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Effect of Dimensionality and Polymorphism on the properties of ZnO

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Aileme

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“Every compound has different polymorphic forms, and that, in general, the number of forms known for a given compound is proportional to the time and money spent in research on that compound”

Walter Mc Crone

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CHAPTER I: Introduction

1. Thesis Overview:

The metal elements can form a large diversity of oxide compounds which play a very important role in many areas of materials science, physics and chemistry.¹ Among the various inorganic materials of current technological interest, metal oxides have a pivotal position.² Due to their broad range of structures and properties metal oxides have wide range of applications. In industrial chemistry, a large proportion of the important catalysts and/or catalyst supports are oxides. In geology, some of the most important minerals are also oxides. For many of the important properties or phenomena in solid-state science such as: metallic ferromagnetism, high temperature ferroelectricity, fast-ion conductivity, and superconductivity,³ one can find prototypical examples among metal oxides. The rich variety of electronic properties of metal oxides, ranging from insulating to metallic and even superconducting behavior, is continually opening up new perspectives for these materials in the electronics and optoelectronics industries.

The possibility for a single compound to exist in more than one distinct crystalline phase is a common phenomenon called polymorphism, which is of crucial importance in many branches of science and technology as polymorphs can and often do show significant differences in chemical and physical properties. With the continuing advances in the development of devices requiring low dimensional nanomaterials (e.g. 0-dimensional nanoparticles, 1-dimensional nanowires, 2-dimensional nanofilms) the importance of gaining a deeper and more general understanding of the relationship between the relative stability of competing crystalline phases (or polymorphs) and size and/or dimension is paramount. The polymorph exhibited by a material is remarkably sensitive to scale and/or dimensionality. This phenomenon is often particularly pronounced when comparing the polymorphism of a three-dimensional (3D) bulk material with that of the corresponding system at the nanoscale with reduced dimensions. Based upon the limited available experimental evidence, it has been reasonably suggested that bulk-nanoscale polymorphic stability crossovers could be due a possible correlation between increasing metastability and decreasing surface energies,

along with the higher surface area to bulk ratios found in nanosystems.⁴ Titanium dioxide, for example, exhibits the rutile crystal structure in the bulk, but, in sufficiently small nanoparticles it displays the anatase phase, which is technologically highly valued for its photocatalytic properties.

In this thesis, the work has mainly focused on zinc oxide (ZnO), which is a group II-VI semiconductor compound having a wide range of technological applications. ZnO is a key element in many industrial manufacturing processes such as paints, cosmetics, pharmaceuticals, plastics, batteries, electrical equipment, rubber, soap, textiles, floor coverings and much more.⁵ Apart from being widely used in a broad range of industries in our society, the development of technologies to grow high quality ZnO single crystals and epitaxial layers has also enhanced its scientific importance. Studies of such well-defined ZnO samples are promising to yield an even wider range of potential applications in further (nano)technologies such as energy harvesting and spintronics. In this sense ZnO can be regarded as a 'future material', which also explains the intense and increasing interest in ZnO in the scientific community (see Figure 1)

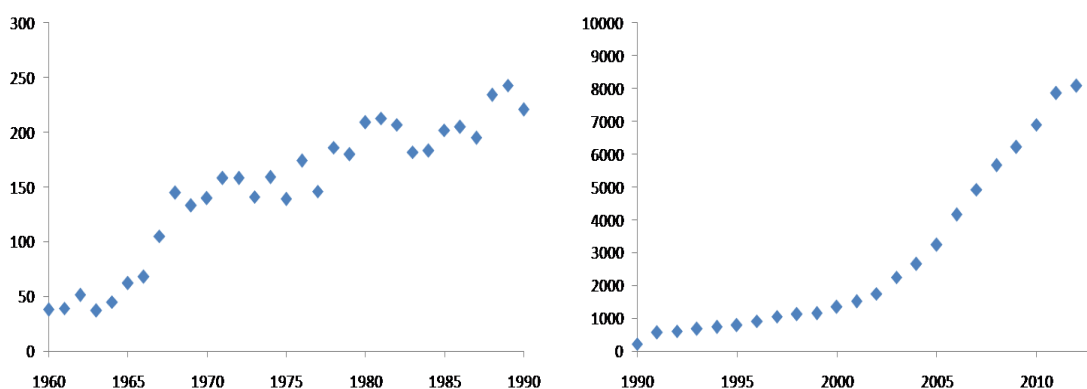


Figure 1. Article Count of “ZnO” word per year between years 1960 and 2013 (taken from web of science).

In Chapter 1, we give detailed introduction about important concepts related our work, such as crystal structure, semiconductivity, polymorphism, and nanoscale, and we introduce related properties of ZnO material in detail. In chapter 2, we introduce the methodology used in this thesis together with related concepts. In chapter 3, we start to

report our results with the case of 0-dimensional ZnO nanoclusters on Ag substrate and compare their properties with free space ZnO nanoclusters. In Chapter 4, we continue with a study of single 2D-ZnO sheet on Ag(111) surface and investigate also how H atoms interact with it. In chapter 5, we move on with the consideration of higher coverage models, including triangular islands prepared to model experimental systems. In chapter 6, we focus on 4ML nanofilms and compare bulk and nanofilm polymorphism of ZnO. Lastly, in chapter 7, we focus on bulk polymorphism and investigate the effect of nanoporosity

2. Structure

Properties of materials are inherently linked to their structures. All substances, except helium, form a solid phase when they cooled sufficiently. The vast majority of these substances form one or more crystalline phases, where the atoms, molecules, or ions are packed in a regular way with long range order. If, however, there is only short range order the solid is said to be amorphous (see Figure 2).

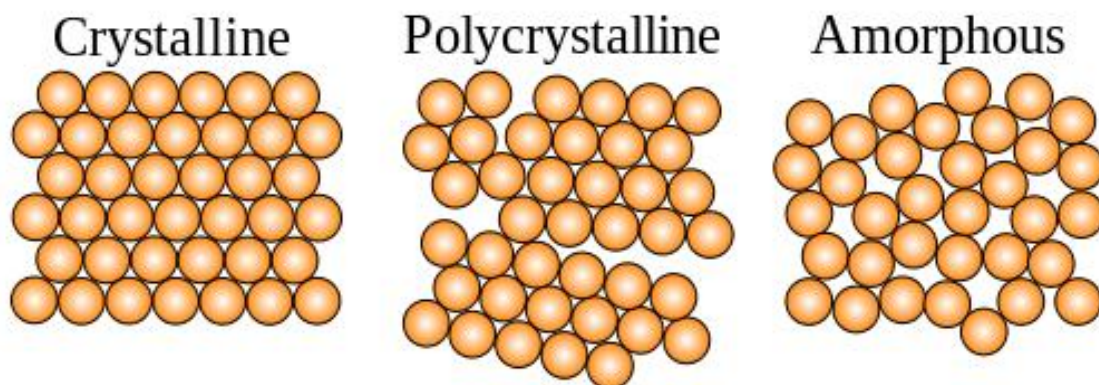


Figure 2. Illustrative example of crystalline and amorphous solid structures.

2.1. Crystal Structures:

Crystal structures consists of: (i) a lattice, which means a spatial periodicity or translation symmetry, and (ii) a basis, which is a repeating pattern of one or more atoms arranged in a particular way. All crystal structures can be obtained by repetition of the basis according to the lattice as seen in Figure 3.

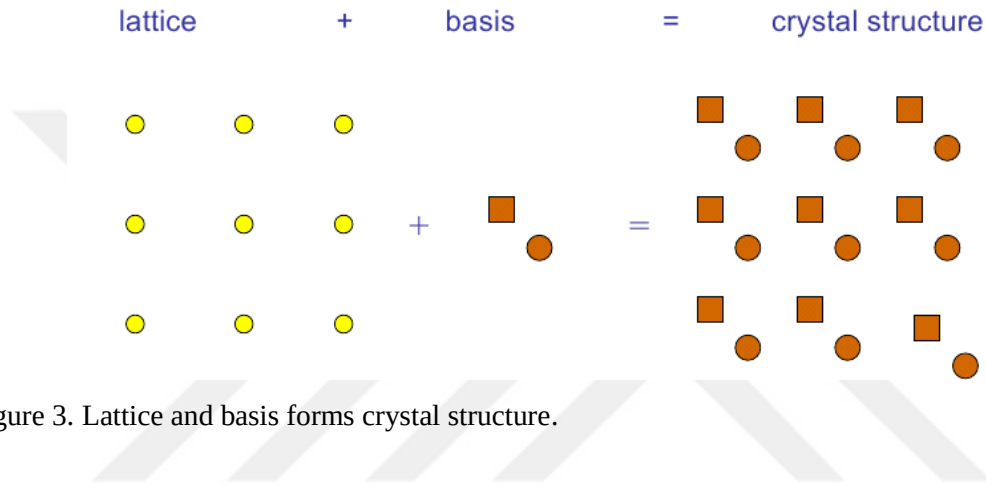


Figure 3. Lattice and basis forms crystal structure.

In 3-dimensional (3D) space we define three non-coplanar vectors; a_1 , a_2 , and a_3 that leave all the properties of the crystal unchanged after the shift as a whole by any of those vectors. As a result, any lattice point R_i can be obtained from another point R_0 by

$$R_i = R_0 + m_1 a_1 + m_2 a_2 + m_3 a_3$$

where m_i are integers. Such a lattice of building blocks is called the Bravais lattice. The volume of the cell enclosed by the three vectors a_i is called unit cell. There is no unique way to choose a_i , which means for a given structure there is never one unique unit cell that is 'correct'. By convention a_1 can be chosen as the shortest period of the lattice, a_2 as the shortest period not parallel to a_1 , and a_3 as the shortest period not coplanar to a_1 and a_2 . Vectors a_i which are chosen in such a way are called primitive vectors and the volume cell enclosed by the primitive vectors is called the primitive unit cell. There are seven unique unit cell shapes that can be stacked together to fill 3D space as shown in Table 1.

Table 1. Unique unit cell Structures.

Lattice	Possible Variations	Axial Distances	Axial Angles	Examples
Cubic	Primitive, Body-centred, Face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc Blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2 , CaSO_4
Orthorhombic	Primitive, Body-centred, Face-centred, Base-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Graphite, ZnO, CdS
Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite(CaCO_3), Cinnabar(HgS)
Monoclinic	Primitive, Base-centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3

In crystallography, to describe the crystal planes and directions, Miller indices are used, which are usually three integers h , k , and ℓ . A plane (hkl) intercepts the lattice at three points a_1/h , a_2/k , and a_3/ℓ . Negative indices are also allowed and, by convention, written with a bar, like in $\bar{3}$ for -3 . The direction normal to a (hkl) plane is shown as $[hkl]$. In a hexagonal crystal structure usually four indices are used instead of three, like $(hkil)$, where $i = -h - k$. This is not strictly necessary to define a plane, but it makes it easier to identify equivalent planes.

A real crystal is never perfect, which means it contains defects. These defects may be 0D (e.g. vacancies or interstitials), 1D (e.g. dislocations), 2D, (e.g stacking faults), or 3D, (e.g. precipitates). For $n > 0$, n -dimensional defects are usually undesirable, and can be avoided with proper care during sample fabrication and processing. However, 0D defects can develop for thermodynamic reasons. Defects of this nature are called intrinsic, as they cannot be avoided and are not caused by impurities. The equilibrium amount of defects depends on the material

2.2. Structural properties of ZnO

Most of the group-II-VI binary compounds have either cubic zinc-blende or hexagonal wurtzite structures. Both of these structures have tetrahedral coordination implying sp^3 hybridised covalent bonding, but these materials also have a substantial ionic character.

The ionicity of ZnO resides at the borderline between covalent and ionic semiconductors, in the region where tetrahedral coordination is expected (see Figure 4).

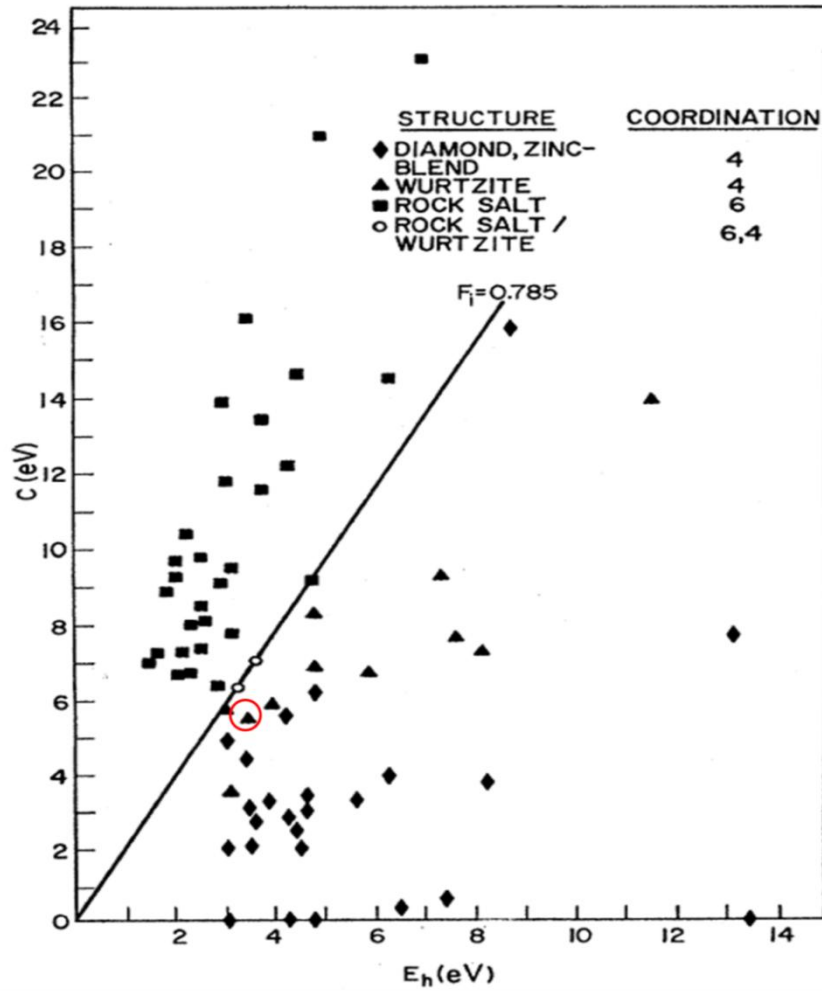


Figure 4. Phillips-van Vechten Plot for AB materials. E_h and C are homopolar and heteropolar parts of the complex energy gap, E_g associated with the A-B bond in the crystal.⁶

ZnO exhibits several crystal structures such as wurtzite, zinc blende and rocksalt phases. Of these, the wurtzite (wz) structure is thermodynamically most stable under ambient conditions, and is the most commonly observed phase.⁷ As shown in Figure 5, wz-ZnO has a hexagonal lattice which is characterized by two interconnecting sublattices of Zn^{2+} and O^{2-} , such that each O^{2-} ion is surrounded by a tetrahedron of Zn^{2+} ions, and vice-versa. It belongs to the space group $P6_3mc$, which causes the wz structure to lack of center of inversion symmetry.

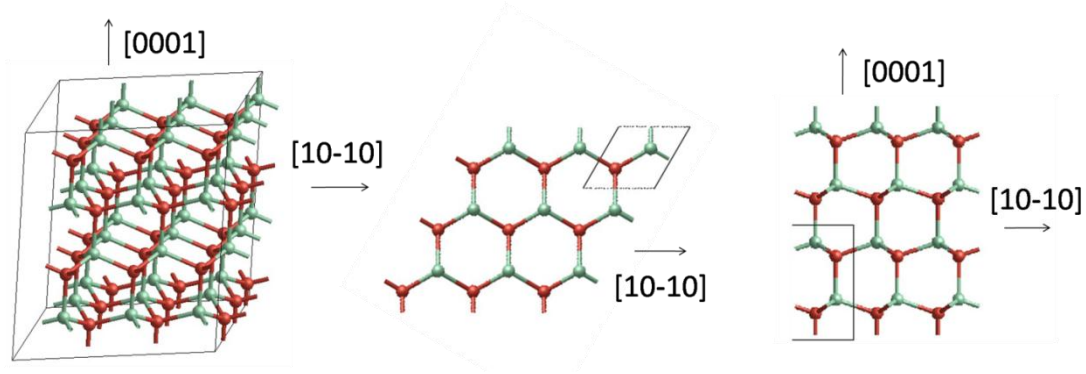


Figure 5. Top view and side view of wurtzite (wz) ZnO structure.

The primitive translation vectors a and b lay in the x - y plane, are of equal length, and include an angle of 120° , while c is parallel to the z -axis. The primitive unit cell contains four ions, ie. two formula units of ZnO, with the corresponding basis vectors: $(1/3, 2/3, 0)$, $(2/3, 1/3, 1/2)$ for the cations, and $(2/3, 1/3, u)$, $(1/3, 2/3, u+1/2)$ for the anions, where u is the separation between anions and cations in the z -direction. The values of the primitive translation vectors in wz-ZnO are $a = b \approx 0.3249$ nm and $c \approx 0.5206$ nm at room temperature. The deviation from the ideal lattice parameters are most likely due to the ionic nature of the ZnO bond, leading to a distortion of the bond angles.⁸

The wz structure can be also considered as an ABAB... stacking of one atom thick, charge neutral sheets, in which zinc and oxygen atoms form a hexagonal pattern like honeycomb, with three equivalent Zn-O bonds for each site (see top view in Figure 5). As can be clearly seen in the side view (Figure 5), these sheets are corrugated in the wz structure, with all zinc atoms occupying one side and oxygen atoms the other. Because of the ionic character of ZnO, each sheet thus possesses a dipole moment, which is normal to the surface.

There are 4 common surface terminations for the wz-ZnO crystal: Zn terminated (0001) and O terminated ($000\bar{1}$) polar faces, and non-polar ($11\bar{2}0$) and ($10\bar{1}0$) faces containing equal numbers of Zn and O atoms. Of these surfaces, the non-polar ($10\bar{1}0$) surface has the lowest surface energy.⁹

In a wz-ZnO unit cell there are 4 atoms which gives 12 phonon modes, which are 1 longitudinal-acoustic (LA), 2 transverse-acoustic (TA), 3 longitudinal-optical (LO) and 6 transverse-optical (TO) modes. These modes are important to understand the electrical, optical and thermal properties of the crystal and therefore extensively studied.⁸ The E_1 and A_1 branches are infrared and Raman active, while E_2 branches are only Raman active and B_1 branches are inactive. Experimental values of most common phonon modes visible at 300 K are given in Table 2.

Table 2. Experimentally determined principal phonon modes of wurtzite ZnO at 300 K.

Phonon mode	Value (cm ⁻¹)
E_2^{low}	101
E_2^{low}	437
TO (A_1)	380
LO (A_1)	574
TO (E_1)	591

When exposed to an electric field all materials undergo a change in dimensions, but the reverse effect, development of an electric polarization when an external stress or strain applied, does not occur for most of them. This latter property allows conversion of mechanical energy to electrical energy and is called piezoelectricity. Being a subclass of these materials, a pyroelectric material expands by heating and the net dipole moment changes with the temperature due to the compensating charges appearing on the opposite faces of the crystal. These materials are generally used as sensors, transducers and actuators. ZnO is a piezoelectric material because of the lack of inversion symmetry of the wurtzite crystal structure and a pyroelectric material due to the specific polar axis. Combined with its other advantageous properties, the piezoelectric¹⁰ and pyroelectric¹¹ properties of ZnO make it a very promising material for applications such as energy harvesting.¹²

Apart from wz, the zinc blende (ZB) ZnO structure can be also obtained. ZB-ZnO can be grown on cubic structures, such as ZnS,¹³ GaAs/ZnS,¹⁴ Pt/Ti/SiO₂/Si.¹⁵ ZB is a cubic structure, which belongs to the space group $F\bar{4}3m$ (Figure 6). Like wz, all the ions in ZB are also tetrahedrally coordinated. Thus, although the wz and ZB structures belong to different space groups, they have the same local tetrahedral environment and

become different only in their third-nearest-neighbor atomic arrangement. In terms of *a-b* aligned hexagonal sheets, for the *wz* structure they are arranged in a *ABABAB* stacking in the *c*-direction, whereas *ZB* shows *ABCABC* stacking of the same sheets in the (111) direction.

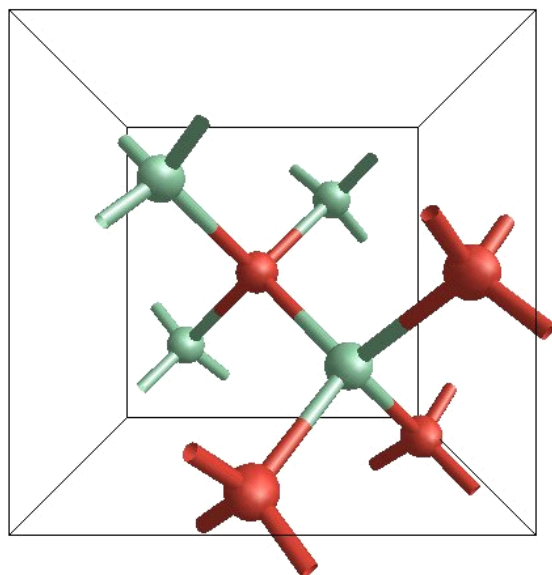


Figure 6. Structure of zinc-blende.

Like other group II-VI compounds, *wz*-ZnO can also be transformed into the rocksalt (RS) structure at high pressures (~ 9 GPa¹⁶). The RS structure belongs to the space group *Fm3m* and the structure is sixfold coordinated as shown in the Figure 7. Recently the RS-ZnO structure has been stabilized at ambient conditions.¹⁷

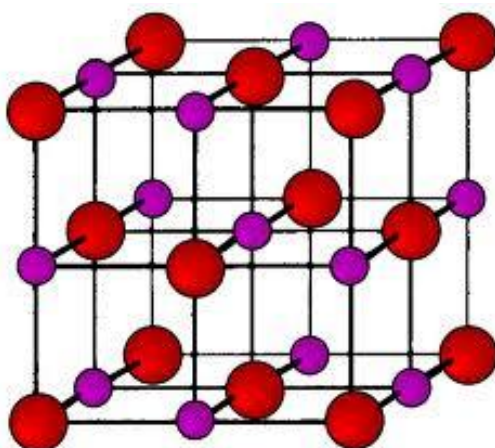


Figure 7. Rocksalt Structure.

3. Semiconductivity

3.1. Semiconductivity and Band structure

Devices made from semiconductor materials are the foundation of modern electronics, including radio, computers, telephones, and many other devices. Semiconductors are a group of materials having electrical conductivities between those of metals and insulators, which can be easily controlled over a wide range of operating conditions.

Electrons in atoms or molecules occupy distinct atomic or molecular orbitals. Orbitals have discrete energy levels each with a different energy due to the Pauli exclusion principle. In solids, due to the large number of atoms brought together, the energy differences between orbitals become very small and they form continuous bands of energy instead of being discrete. The energetical variance of these continuous bands inside a periodic crystal with the wavevector is referred as band dispersion and the overall plot sketched for each band energy with respect to several crystal directions is called the band structure. The energy bands occupied by electrons are called valance bands while empty ones are called conduction bands. In metals these bands overlap and thus the electrons are free to move and electrical conduction can occur. Some intervals of energy between bands can remain forming energy gaps. For insulators and semiconductors the gap between valance and conduction bands is called the bandgap and electrons have to gain enough energy to overcome this gap.

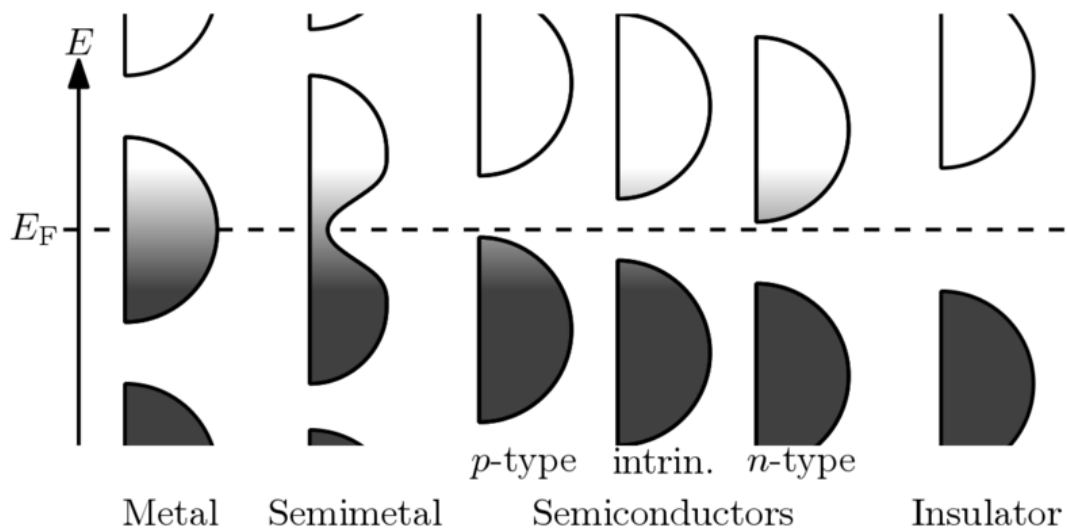


Figure 8. Electronic band structure in various types of materials.

Since the dispersion of the bands, two types of gaps emerge as direct and indirect gap. If the maximum of valance band and the minimum of the conduction band corresponds the same wavevector, the gap is called to be direct, or vice versa. In a direct gap, an electron transition between bands can occur without a change in electron momentum. However electron transition is less likely in indirect gaps since it requires a change in electron momentum. Examples of direct and indirect gaps are given in Figure 9 as bandstructures of Si and ZnO.

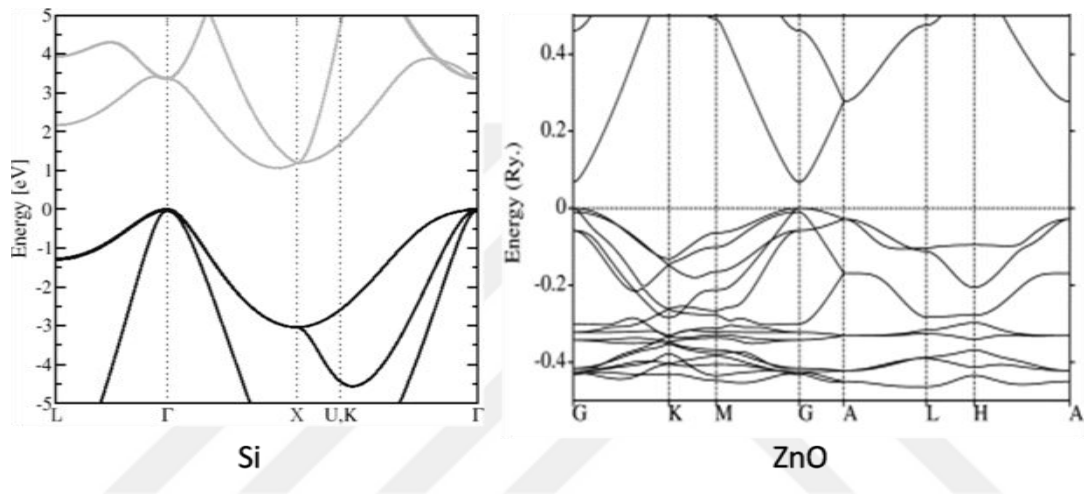


Figure 9. Bandstructures of Si and ZnO.

The difference between insulators and semiconductors is just the size of bandgap, which in semiconductors the electrons can thermally or optically excited from valance band to conduction band and thus transport current, whereas in insulators not.

In semiconductors, conductivity is controlled by two types of charge carriers; electrons in the conduction band and holes in the valence band. A hole refers to the situation where one electron is missing in the valence band. In order to control the conductivity, dopants can be introduced. To have an excess of negative charge carriers, the semiconductor can be doped with a donor impurity, which is called n-type doping. Vice-versa p-type doping (to introduce positive charge carriers) can be done by introducing an acceptor impurity.

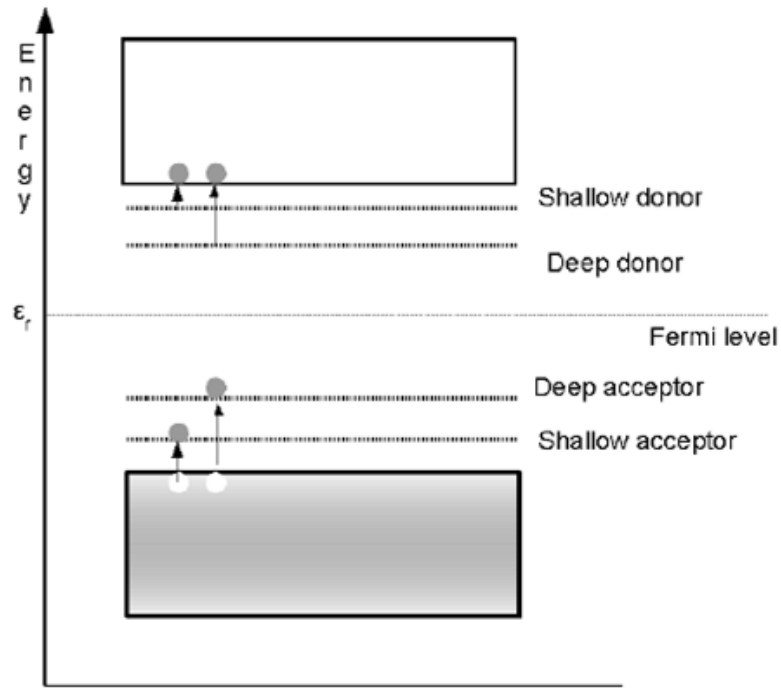


Figure 10. Doping introduces new levels within the bandgap.

3.2. ZnO as a wide bandgap semiconductor

Some of the useful applications and properties of ZnO are summarized in Figure 11 and some basic physical properties at 300 K^{5,8,18,19} are given in Table 3. Large variation of thermal conductivity values are expected due to crystal defects.²⁰ Mobility and effective mass values are uncertain because of the problems to obtain reproducible and robust p-type ZnO, which will be discussed later in this chapter.

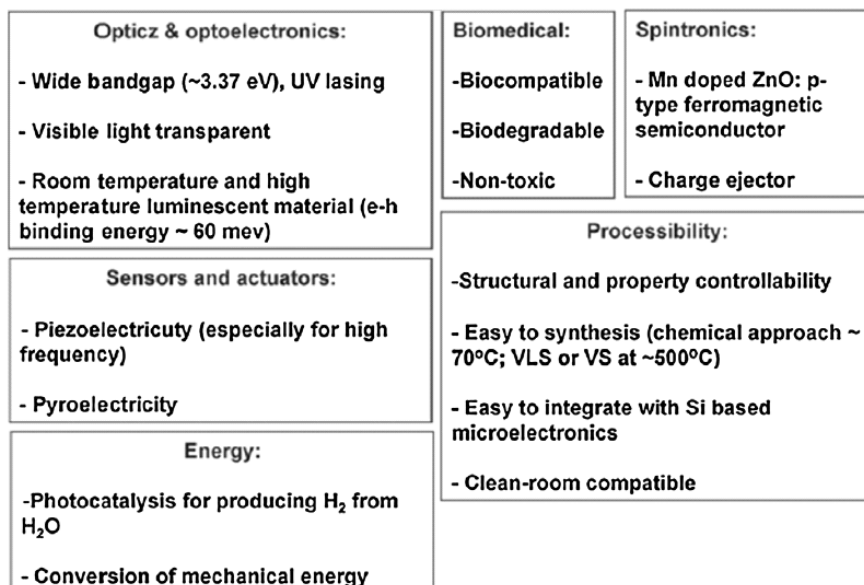


Figure 11. Useful applications and properties of ZnO material.

Table 3. Basic physical properties of ZnO at 300 K.

Parameters	Values
Lattice constant	a = 0.32495 nm, c = 0.52069 nm
Density	5.67526 g/cm ³
Molecular mass	81.389 g/mol
Melting point	2250 K
Electron effective mass	0.28 m ₀
Hole effective mass	0.59 m ₀
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Bandgap energy	3.37 eV
Exciton binding energy	60 meV
Thermal conductivity	0.6 – 1.16 W/Km
Specific heat	0.125 cal/g°C
Thermal constant at 573	1200 mV/K
Electron mobility	~ 210 cm ² /Vs

At present GaN is used in many opto-electronics devices as a semiconductor which has a direct bandgap of 3.44 eV.²¹ Like ZnO, GaN also crystalizes in wz structure. ZnO is a very promising semiconductor material with its similar direct wide bandgap of 3.37 eV at room temperature.²² However its use in electronic devices has been hindered by the lack of control over its electrical conductivity and, therefore, firstly, it has been considered as a substrate to GaN due to its close match.²³ ZnO is intrinsically n-type semiconductor without any intentional doping. However, to achieve p-type ZnO is a difficult task, which is essential for utilizing most of the semiconductor applications via junctions of p- and n- doped materials. Although p-type ZnO samples have been reported by several groups, mobility and the hole concentration are usually not high and the reproducibility of the results are under debate.²⁴ Still considerable efforts are underway, both theoretically and experimentally,²⁵ to obtain p-type ZnO with various techniques and dopants. The availability of high-quality p-type ZnO would enable the use of ZnO itself directly in optoelectronic devices, which would heavily profit from the availability of large size high-quality single crystals^{26,27} and compatibility with Si technology due to wet chemical processability.¹⁸

The reason for the n-type behavior of ZnO has been often attributed to the self-compensation from native donor defects and/or hydrogen incorporation²⁸ but the exact reason is not clear yet. Because all different growth techniques produce n-type ZnO, the first assumption was that there is only one responsible defect, which was thought to be a native zinc interstitial defect or oxygen vacancy.^{29, 30, 31} However, theoretical calculations⁸ have showed that the formation energies of these defects are relatively high, with, the most stable oxygen vacancy (V_O) is seeming to induce a donor state which is too deep to account for the observed n-type behaviour. Although V_O cannot contribute to the n-type conductivity, it can be a relevant source of compensation in p-type ZnO. The Zn intersitital is a shallow donor (Figure 10) but considering its high formation energy one should not expect considerable amount to be present in the material to control the n-type conductivity.

Recently, attention has been drawn to the role of hydrogen^{24,32} and other unintentional impurities^{33,34,35} in affecting the electronic properties of ZnO. Hydrogen, in particular, is present in high concentrations in ZnO irrespective of the growth conditions. In most of

the semiconductors studied, interstitial hydrogen has been observed to act as amphoteric impurity,^{36,37} which means it always counteracts the conductivity by incorporating H_i^+ in p-type samples, and H_i^- in n-type samples. This behavior prevents hydrogen from being the source of conductivity. However, in ZnO only the H_i^+ is thermodynamically stable, thus interstitial hydrogen behaves as a shallow donor.

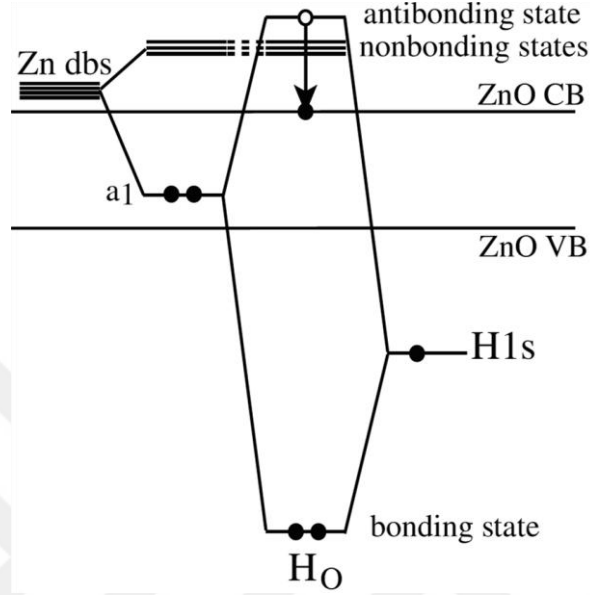


Figure 12. Coupling between the H 1s orbital and the Zn 4s dangling bonds (Zn dbs) to form the hydrogen multicenter bond in ZnO.

It was found that hydrogen can also replace oxygen in ZnO (H_O) in addition to being in interstitial positions. When in a V_O position H forms a multicenter bond with four neighboring Zn centres equally. Exclusively occurring in the positive charge state H_O^+ , such substitutional hydrogen is also a shallow donor in ZnO.

The hydrogen multicenter bond can be thought as a coupling between the H 1s orbital and the Zn 4s dangling bonds (Zn dbs) as in Figure 12. The H 1s orbital interacts with the a1 state and produces a fully symmetric bonding state in the valence band, and an antibonding state in the conduction band. The electron that would occupy this antibonding state is then transferred to the conduction-band minimum, making the substitutional hydrogen H_O a shallow donor.³⁸ Because of the formation energies of both interstitial and substitutional hydrogen are low, they can occur in significant concentrations making hydrogen a very attractive candidate for the reason of unintended n-type conductivity. There are also other possible donors, such as Al, Ga and Si, which have been suggested to explain the n-type behavior of ZnO, but the occurrence of these donors depends of the sample growth method.

3.3. Bandgap engineering of ZnO

The success of ZnO as a semiconductor depends also the possibilities of band gap engineering, ability to increase or decrease the band gap, as well as controllable n-type and p-type doping. Most semiconductor devices (e.g. high electron mobility transistors, lasers, LEDs, etc) use heterostructures to provide carrier and optical confinement. These heterostructures consist of layers of different materials or compositions and the important parameters are the bandgaps of each layer and the band offsets between the layers. Similar to GaN, which can be alloyed with AlN or InN, ZnO can be alloyed with MgO or CdO to increase the band gap. However, while GaN, AlN and InN all display the same wz structure, MgO and CdO exhibit the rocksalt structure, which is different from wz-ZnO. This becomes problematic when high proportions of MgO or CdO are used for alloying because a phase separation is expected to occur. However, the wz crystal structure can be preserved for moderate amounts of MgO and CdO, which still provides a range of band gaps and useful band offsets for practical device application³⁹. $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films can be grown on various substrates such as sapphire, ZnO itself or ScAlMgO_4 using different techniques.⁴⁰ It has been found that after ~33% incorporation of MgO in ZnO a phase transition to the cubic structure occurs, but a bandgap increase up to 3.99 eV can be achieved before this phase transition.⁴¹ Like the inverse of MgO, alloying ZnO with CdO decreases the bandgap. For example, a 3.0 eV band gap has been observed for ZnO with 7% of Cd content grown on sapphire and ScAlMgO_4 substrates by pulsed-laser deposition.⁴²

3.4. Optical and Electronic properties of ZnO

Besides having a wide band gap, the optical properties of ZnO are very important because it has a high exciton binding energy of 60meV^{7,43} which is much larger than the 25meV⁴⁴ of GaN. This high exciton binding energy allows efficient excitonic emission even at room temperature, which also makes ZnO a very promising material for optical devices based on excitonic effects.

ZnO has a strong luminescence in the green-white region, which makes it also suitable material for phosphor applications. It has an emission peak at 495 nm and a broad half-width of 0.4 eV.⁴⁵ It makes ZnO also appropriate material for applications in vacuum

fluorescent displays and field emission displays combining with the n-type conductivity. Although the reason mechanism for the green luminescence is not really understood, Zn vacancies are suggested to be likely cause due to acceptor behavior in n-type ZnO.³⁸ Both in crystal and thin films, ZnO shows large second- and third-order non-linear optical behavior⁴⁶ depending on the crystallinity of the samples, which makes it suitable for non-linear optic devices.

ZnO exhibit exceptionally high radiation hardness, which makes it very suitable in applications where radiation damage is a factor, such as solar cells or space satellite applications.^{47, 48} Also ZnO Schottky rectifiers have been found to remain fully functional after high radiation exposure and showed little degradation in electrical performance even less than that of SiC and GaN devices,⁴⁹ which makes ZnO material very promising for aerospace and terrestrial applications.

A device which responds to specific chemical species or biological analyte in a selective way through a chemical reaction is called a chemical sensor. They can be used for a quantitative or qualitative determination of an analyte. Semiconductor materials are heavily used in this field because of their excellent properties.⁵⁰ Among them ZnO material is very important because it can be easily synthesized with a variety of nanostructures on different substrates⁵¹, and is also biocompatible and biodegradable.⁵²

4. Polymorphism

4.1. Introduction to Polymorphism

The idea that a substance can exist in different physical states can be traced back to the speculations on the conceptions of matter in ancient Greek philosophy.⁵³ Aristotle (384-322 BC) developed a philosophical approach to explain natural phenomena like evaporation and the existence of different physical states. According to Aristotle, matter itself is something that is not a substance however it has the ability to receive forms. Thus, even drastical changes are possible, because one form can replace another and the drastical changes happens when when it receives a new substantial form.⁵⁴ The connection from a philosophical to scientific interpretation of nature was done by

mainly Aristotle's commentators in the following centuries. The philosophical theory, *minima naturalia*, which states that every kind of substance has its specific minimum sized particles was developed and had a big impact on the development of modern chemistry, since it can be regarded as predecessor of the atomistic theories.⁵⁵ The transition from philosophical to scientific atomistic theories took place between 17th and 19th centuries. At this period, M. H. Klaproth^{54,56} addressed the question whether different solid matters should have different chemical compositions or not, and discovered that calcite and aragonite have the same chemical composition which is CaCO_3 . His discovery had large effects on the development of the solid state theory. Later on the work on arsenates, phosphates and sulfur by E. Mitscherlich^{57,58} gave additional evidence for the fact that a given substance can form different solids with different physical properties. He also realized that arsenates and phosphates crystallize in the same form and thus display enunciated isomorphism, which is the term to describe crystals of different composition generating the same form. From then on many other examples of solids that differ in physical properties while having same chemical composition have been found primarily for inorganic compounds followed by organic compounds. In 1839 the first transition between such so-called polymorphs was observed by Frankenheim.^{54,59} He studied the crystallization of potassium nitrate from solution and demonstrated that the polymorphic transitions can be solvent mediated. Following decades, Lehmann⁶⁰ studied phase transitions and classified them into one direction only transitions and reversible transitions upon heating or cooling. With the discovery of X-Ray diffraction, the organization of atoms in the crystalline assembly become reachable and stimulated the field of polymorphism by giving a new impulse and a new direction from the structural point of view.

At first, polymorphism was called dimorphism because it is thought that a substance could crystallize into only two possible phases. Later it was named as polymorphism with the experimental evidence for substances that have more than two phases. Berzelius introduced a lesser general term allotropism,⁶¹ for the chemical elements existing in two or more different forms. Most widely known cases of allotropism is maybe that of the carbon which can have several solid structures such as graphite and diamond as well as more recent discovered nanotubes and fullerenes. For molecular crystals polymorphism has been defined by McCrone⁶² as "A solid crystalline phase of

a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state”. To eliminate the ambiguity with tautomerism, which is defined as the rapid interconversion of structural isomers in liquid or vapor state, the definition was strengthened by classifying two crystal structures as polymorphic if they lead to the same liquid or vapor phases.⁶³ A related term pseudopolymorphism is sometimes used for solvated forms, but the use is discouraged because there is a clear difference between a polymorphic transition and the process of desolvation.⁶⁴ Polymorphism is usually classified as packing polymorphism, in which the structures are different in the way that molecules are packed, and conformational polymorphism, in which there is a difference in molecular conformation for the structures. However this classification can be ambiguous because at the atomic level, there do not exist really frozen structures with exact bond lengths and bond angles but these entities are just averages over time of different vibrational modes happening on a very short time scale, which depend on different short and long range interactions. There can be also possible rotation flexibility around single bonds in some systems which add additional degrees of freedom in the packing of molecules in a crystal lattice. Thus the classification of packing polymorphism and conformational polymorphism should be regarded as extremes on a floating scale. Polymorphism is an extremely widespread phenomenon within the chemistry branches of both inorganic and organic systems. A famous quote belonging to McCrone (1965) about the existence of polymorphism is as follows: “Every compound has different polymorphic forms and in general, the number of forms known for a given compound is proportional to the time and money spent on it.”

Silica (SiO_2) can be regarded as an example of a material which shows a very high degree of polymorphism. It is one of the most common materials in nature and has many industrial applications. Thus, it is one of the most heavily and widely investigated materials. The five stable dense polymorphs: quartz, coesite, stishovite, cristobalite and tridymite, have been studied intensively for decades. There is also an increasing and large number of other lower density polymorphs which have been synthesized (e.g. zeolites).

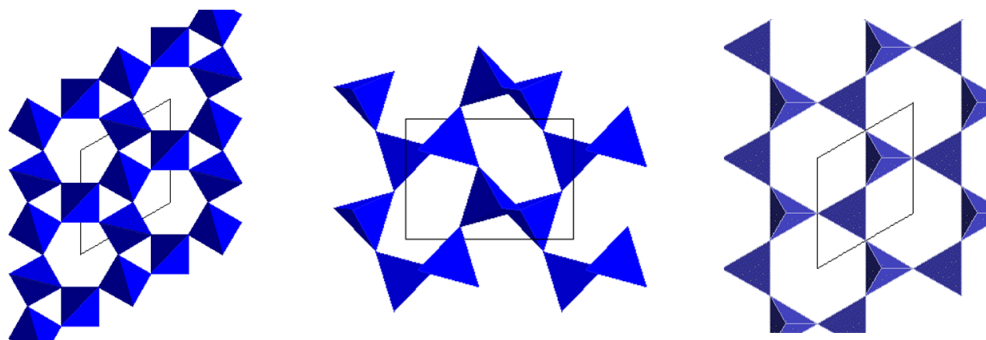


Figure 13. Structures of Silica polymorphs, a) quartz, b) tridymite, c) cristobalite.

At atmospheric pressure, silica has three distinct crystalline phases, which are quartz, cristobalite and tridymite. The stability ranges of these polymorphs have been subject to many studies, but one of the earliest and mostly quoted one is that of Fenner's,⁶⁵ who determined the stability relations among these phases as:



The low pressure phases are all built of corner-sharing SiO₄ tetrahedra. Also in the glass and the liquid phases, almost all Si atoms are tetrahedrally coordinated. However at higher pressures crystal structures six-fold coordination of Si atoms becomes more favorable so that octahedrally coordinated polymorphs occur (e.g. stishovite).

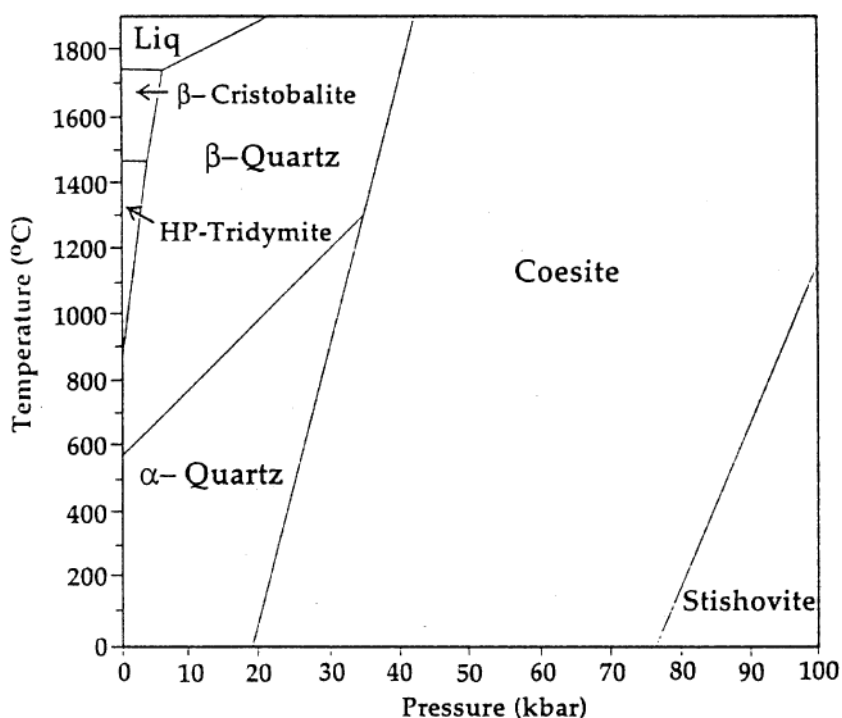


Figure 14. Phase diagram of silica at various pressures and temperatures.⁶⁶

Depending on temperature, at pressures above 8-12 GPa, silica forms the stishovite phase, where oxygen atoms form a distorted hexagonal close packed structure and silicon atoms occupies octahedral sites. At higher pressures above 45-50 GPa stishovite undergoes an orthorhombic distortion and transforms to a CaCl_2 phase.⁶⁷ In the same pressure range in a He pressure medium quartz was found to transform to a monoclinic post-quartz phase, which is built up of 3×2 kinked chains of edgesharing SiO_6 octahedra units.⁶⁸ Without a pressure medium, compression of quartz converts to a complex phase Quartz II or a mixture of phases.⁶⁹ At pressures around 35-40 GPa in a soft pressure medium cristobalite transforms to a PbO_2 -type structure.⁷⁰ Niccolite structure was reported in shock wave compression⁷¹ and laser heated DAC experiments.⁷² With several other methods, many other polymorphs of silica are continuing to be reported and the research to obtain new polymorphs and to characterize them is still going on.

For ZnO material, as previously mentioned, there are three experimentally known polymorphs, which are wurtzite, zincblende and rocksalt structure. However, will be discussed throughout this thesis, ZnO has a very wide range of possible and promising polymorphs.

4.2. Polytypism

Polytypism is a special class of polymorphism. It is used for the polymorphism between two different crystal structures, which are composed of identical 2D layers but have differences only in stacking. Silicon carbide (SiC) is the most well-known example for this type of polymorphism, which can form such stable and long range modifications. More than 200 SiC polytypes have been determined so far.⁷³ The SiC polytypism occurs between two extreme polytype structures ZB, where cubic stacking of Si-C double layers occurs in the [111] direction and hexagonal wurtzite with hexagonal stacking in the [0001] direction. The other polytypes are hexagonal or rhombohedral combinations of these two stacking sequences with n Si-C double layers in the primitive cell (Figure 15). The most well known examples are 4H and 6H structures, which are named according to Ramsdell notation.⁷⁴ According to this notation the number of SiC double layers in the stacking direction in the primitive unit cell is combined with the letter

representing the Bravais lattice type; ‘C’ for cubic, ‘H’ for hexagonal and ‘R’ for rhombohedral. With this notation cubic zinc blende is noted as 3C and hexagonal wurtzite as 2H as you can see also the corresponding ABC stackings of double layers in Table 4 for selected SiC polytypes.

Table 4. Ramsdell notations and layer stackings of simple SiC polytype structures.

Ramsdell notation	ABC stacking	% of hexagonality	No. of atoms per unit cell
3C	ABC	0	2
8H	ABACBABC	25	16
21R	ABCACBACABCBCABACB	29	14
6H	ABCACB	33	12
15R	ABACBCACBABCBCACB	40	10
4H	ABAC	50	8
2H	ABAB	100	4

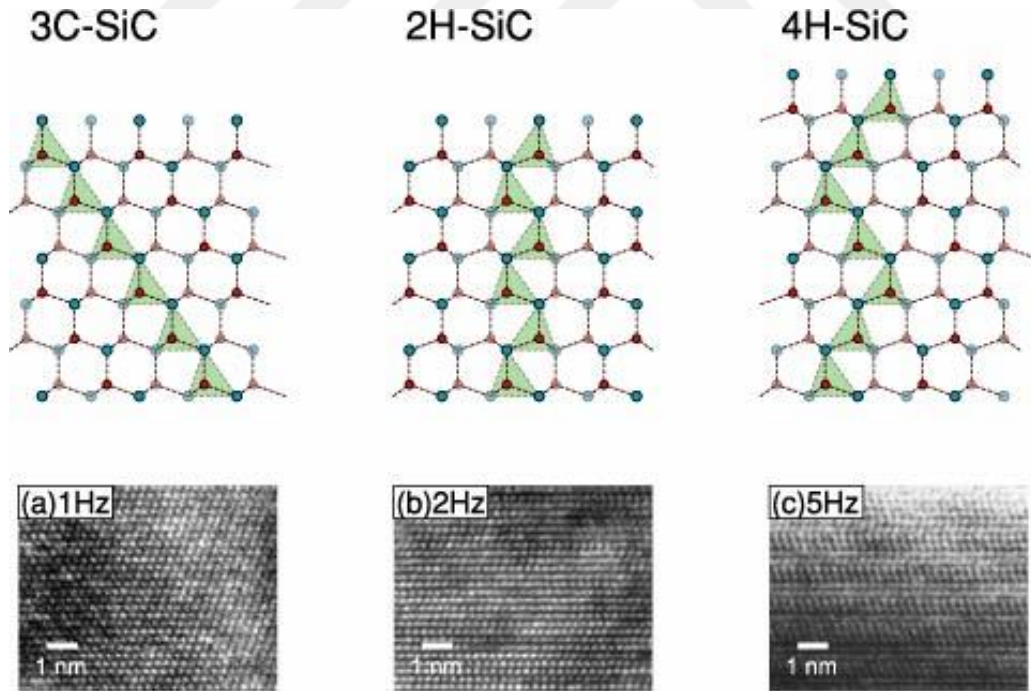


Figure 15. Crystal structures of 3C (zinc blende), 2H (wurtzite) and 4H polytypes of SiC and high resolution images of their corresponding films fabricated at different laser pulse frequencies.⁷⁵

The driving forces for the occurrence of so many polytypes of SiC is not very clear yet despite many research in this field. There are roughly two categories of explanations of the polytypism of the SiC.⁷⁶ The first one focuses on the considerations of the thermodynamical stability of the common short-period polytypes, which are believed to act as basic structural elements for the generation of long-period polytypes. The second category deals with the growth mechanism for long-period polytypes around screw dislocations. However, there is no final conclusion so far, and a satisfactory explanation may contain both types of considerations to some degree depending on the actual growth conditions.⁷⁷ There also exist polymorphic transformations between SiC polytypes, among which the solid-solid phase transition of 3C to 6H structure at elevated temperatures is just one example.⁷⁸ The properties of various SiC polytypes differs also by the remarkable influence of different stacking of Si-C double layers. One common example is of their electronic structure, where the indirect bandgaps vary in a wide energy range from 2.4 eV to 3.3 eV going from one extreme cubic 3C polytype to the other extreme 2H with complete hexagonal stacking. Choyke et al.⁷⁹ determined a linear relationship between hexagonality of the polytype and the bandgap experimentally for a couple of polytypes. The position of the conduction band minimum in *k*-space is also established by the polytype, which is important in microelectronic device applications as of certain polytypes.⁸⁰

4.3. Hypothetical polymorphs

If we are to believe the quote by McCrone at the start of this that new polymorphs can be found for most of the materials by investing more and more on research, a question arises whether we can predict new feasible structures before experimentally fabricating them. Similarly, can the theoretical study of potential new polymorphs help characterize experimentally found new structures. As well documented in a review of the current status of the field of material's prediction by Woodley and Catlow⁸¹ the answer to both these questions is yes, up to some degree of accuracy. . Predicted structures are often called as hypothetical structures. There are several methods developed throughout several decades to generate reasonable hypothetical structures which can be roughly partitioned into three groups: (i) direct explorations of configurational space, (ii) topological modeling methods, and (iii) structural models by analogy.

4.3.1. Structural Models by Analogy

The simplest among all is the latter, which is generating approximate structural models by analogy with known structures of somehow related chemical composition and then refining their structures with usually quantum mechanical electronic structure methods⁸². This approach is not ‘ab initio’ in terms of generation because, so to speak, the structures are derived from “mining” in the literature for experimentally known or other predicted structures of similar systems and is thus usually called the ‘data mining’ approach. Although simple, data mining approaches can be very effective for some systems like alloys,^{83,84} but intrinsically lack the ability to explore among the diversity of as-yet unknown structures.

4.3.2. Topological Modeling Methods

Topological principles have been also used for decades by enumerating and defining networks according to the bonding connectivity of considered materials. This approach is particularly useful in analyzing real structures and for predicting hypothetical structures with directionally-bonded frameworks (e.g. zeolites). As an example, Smith⁸⁵ developed a systematic enumeration method for four connected three dimensional silicate materials (building on the earlier topological approach of Wells)⁸⁶ where he describes some 3D nets based on other 2D nets. For silicates, 2 dimensional simple hexagonal nets are used to describe the frameworks together with perpendicular upward or downward connections for each node to another 2 dimensional net. Thus, two adjacent nodes within a horizontal hexagonal net can have their internet linkages either pointing in the same (S) or in a changed (C) direction, which is how they are enumerated. Going around the six nodes of a single hexagonal ring in a single net, there are 8 ways, in which the internet connection sequences can occur: CCCCCC, SCCSCC, SCSCCC, SSCCCC, SSCSSC, SSSCSC, SSSSCC and SSSSSS (see Figure 16). Most of these sequences allow only one type of 3 dimensional nets, except for SSCCCC and SSSSCC, for which there exist two different choices of bringing hexagons together in adjacent nets. According to this enumeration there exist ten different simple framework structures, excluding the infinite number of possibilities due to polytypism in CCCCCC (which stands for wurtzite and zincblende polytypism) and SSSSCC. One should also note that there exist infinitely many possible structures by combining two or more of

these simple framework enumerations. In principle, these type of enumeration methods may generate all the possible frameworks, however filtering the results in order to identify the more likely candidates can be sometimes problematic.

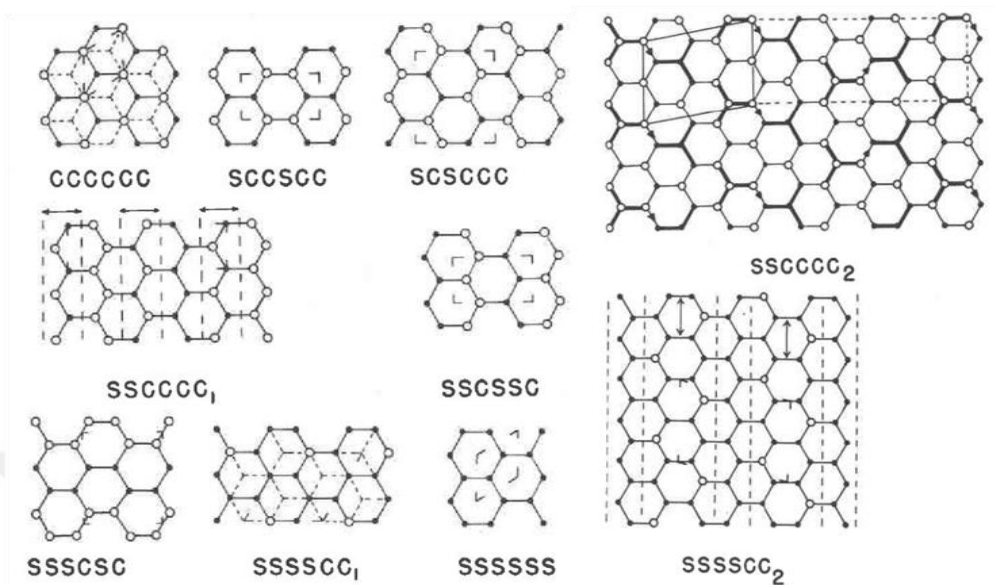


Figure 16. 3D nets of simple framework structures.

Another example would be tiling approach,⁸⁷ in which the four-connected 3D nets are divided into polyhedra and Euclidean space polyhedral tilings are used to enumerate the corresponding nets, and graph approach,⁸⁸ in which the atoms are treated as tetrahedral nodes and the frameworks are generated by permuting over all possible topological connections.

4.3.3. Directly Exploring Configurational Space (Global Optimization)

Directly exploring the configurational space of structures has the potential to explore and selectively identify promising structures but can be computationally expensive. Such search methods are also called global optimization methods because they try to find the global minimum of the configurational space computationally. As such approaches (e.g. simulated annealing, evolutionary algorithms) require efficient procedures to explore the energy landscape of configurations, which is defined by the internal coordinates of the atoms in the unit cell and the corresponding energy. Usually energy functions at a classical or quantum level depending required accuracy and computational cost are used to evaluate the structures, however they sometimes also use simpler cost functions or collective variables for some systems. Global optimization techniques evaluate the energy function many times in order to search the energy landscape of configurations. As examples, we outline two specific approaches to

global optimization below. The Monte Carlo Basin hopping method, as used in my work, is discussed in more detailed in the methodology chapter.

4.3.3.1. Simulated annealing

The simulated annealing⁸⁹ is an approach based on simple concepts arising from physical annealing. The atoms are in a disordered manner when the substance is in melted state. While cooling slowly, the atoms may crystallize in an ordered manner, to reach the global minimum. However, if the cooling is rapid or if the starting temperature is not high enough, the system may be quenched into a local minimum or freeze into a crystalline system containing defects like vacancies and dislocations. In simulating annealing the positions of atoms are perturbed using molecular dynamics or a Monte Carlo scheme while decreasing the temperature gradually, so that the system can move around between local minima by overcoming the energy barriers depending on the temperature. After the continuation of this process slowly enough, the final structure is likely to be the global minimum. However it is possible for complex energy landscapes that some low-energy regions may not be reachable for a specific starting point and thus the global minimum may be missed. To overcome this danger, usually multiple runs starting from different initial positions are being used. The simulated annealing approach has been used in a number of elegant, predictive studies of inorganic solids.^{90,91}

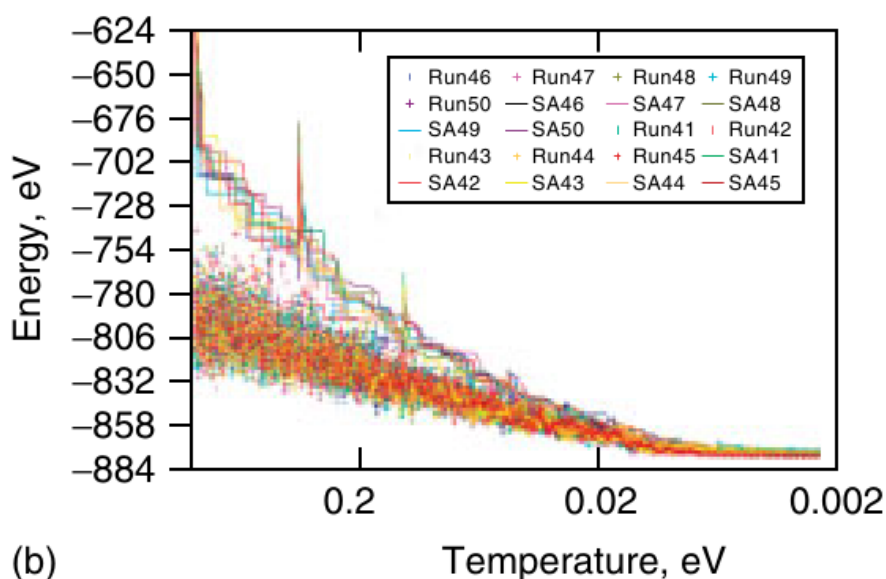


Figure 17. An example of simulated annealing method used for prediction of crystal structure of $\text{BaMgAl}_4\text{Si}_4\text{O}_{16}$.⁹² The different color lines corresponding the trajectories of ten runs starting from different starting points. Data points represents the local minima along each trajectory.

4.3.3.2. Genetic algorithm methods

Genetic algorithm⁹³ are another approach to explore the configurational landscape by mimicking biological evolution, which can also avoid the problems related with a single starting point, by introducing a population of structures. The initial population is usually produced by random configurations of atoms and then is being used to create new generations by mimicking evolutionary mechanisms like crossover, mutation and natural selection. According to natural selection, the organism that fits better to the environment continues to evolve. Thus, in genetic algorithms it is principal to define a fit function, which clearly becomes energy of a structure for physical sciences, so that the lower the energy, higher the fitness. Crossover is described as taking two parent structures and combining them to obtain a new candidate structure for the new generation, whereas mutation is described as a random change on a single structure. However to optimize the efficiency of the algorithm there are several implementations of genetic algorithms varying how the crossover and mutation operators actually defined, how competition is simulated to become a parent structure and how the population is renewed or updated. Usually roulette wheel method is being used for the selection of parent structures. In this method, fitness value is taken for a random selected structure and compared with again a random number which is generated in a range covering all of fitness values in the population, and the procedure continues until two parent structure being selected for crossover. Thus, it is more likely that the low energy structures are being selected. After the selection, a crossover operation is used for mixing the parent structures, for which there is generally two types of approaches according to whether a genotype representation was used to define the phenotype of the structure or not. If there is not, crossover operators are defined as working directly on phenotypes, which are simply atomic positions for our case. By mixing structures it is likely to found better structures constituting from low-energy regions of the present structures, however no new low-energy regions are being introduced usually. Mutation operators serve better for this purpose as they operate on a single structure and the ability to introduce new low-energy regions by random changes like moving atoms, twisting the structure, swapping of atom types or even replacing with a random structure to keep the structural diversity. The selection of the new population includes always elitism, which is at least keeping the best structure from the last generation and usually

taken more than one and merged with new generated structures with higher fitness. Duplicate structures are also eliminated to avoid a deadlock in a local minimum. The efficiency of genetic algorithm method has been shown in a series of studies for metallic and alloy clusters,⁹⁴ for oxide structures,⁹⁵ and for molecular crystals.⁹⁶

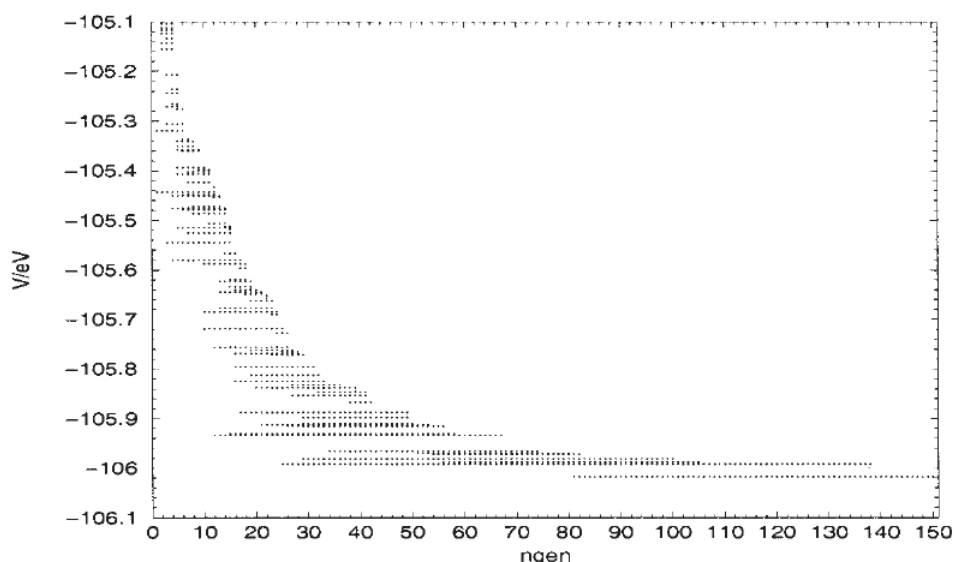


Figure 18. An example of genetic algorithm method used for $\text{Pt}_{12}\text{Pd}_{12}$ nanoclusters.⁹⁷

5. Scale and Dimensionality

5.1. Introduction

Going from the macroscopic scale to the atomic or molecular scale, one passes through the nanoscale where the properties of materials can change drastically because of both size and surface effects. The former is often termed the quantum size effect, which is the change in bulk electronic structure at the atomic scale due to influence of discrete electronic levels. The latter is surface or interface induced effect, which becomes important by the enormous increase of the surface to bulk ratio at reduced scales. Research into the properties of materials at the nanoscale (the term “nano” refers to 10^{-9}m by definition and roughly corresponds to systems with 1-100 nm dimensions.) have had a great impact on the development of science and technology. The application performance of materials is determined by their properties which, in turn, strongly

depend on their size and structure. The importance of the nanoscale is underlined by the way it opens up to opportunities to synthesize new (nano)materials with unique structure and properties. The research area concerned with the study of these new nanostructures and their properties is called nanoscience. The utilization of these new materials towards potential new applications found the basis of the field of nanotechnology.

Structures can be naively classified by their scale as 3-dimensional (3D), 2-dimensional (2D), 1-dimensional (1D) and 0-dimensional (0D) in terms of the size of that corresponding dimension as shown in Figure 19. Materials having a nanosized length scale at least in one dimension are called nanostructures.

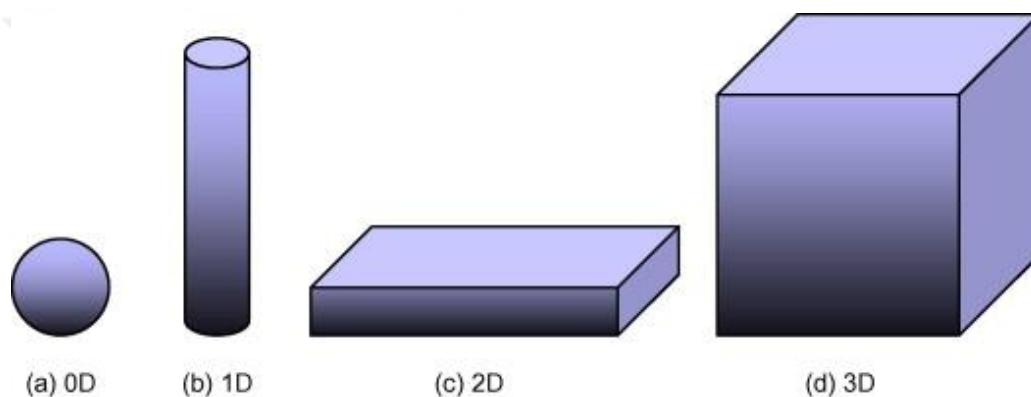


Figure 19. Schematic representations of (a) 0-dimensional (0D), (b) 1-dimensional (1D), (c) 2-dimensional (2D) and (d) 3-dimensional (3D) structures.

In general there are two approaches to produce nanostructures: top-down and bottom-up. The top-down approach obtains nanostructured materials from a parent bulk material by size-reduction via various techniques, while the bottom-up approach forms nanostructures by the assembling of atoms or particles.

5.2. Synthesis of nano-ZnO

To prepare ZnO nanostructures, both physical and chemical methods can be used within these two approaches. Wet chemical etching⁹⁸ is one example of a top-down approach. However high cost, high time-consumption, low controllability and repeatability of top-down approaches makes bottom-up approaches more promising and more researched. Molecular beam epitaxy,⁹⁹ metal-organic chemical vapor deposition,¹⁰⁰ pulsed laser deposition in a controlled atmosphere¹⁰¹ or in liquids¹⁰² are some examples

of physical bottom-up approaches to obtain nanostructured ZnO thin films with high crystallinity, high homogeneity and adaptable chemical compositions. Chemical methods like sol-gel,¹⁰³ electrochemical¹⁰⁴ or hydrothermal pathways¹⁰⁵ are known to have the advantage of allowing one to obtain extremely small structures with tunable dimensions. However the crystalline quality may be less because of the potential presence of impurities in the solution phase.

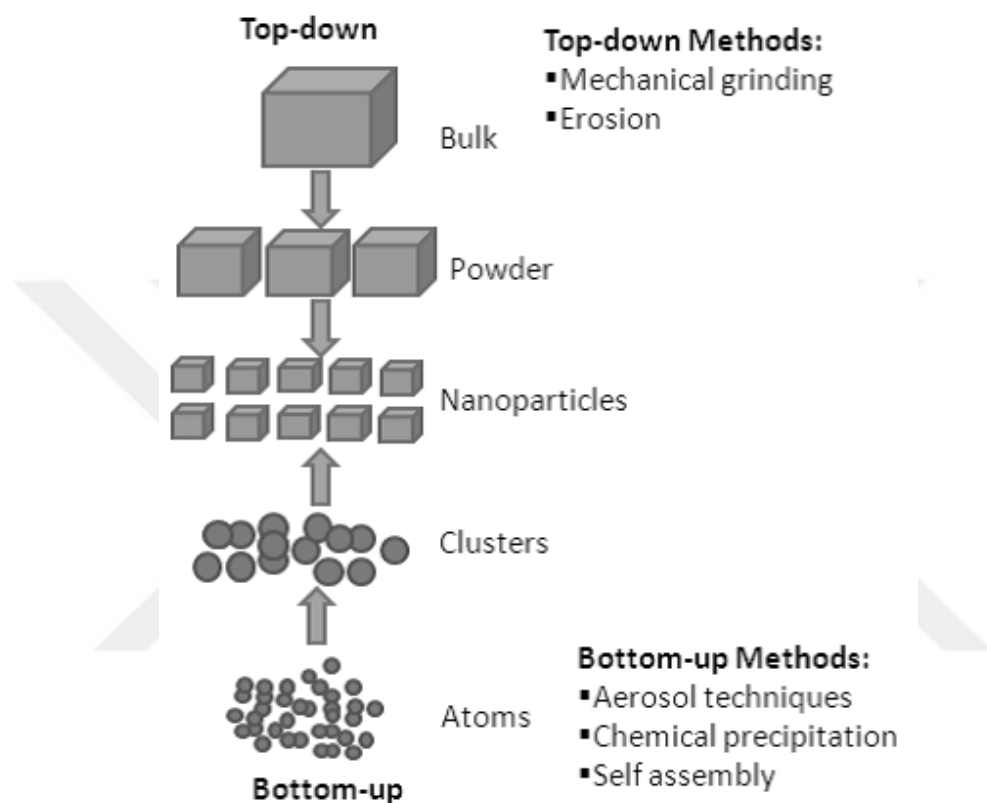


Figure 20. Illustrative example of top-down and bottom-up approaches.

5.3. Nanostructured 3D materials

As previously discussed, the bulk is considered to have a packing of atoms extending to the macroscopic scale. In other words the bulk has dimensions considerably larger than the nanoscale in all three orthogonal crystallographical directions. The periodicity, and extent of structural order defines the crystallinity, ie separates the crystalline, polycrystalline and the amorphous structures as mentioned in previous section. Polycrystalline bulk materials, if the grain sizes are in the nanoscale, can be classified as 3D nanostructures. In nanostructured materials a large volume fraction of the atoms are on the interfaces, mainly on grain boundaries due to very small grain sizes. Thus nanostructured materials have significantly different or improved properties than their

polycrystalline counterparts, such as increased hardness, enhanced diffusivity, improved ductility, higher electrical resistivity¹⁰⁶.

5.4. Nanofilms (2D)

A thin film is a layered structure of a material ranging from fractions of a nanometer to several micrometers in thickness in the direction normal to the layers, whereas having long range periodicity on other two dimensions. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction. The chemical, physical, mechanical, and electronic properties of thin films can be extremely different from those of the corresponding bulk materials. With the increase of the surface to volume ratio due to the reduction in size and dimensions, the low coordinated surface atoms play a dominant role in the thermodynamics and kinetics of these systems, resulting in complex phenomena such as surface reconstructions, island formation, nanostructure formation etc. The emergent films often contain nano or microscale morphological features that display novel size and morphology-dependent properties which can be exploited in a number of technological applications. Metal oxide thin films provide a rich platform for exploring novel device applications because they have a variety of functionalities. Many metal oxide thin film systems have traditionally been used as important device materials like dielectric insulators, temperature sensors, transparent conducting oxides, phosphors, etc.

Fabrication of 2D nanomaterials is usually accomplished on a substrate which is called epitaxial growth and over the past decades sophisticated techniques have been developed to achieve a controlled deposition down to single atomic layers. With the advances in microelectronic fabrication processes, several vapor-phase techniques were used to obtain controlled deposition of 2D nanomaterials.¹⁰⁷ Although vapor-phase techniques are energy intensive and usually require exceptionally clean environments, the technology is commercially viable by large scale production. Alternative methods to fabricate 2D nanomaterials are spin-coating of colloidal nanoparticles or layer by layer dip-coating processes into colloidal suspension of nanoparticles. Both these techniques require synthesis of nanoparticles in colloidal form by solution chemistry. The obtained 2D material is usually textured and non-epitaxial. Such strategies have potential applications in where cost efficiency is more important over high-quality and repeatable

performance, for example qualitative sensors.¹⁰⁸ In recent years a single layer of graphite sheet, which is called graphene, has been synthesized via solution based chemical techniques and without a supporting substrate.¹⁰⁹

2D materials exhibit surfaces perpendicular to the growth direction. The stability of the exhibited surface is one of the main factor that determines the morphology of the 2D material and it can be defined by the surface energy (E_{sur}):

$$E_{sur} = E_{slab} - n \times E_{bulk}$$

where n is the number of atoms, E_{slab} is the cohesive energy of finite crystal and the E_{bulk} is the cohesive energy per atom in infinite crystal. Thus the surface energy (E_{sur}) becomes the excess energy associated with the surface. Surface energy plays an important role in growth and nucleation processes. For ionic materials, when there is a dipole moment perpendicular to the surface in the unit cell, the surface energy diverges and becomes infinite, which means such surfaces cannot exist.¹¹⁰ The apparent occurrence of such polar surfaces has been attributed to some stabilization processes like adsorption of other atoms or surface roughening. Tasker categorized the surfaces of ionic or partly ionic crystals into three types as illustrated in Figure 21. Type 1 consists of stoichiometric proportions of cations and anions in each plane and thus exhibit neutral surfaces. Type 2 exhibit charged surfaces but has no dipole moment in the repeating units perpendicular to the surface due to the cancellation inside the unit cell. However the Type 3 surfaces exhibit charged surfaces with a dipole moment in the repeating unit perpendicular to the surface. Therefore these Type 3 surfaces have an infinite surface energy and an electric field throughout the crystal due to charged surface. Thus Type 3 surfaces cannot exist as a simple termination of the frozen bulk structure and can only be prepared as a reconstructed surface in such a way to compensate the polarity.

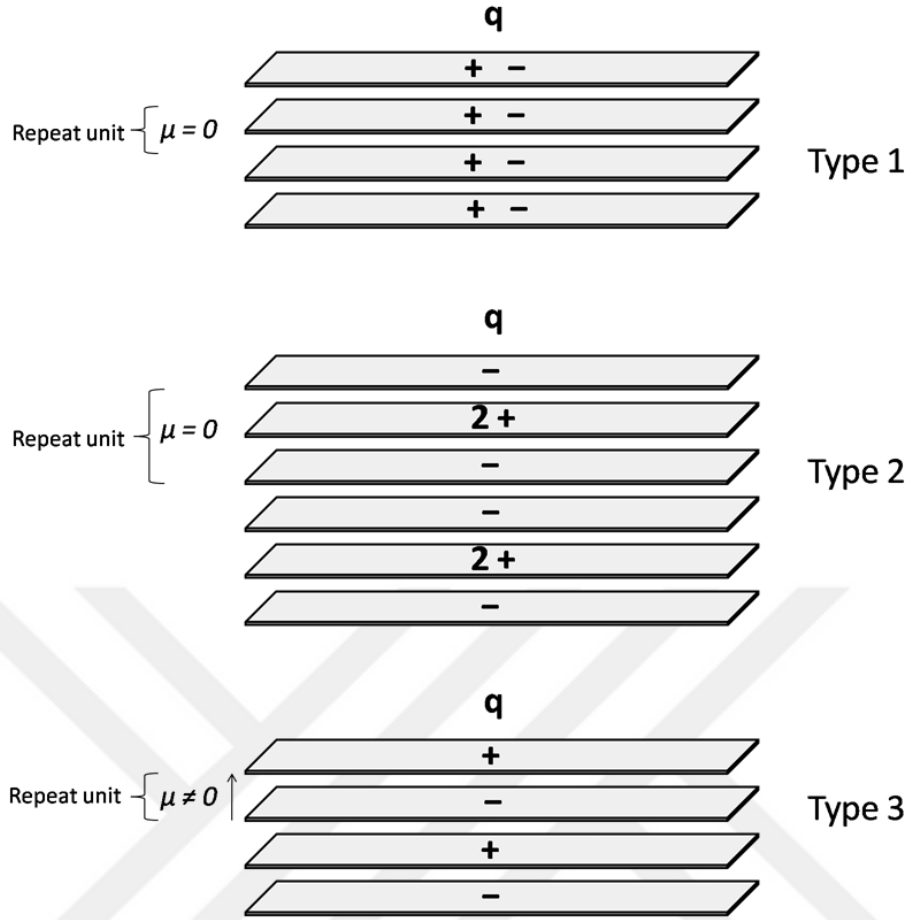


Figure 21. Distribution of charges q on planes for three stacking sequences parallel to surface.

ZnO thin films have been prepared by many methods like chemical vapor deposition¹¹¹, sputtering,¹¹² sol-gel method,¹¹³ pulsed layer deposition¹¹⁴ and spray pyrolysis.¹¹⁵ In Industry, for large-scale deposition sputtering is mainly used due to its high deposition rate and high uniformity. At room temperature, films grown by pulsed layer deposition technique tend to be amorphous, however at elevated substrate temperatures deposition can result in highly textured films with the c-axis oriented perpendicular to the substrate plane.¹¹⁶ In other layer-by-layer growth techniques the prevalence of c-axis oriented material is also observed whereas it is considered to be a polar surface.¹¹⁷

For wurtzite ZnO, c-axis oriented [0001] Zn and [0001] O face terminations are both Tasker type 3 surfaces. These two surfaces can be seen as a stacking sequence of hexagonal Zn and O layers along the crystallographic c axis with alternating distances of $R_1 = 0.61 \text{ \AA}$ and $R_2 = 1.99 \text{ \AA}$ and thus a reconstruction of the surface layer charge by a factor of $R_1 / R_1 + R_2 \approx 1/4$ less positive for Zn terminated (or less negative for O

terminated) is needed for a charge compensation.¹¹⁸ This charge compensation can be achieved by three suggested mechanisms:¹¹⁹

- Creation of surface states and transfer of negative charge from the O to the Zn face.
- Removal of surface atoms
- Oppositely charged foreign atom adsorption on the surfaces

Among them, which is the exact mechanism involving the stabilization of the [0001] surface of ZnO is still debated and a combination of different mechanisms can be also responsible such as surface reconstruction and hydrogen adsorption.¹²⁰ More recent work shows nanoisland reconstructions are responsible for stabilization process.¹²¹ In terms of theoretical values of cleavage energies, non-polar surfaces $[10\bar{1}0]$ $[11\bar{2}0]$ are found to be more stable than the polar $[0001]$ -Zn and $[000\bar{1}]$ -O surfaces,¹²² whereas for thinner layers graphitic-like (layered)ⁱ layers, which can be seen as a flattening reconstruction of $[0001]$ surfaces to get rid of the dipole moment, are found to be lower in energy up to the 36 layers.¹²³

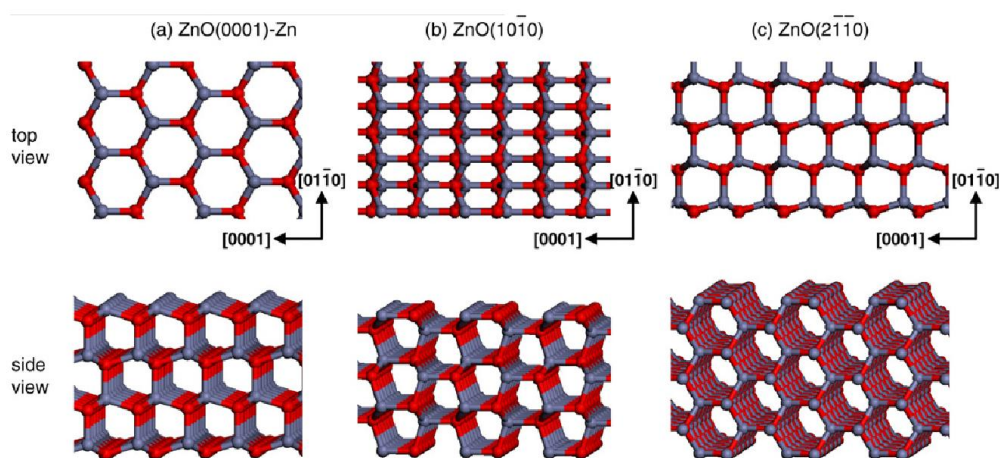


Figure 22. surfaces of wurtzite ZnO.

In a later theoretical work, Morgan suggested another promising nonpolar film structure (the Body Centred Tetragonal (BCT) structure), which is found energetically lower even

ⁱ In ref ¹²³ the layer-ZnO structure is reported as being graphitic. Strictly speaking, the layer-ZnO phase has a different layer stacking to graphite, and is thus analogous to the layered hex-BN phase.

than the layered phase up to 28 layers.¹²⁴ Experimentally, layered phase (see Figure 23) of ZnO for very thin layers are confirmed both on Ag(111)¹²⁵ and Pd(111)¹²⁶ surfaces. The BCT structure has still not been observed as a film structure itself possibly due to epitaxial symmetry issues, but has recently been observed as a surface reconstruction on the wurtzite ZnO (10 $\bar{1}$ 0) surface.¹²⁷

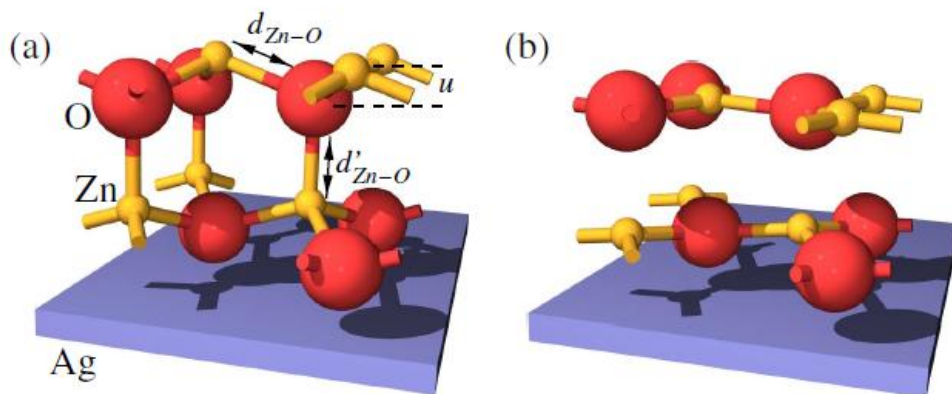


Figure 23. Illustrative model of (a) wz-ZnO and (b) layered-ZnO on Ag surface.

5.5. Nanowires (1D)

One dimensional nanomaterials have nanoscale sizes along two dimensions and they usually have a rod-like or wire-like appearance. Unlike films and particles, 1D nanomaterials have two possible axes of alignment with respect to a substrate. Deposition of nanowires parallel to a substrate can be achieved by various microelectronic fabrication technologies such as chemical etching,¹²⁸ electron or ion beam lithography¹²⁹ for semiconducting materials. Also electron or focused ion beam patterning/writing¹²⁹ X-ray or extreme UV photolithography can be used in combination with vapor-phase depositions to obtain nanowire patterns along the substrates which are compatible with the planar geometries of microelectronic devices.¹³⁰ These lithography based techniques belongs to ‘top-down’ approach. Besides, to obtain size and shape selective fabrication, ‘bottom-up’ approaches are used via crystallization of atoms or molecules in a controlled manner which usually results in vertical oriented nanowire-arrays to a substrate.¹³⁰ Several optoelectronic¹³¹ and piezoelectric applications¹³² make use of these vertically aligned nanowire arrays of semiconductors.

The interest in ZnO has increased with the discoveries of new nanostructured morphologies. It has been shown that ZnO can be grown in a wide variety of shapes and structures by using different growth techniques.¹³³ For example, as 1D nanostructures ZnO can take the shape of nanorods, nanotubes, nanocages, nanowires, nanotetrapods, nanoflowers and more.^{134,135} 1D nanostructures of ZnO shows different novel properties to 3D and 2D structures due to their higher surface area to bulk ratios and single crystalline surface facets. The usually observed crystal faces on 1D nanostructures ZnO are the (0001), (10 $\bar{1}$ 0) and (2 $\bar{1}$ $\bar{1}$ 0) facets of wurtzite.

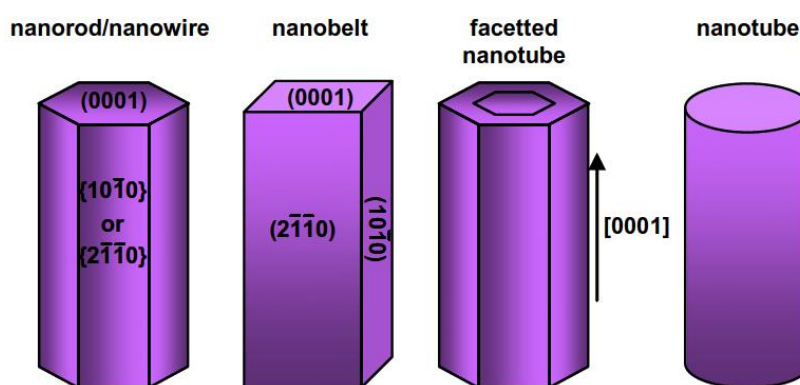


Figure 24. Schematic diagram of common 1D ZnO morphologies.

The most observed 1D nanostructures are nanorods and nanowires. The only difference of these two structure is that nanorods have a hexagonal cross section along the growth direction while nanowires have not. The growth direction is observed as [0001] while the nanorods show faces of (10 $\bar{1}$ 0) and (2 $\bar{1}$ $\bar{1}$ 0). Nanowires and nanorods can be grown with diameters as small as 4 nm¹³⁶ and 6.5 nm¹³⁷ respectively. Nanobelts are another observed 1D nanostructure which have rectangular cross-sections. Nanobelts can be grown with uniform width along their entire length with typical widths of 50-300 nm and thicknesses of 10-30 nm.¹³⁸ Hollow 1D nanotube nanostructures can also be grown with small wall thicknesses as small as 5 nm.¹³⁹ Another important nanostructure for ZnO is the nanotetrapod, which consist of a zinc blendestructured core connected with four wurtzite-structured arms. Nanotetrapods have the advantage that they may spontaneously orientate with one arm directed to the normal to the substrate, and have found immediate application in composite polymer/nanocrystal solar cells.¹⁴⁰

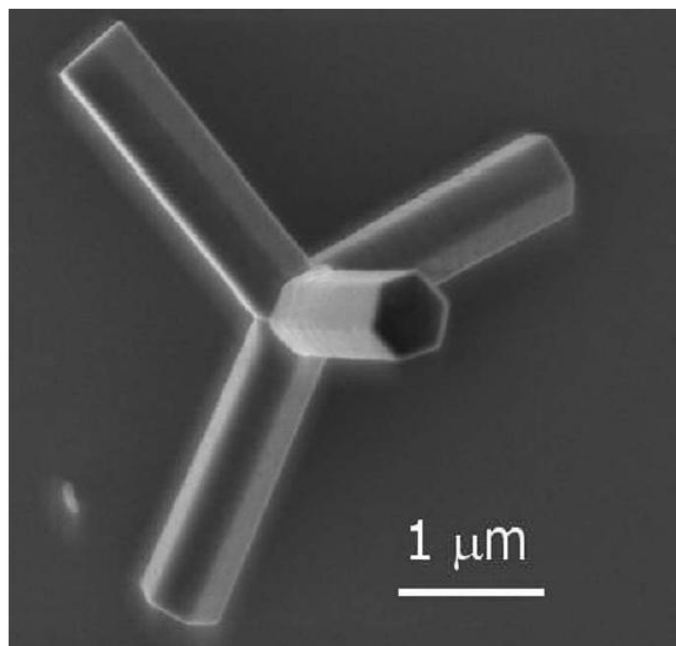


Figure 25. SEM image of a ZnO tetrapod.

5.6. Nanoclusters (0D)

Zero dimensional nanomaterials, or nanoparticles, have nanoscale sizes along all three dimensions. Zero dimensional nanoparticles can be single crystalline, polycrystalline or amorphous and may exhibit all possible morphologies. If the nanoparticles are single crystal, they are called nanocrystals. Nanoparticles with sufficiently small dimensions to observe quantum effects are called quantum dots. Nanoparticles are of great scientific interest because they form a bridge between atomic or molecular structures and bulk materials. First modern scientific experiments with nanomaterials were done by Michael Faraday in 19th century as the determination of the particulate nature of colloidal gold and size dependent optical properties.¹⁴¹ 0D nanomaterials can be fabricated by physical processes like tribology¹⁴² or vapor phase epitaxial depositions¹⁴³ as well as chemical synthesis techniques such as (co-)precipitation,¹⁴⁴ sol-gel processes¹⁴⁵ and thermal decomposition of organic complexes.¹⁴⁶

The recent heavy interest on the synthesis and characterization of zero dimensional nanoparticles is mainly due to the wide range of applications of these materials in energy conversion, electronics and catalysis. The explanation of the structures and properties of nanoparticle materials is difficult because it is often highly problematic to determine the structure from experiment. Although small angle scattering and X-ray

absorption spectroscopy can provide useful information, they lack to give a detailed structural model. High resolution electron microscopy can provide detailed images of cluster structures, however they are often difficult to apply. A range of spectroscopic techniques that being employed usually give indirect and incomplete information. The difficulties are mainly related with the different behaviour of nanoparticles varying with size. Thus, the need to obtain atomic level models of crystal nucleation and the early stages of growth, which involves the formation and evolution of nano-clusters increases and stimulates the field further.

The structural and optical properties of ZnO nanoparticles are mainly determined by their size. Wood et al.¹⁴⁷ recognized three length scales, or regimes for ZnO nanoparticles which are macroscopic, quantum dots and clusters. Macroscopic particles maintain the crystal structure of the bulk and the optical band gap is practically constant while surfaces and point defects give rise to specific size-independent phenomena like UV, blue-green, yellow-orange and red luminescence. Quantum dots are nanoparticles with sizes of the order of the exciton radius, 15-30 Å at least in one dimension. In this regime even though the X-ray diffraction lines are broadened, the bulk crystal structure is preserved. The order of the stability between the phases change and the optical absorption bands shift and deform because of quantum size effects. The cluster regime is where the structures of the particles may differ significantly from that of the bulk phases. In this regime clear diffraction patterns are not obtainable and the optical properties cannot be directly correlated with those of the bulk. For ZnO and for many other materials experimental techniques are not capable of reliable characterization of the structure yet and thus is the least understood regime. The characteristic size separating the quantum dots and cluster regimes is not general and is found to be system dependent.

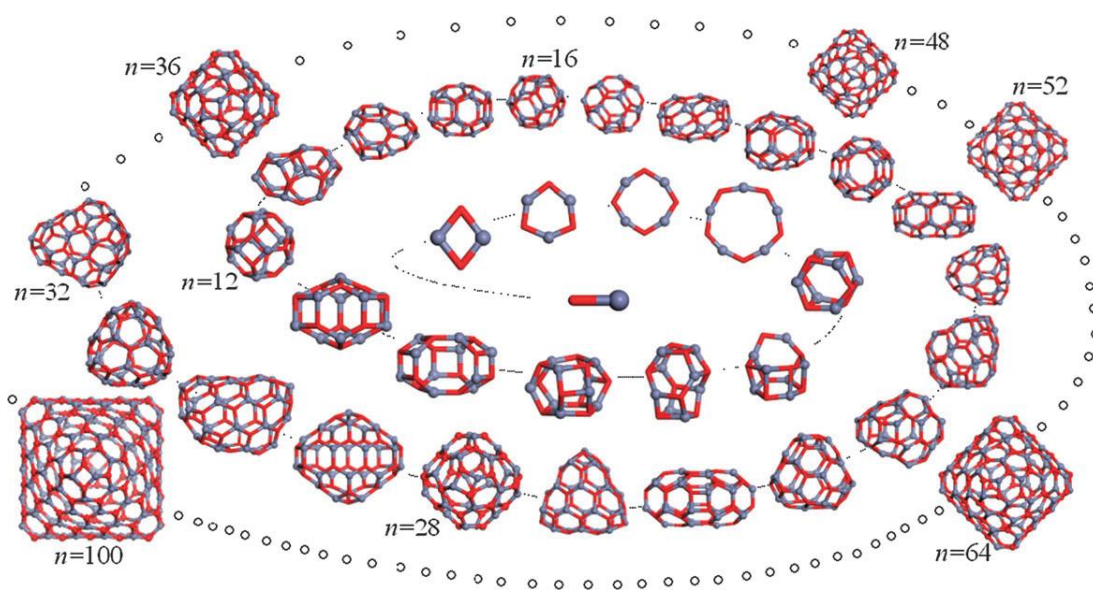


Figure 26. Global minimum structures of $(\text{ZnO})_n$ nanoclusters.¹⁴⁸

6. Nanoporous systems

6.1. Introduction

Low density crystalline bulk materials can possess periodic nanosized void spaces. This special class of materials, known as nanoporous materials, are abundant in nature, both in biological systems and in natural minerals. Some very well known examples of nanoporous systems are zeolites and metal organic frameworks (MOFs). Nanoporous materials are subdivided into three categories according to their pore radius:

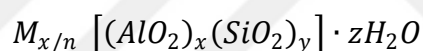
- Microporous 0.2-2 nm
- Mesoporous 2-50 nm
- Macroporous >50 nm

One of the main reason of the interest on porous solids is because their capability to interact with molecules, ions or atoms throughout the bulk of the material as well as their surfaces, which makes them very useful especially in catalysis or as membranes. In a porous structure, voids with molecular dimensions can manipulate, arrange, separate or activate molecules and the size and shape of voids determine these processes while the chemical identity of surfaces or reactive sites control selectivity and reactivity. Nanoporous materials are becoming increasingly important with the growing ability to control their pore sizes, which in turn tailors their physical and chemical properties for particular applications.

6.2. Zeolites

Zeolites are a specific class of microporous oxide materials made up of silicon, aluminum and oxygen atoms. Zeolite minerals are broadly present in nature and have been known for more than 200 years. Primarily Swedish mineralogist Axel Fredrick Cronstedt discovered a natural occurring mineral which loses large amounts of steam upon heating. Thus, he named that material (which is nowadays known as stilbite) as ‘zeolite’¹⁴⁹ which comes from the classical Greek, where ‘zeo’ means ‘to boil’ and ‘litos’ means ‘stone’ and later it became a general name for this type of material. Nowadays, zeolites are produced on a large scale and are available and used in a variety of applications such as ion exchangers in laundry detergents, where they replace calcium and magnesium ions in water with sodium ions present in the zeolite¹⁵⁰ or as adsorbents in gas stream purification to remove water and volatile organic molecules.¹⁵¹

Structurally, zeolites are based on fundamental building blocks of tetrahedral SiO_4 and AlO_4 units giving rise to a three dimensional network. It has a structural formula of



Where M is an exchangeable cation of valence n, z is the number of water molecules and x+y gives the number of tetrahedral building blocks present in the unit cell. Water and cations are found inside the pores. Si and Al atoms, which are called framework atoms, are coordinated tetrahedrally to four oxygen atoms bridging two framework atoms as shown in Figure 27.

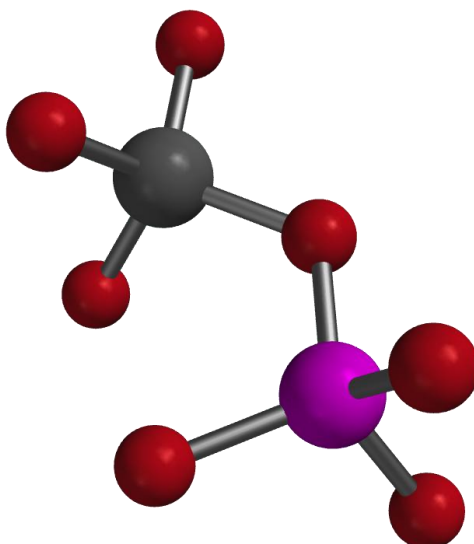


Figure 27. The building unit TO_4 where T denotes for framework atoms.

This tetrahedral TO_4 unit is called a primary building unit (PBU). By further grouping PBUs one can also view zeolites in terms of an infinite lattice of identical building blocks called secondary building units (SBU). SBUs are chosen such a way that entire framework is described by one type of SBU only. Also it should be noted that SBU's are non-chiral and an integral number of SBU always exists in a unit cell. Some SBU structures are given in Figure 28.

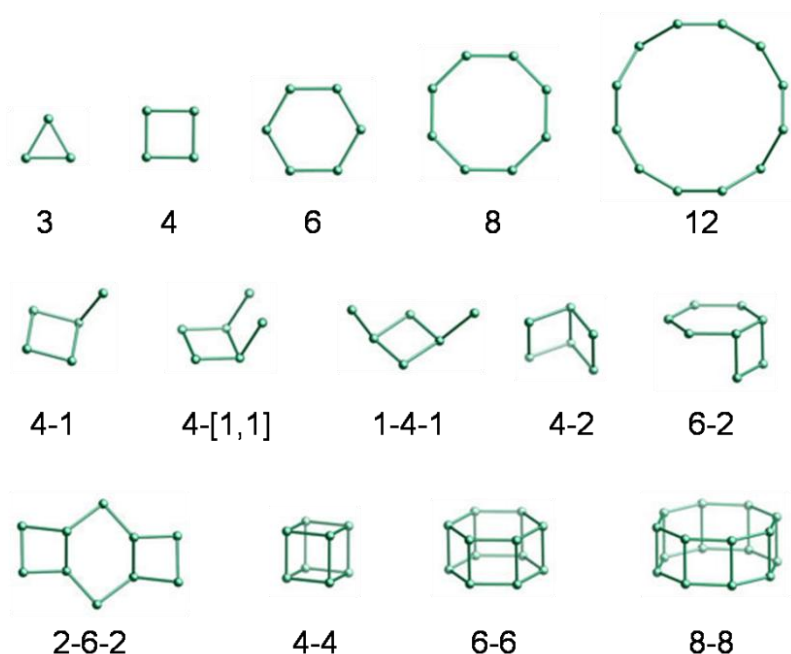


Figure 28. Examples of secondary building units (SBU) of zeolite frameworks. Each cyan ball represents one framework atom.

To understand the topology and identify the relations between framework types it is also useful to describe zeolite frameworks with composite building units (CBUs) and chains. The difference is that the latter cannot necessarily be used to build the entire framework and are not required to be non-chiral. Some examples of CBUs and chains are given in Figure 29. It should be noted that the three lower case letter codes of CBUs are related with the three capital letter codes of some zeolite structures.

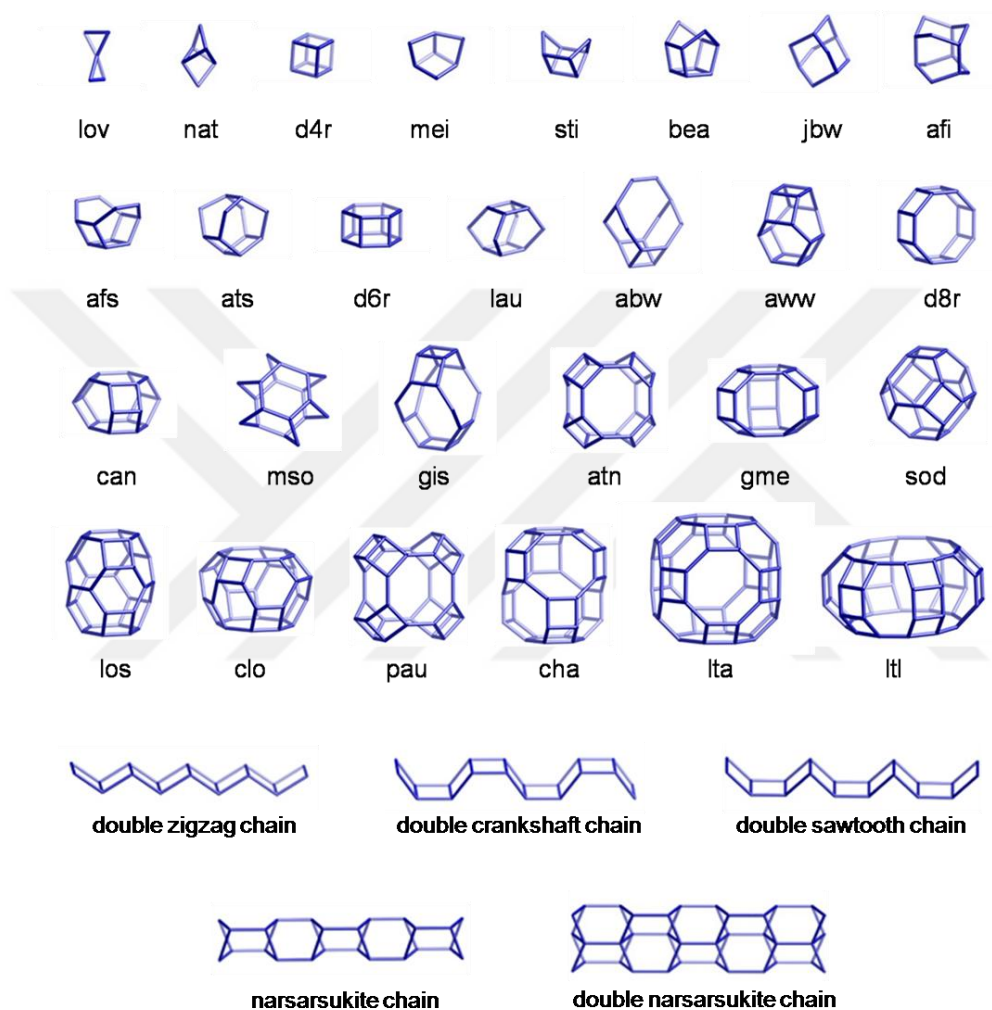


Figure 29. Examples of (a) composite building units (CBUs) and (b) chains for zeolite frameworks.

Zeolite frameworks are denoted with three capital letter codes assigned by the structural committee of International Zeolite Association (IZA). The three-letter codes are mainly derived from original mineral names and for interrupted frameworks three-letter code is preceded by a hyphen. Some of the naturally found zeolite minerals and their three-letter codes are given in Table 5.

Table 5. Some natural zeolites and date of discoveries.

Stilbite	STI	1756	Edingtonite	EDI	1825
Natrolite	NAT	1758	Faujasite	FAU	1842
Chabazite	CHA	1772	Mordenite	MOR	1864
Analcime	ANA	1784	Offretite	OFF	1890
Laumontite	LAU	1785	Erionite	ERI	1890
Thomsonite	THO	1801	Dachiardite	DAC	1905
Heulandite	HEU	1801	Stellerite	STI	1909
Gmelinite	GME	1807	Ferrierite	FER	1918
Gismondine	GIS	1816	Yugawaralite	YUG	1952
Brewsterite	BRE	1822	Bikitaite	BIK	1957
Epistilbite	EPI	1823	Paulingite	PAU	1960
Philipsite	PHI	1824	Mazzite	MAZ	1972
Levynite	LEV	1825	Merlionite	MER	1974

The porous structure of zeolites comes from the n -rings (where n is the number of tetrahedrally coordinated atoms in a ring) formed by these building units which form pore channels and inner cavities. A zeolite framework structure can have a pore system with infinite channels in one, two or three dimensions, corresponding to pore dimensionalities of 1, 2 and 3 respectively. The diameters of the cavities and pores for zeolite structures usually vary from 3 Å to 12 Å which coincides with the scale of many hydrocarbon molecules and thus make these materials attractive for applications as adsorbents and catalysts. Also zeolites can be used to fabricate nanostructures. For example, in the synthesis of ZnO nanostructures, zeolites¹⁵² are also used as well as other mesoporous structures like porous carbons,¹⁵³ porous silicon¹⁵⁴ as nanoscale templates. The fabrication of ZnO inside a porous structure is a way to achieve extremely small nanostructures, which should improve the properties related with quantum size effect due to the immense size reduction. Control of the pore size, also restricts the maximum particle size, giving the opportunity to tune the properties of nanostructures. Thus, zeolite structures with regularly distributed small pore sizes become promising.

6.3. Nanoporous ZnO

Although zeolite term is defined for aluminosilicates, it also encompasses for other microporous structures containing different elements such as gallium, germanium, boron, titanium.¹⁴⁹ While zeolite structures can be used in fabricating extremely small ZnO nanostructures, zeolite polymorphs of ZnO can also be imagined, knowing that zeolitically inspired ZnO-based structures can be synthesized with various techniques¹⁵⁵¹⁵⁶¹⁵⁷. A structural analogy with aluminosilicate zeolites and ZnO can be made by assigning both Zn and O atoms as tetrahedral framework atoms since in ZnO both Zn and O atoms are tetrahedrally coordinated (O atoms bridge two framework atoms in aluminosilicate zeolites). The primary building units of such an analogy is given in Figure 30.

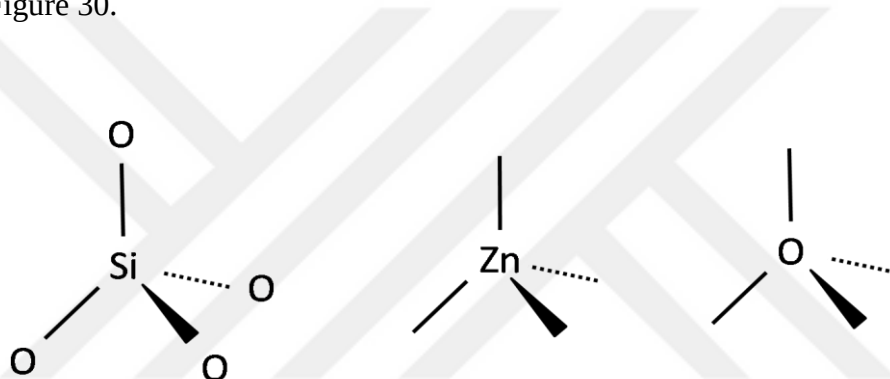


Figure 30. Primary building unit of Silicates (left) and the two analog primary buildings of ZnO (right).

Some zeolite frameworks, have been previously suggested as possible bulk polymorph structures for ZnO in theoretical calculations; (e.g. BCT¹⁵⁸ and SOD¹⁵⁹). The BCT and SOD zeolite frameworks are shown in Figure 31.

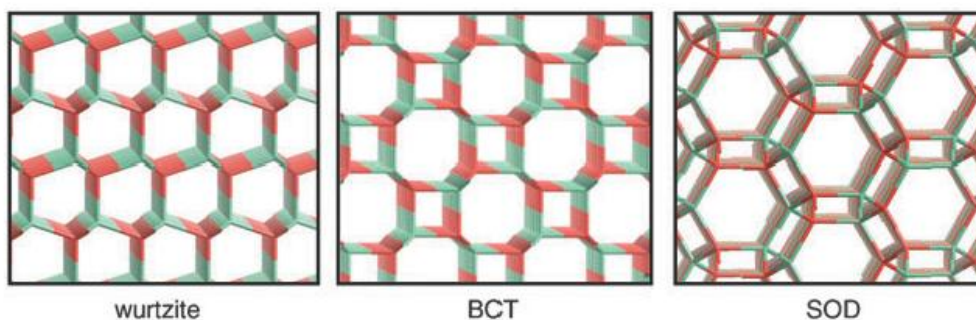


Figure 31. Structures of BCT and SOD zeolite frameworks.

The possibility of the BCT structure being a new ZnO polymorph follows theoretical results on similar materials such as ZnS and LiF. For ZnS nanocrystals, the BCT structure has been calculated to be more stable than the bulk phases,¹⁶⁰ and for bulk LiF, BCT structure is predicted as metastable.¹⁶¹ Later for ZnO a wurtzite→BCT transition was observed for nanorods under uniaxial strain with molecular dynamics simulations.¹⁶² For ZnO nanoclusters, the BCT structure has been also observed to form spontaneously in down-stroke pressure-driven transitions by molecular dynamics simulations.¹⁶³ Following these results, Morgan showed theoretically that for nanofilms of ZnO, the BCT structure is energetically more favorable than wurtzite structure up to 56 monolayers by density functional calculations.¹⁵⁸ With respect to the SOD framework, for (ZnO)₁₂ nanoclusters SOD cage structure has been found to be the ground state by means of density functional theory calculations and an extended SOD-ZnO phase was also suggested to be accessible via coalescence of nanocluster building blocks.¹⁵⁹ In a later theoretical study, the SOD structure has been found to be lower in energy than a previously suggested nested cage structures for (ZnO)₆₀ and the SOD motif was suggested as being very energetically competitive for larger (ZnO)_n clusters due to smaller influence of surface reconstruction.¹⁶⁴ For bulk phases, the study of the energy versus volume equations of state for possible polymorphs revealed that SOD phase would be thermodynamically stable under suitable negative pressures.¹⁶⁵ It should be also noted that the energetical stabilities of SOD and BCT phases are closer to the ground state wurtzite structure than the experimentally obtained rocksalt phase as can be seen in Figure 32.

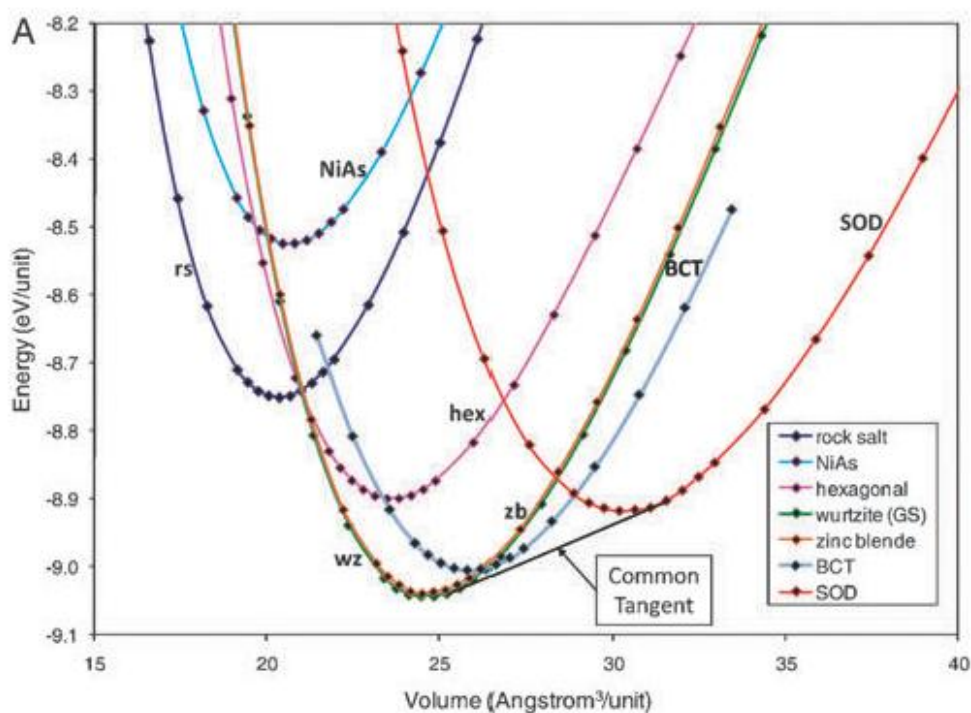


Figure 32. Energy versus volume plots for ZnO phases.¹⁶⁵

As an alternative approach to the structural analogy in Figure 30, we can also follow an analogy with aluminosilicate zeolite structures. Starting from pure SiO_2 , an aluminosilicate can be seen as a replacement of some fraction of Si^{+4} cations with cations having a similar ionic radius and a +3 charge (e.g. Al^{+3}), and a larger cations (e.g. K^+) to compensate the charge. The +3 cations incorporate into the 4-connected network and the charge-compensating larger cations reside in the void space, and determine the shape of framework together with the absorbed water. Such substitutions of silica are well-known to be energetically favorable from experimental calorimetry and theoretical calculations have showed that aluminosilicate zeolite frameworks are energetically the most likely products for large alkali metal cations (K^+ , Rb^+ , Cs^+).¹⁶⁶ An analogy with ZnO can be made by substitution of a fraction of Zn^{+2} cations with similar sized cations such as Li^+ and larger cations such as K^+ to obtain a zeolitic framework. For ZnO such co-substitutions have reported in a small number of experimental studies.¹⁶⁷ For example $[\text{K}][\text{LiZn}_3\text{O}_4]$, where 25% of Zn^{+2} cations were replaced by K^+ and Li^+ cations, was prepared experimentally and is found to have the ATN zeolite framework by means of single crystal X-ray techniques.¹⁶⁸ As can be seen in Figure 33 small Li^+ cations incorporate into the 4-coordinated network as a Zn^{2+}

cation while larger K^+ cations open the structure and causes the porous ATN network. Theoretical results also supports that the co-substitution of Zn^{+2} cations in ZnO with Li^+/K^+ or Li^+/Rb^+ are energetically favored and that the thermodynamically stable dense polymorphic structure types found in the pure material are energetic destabilized, while open structures with large rings and cages are stabilized.¹⁶⁹

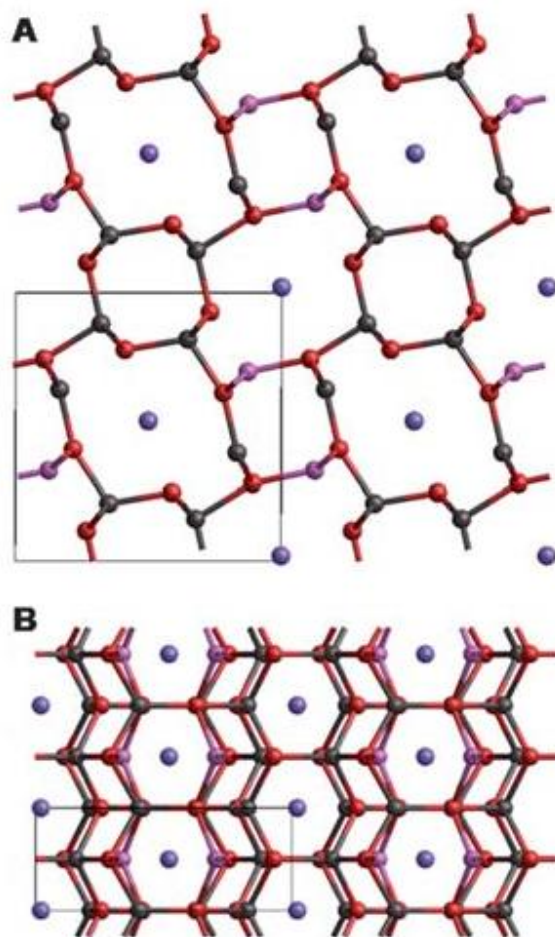


Figure 33. Top and side views of $[K][LiZn_3O_4]$ structure in ATN zeolite framework.



CHAPTER II: METHODOLOGY

In order to understand the properties of the materials, their atomic configurations must be known. One of the simplest to describe but difficult to solve problem in computational chemistry is the determination of atomic configuration. Any computational approach to study a chemical system requires a mathematical model to calculate the energy of the system as a function of its configuration. The success of the approach will depend on the quality of the mathematical model used. For smaller chemical systems studied, quantum mechanical (QM) approaches are appropriate and feasible. Walter Kohn and John A. Pople jointly won the Nobel prize in chemistry in 1998 for the development of the density-functional theory and computational methods in quantum chemistry. However, QM methods are typically limited to system of approximately a few hundreds of atoms, although approaches to treat large systems are under development. Also some of the chemical or biological processes require higher time scales between microsecond to millisecond, while the individual time step of the methods commonly used today are of the order of femtosecond. Thus the energy function might be subjected to over 10^8 energy evaluations even in a single simulation. Large numbers of evaluations are also required for using global optimization techniques to search the configurational energy landscapes. Atomistic models can fulfil the demands required by computational studies of larger systems or larger evaluations. Atomistic models use force fields, in which atoms are the smallest particles in the system rather than the electrons and nuclei used in quantum mechanical descriptions. The mathematical equations in these energy functions include relatively simple terms to describe the physical interactions that dictate the structure and dynamical properties. These simplifications allow for the computational speed required to perform a large number of energy evaluations.

1. Energy Landscapes

The investigation of the structural and dynamical behavior of complex chemical systems, such as large clusters, strongly correlates with the investigation of the underlying potential energy surface (PES). The exact description is very complex, however, predictions can be made using knowledge of the stationary points of the PES.

Stationary points of a PES are points with a vanishing gradient such as minima, maxima, or saddle points. Methods which investigate these points can be summarized as energy landscape methods. The concept of energy landscapes was first proposed by Bryngelson and Wolynes¹⁷⁰ in the context of free energy surfaces, and a detailed summary on energy landscapes is given in the textbook of David J. Wales.¹⁷¹ The most important stationary points of a (potential) energy landscape are local minima and maxima, the global minimum and maximum, as well as transition states (first order saddle points). An illustration of a multi-dimensional PES is given in Figure 34.

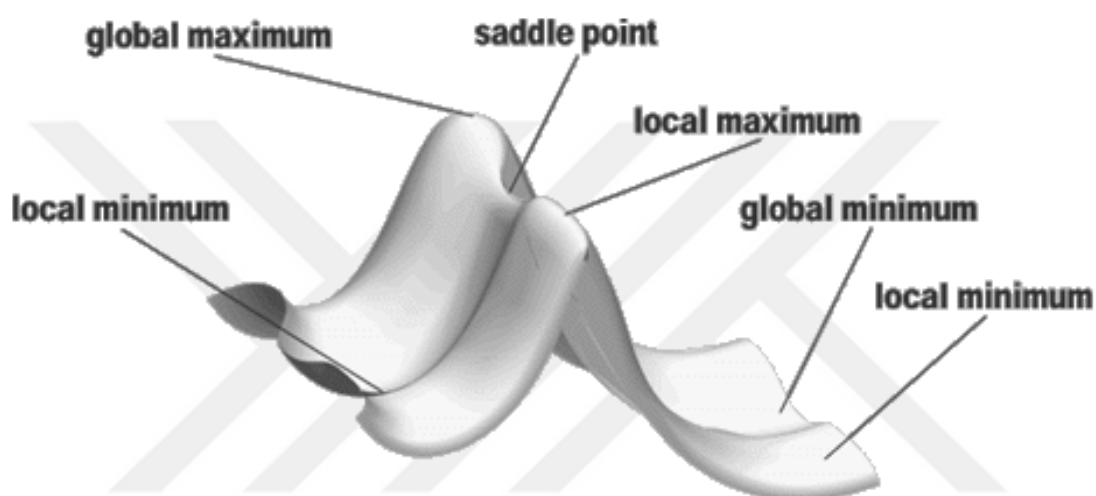


Figure 34. Illustration of a multi-dimensional potential energy surface with important stationary points.

The overall shape of the energy surface is determined by the energetic ordering of the local minima and their connectivity through transition states. One feature to describe the global topology of a PES is for instance the monotonic sequence introduced by Kunz and Berry.¹⁷²¹⁷³ It is defined as a sequence of local minima connected by transition states for which the energy of the minima monotonically decreases. All monotonic sequences leading to the same local minimum therewith define a monotonic sequence basin or funnel (see Figure 35). Another common term is superbasin which emphasizes the analogy to a basin of attraction on the global scale of the PES. In contrast to the latter where every point of the configurational space with a non-vanishing gradient only belongs to one basin of attraction, a local minimum can belong to several monotonic sequence basins. Systems with only one funnel converging to the global minimum are often referred to as single-funnel systems. A PES with such a topology is benign for global optimization as it can guide the system towards the global minimum. In

contrast, multi-funnel systems contain multiple sequence basins. Once in a wrong funnel, the system then has to surmount several energy barriers to climb out of it and reach the global minimum, which makes global optimization in general more difficult.

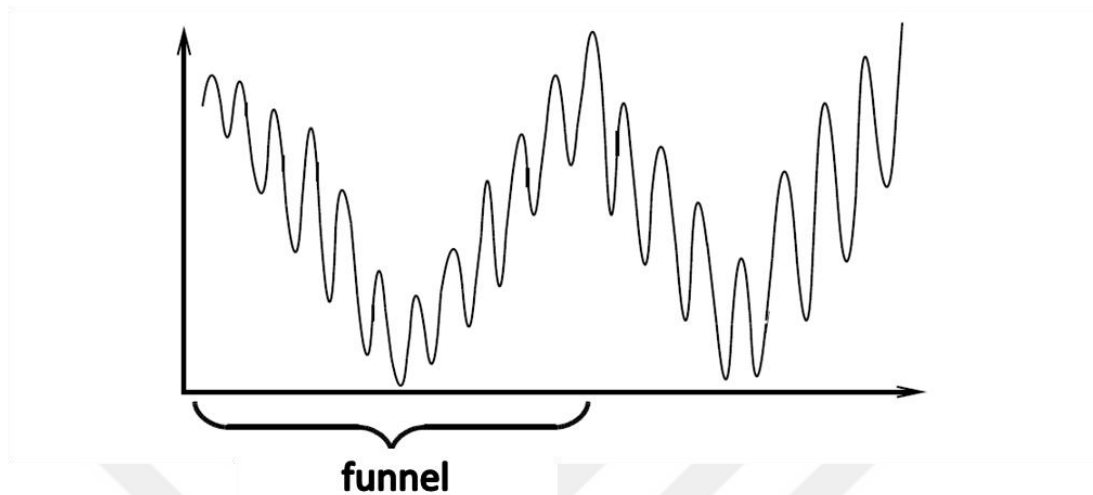


Figure 35. Schematic picture of a multi-funnel potential energy surface.

On the one hand, the behaviour of the energy landscape is defined by the system under investigation. On the other hand it depends on the underlying theoretical model for the energy calculations. More details on possible models are given in section 3.3. and 3.4. as Force Fields and Electronic Structure Methods. To identify the various points of the PES, different algorithms and approaches are required. Local extrema are located using local optimization algorithms, and the global extrema are investigated employing global optimization methods.

2. Exploring the Configurational Space

Determining atomic configurations requires identifying the local minima of the PES, which is a high-dimensional function of the atomic coordinates. The main interest is the global minimum, which constitutes the most stable isomer at zero temperature. Energetically higher-lying and thus metastable isomers, however, might be observed in experiment due to finite temperature or kinetic effects, thus additionally being of interest.

2.1. Local Optimization Methods

Energy minimisation, which is also called geometry optimisation, is simply used to find the local energy minimum of a system by iteratively adjusting the coordinates of the atoms in the system. Starting from a non-equilibrium configuration, energy minimisation employs the mathematical procedure of optimisation to move atoms so as to reduce the net forces (the gradients of potential energy) on the atoms until they become zero and the second derivatives are positive:

$$\frac{\partial U}{\partial r} = 0; \frac{\partial^2 U}{\partial r^2} > 0$$

where U is the internal energy of a system and r is the coordinate of the system (the Cartesian or internal coordinates). The term zero force is used since the first derivative of the internal energy with respect to distance is force. If the internal energy of a system with coordinates r , is $U(r)$, then the internal energy at a new set of coordinates $r + dr$, is:

$$U(r + dr) = U(r) + \frac{\partial U}{\partial r} dr + \frac{1}{2} \frac{\partial^2 U}{\partial r^2} dr^2 + \dots$$

The first derivative can be collectively written as the gradient vector g and the second derivative matrix is referred to as the Hessian matrix H .

Derivatives are useful in energy minimisation as they provide information about the shape of the PES and significantly enhance the efficiency in finding where a minimum is located. The direction of the gradient vector g indicates where the energy minimum lies and the magnitude indicates the steepness of the local slope. The second derivative indicates the curvature of the function, predicting where the function will change direction. The gradient-based algorithms are the most popular methods for energy minimisation, and they can be classified according to the highest-order derivative used. For example, first-order algorithms use the first derivative and second-order algorithms use both first and second derivatives.

2.1.1. Steepest Descent

The simplest approach to using gradient information within a local optimization is the Steepest Descent (SD) algorithm.^{174,175} To find an energy minimum by first-order algorithms, the gradient vector g is used to determine the direction of movement and a line search is used to determine the magnitude of the step length. As the gradient vector

g always points into the direction of the biggest function increase, the function value can be lowered by following the opposite direction. Once the steepest slope has been chosen, the energy can be searched along this direction by:

$$X_{n+1} = X_n - \lambda \cdot g$$

The step size λ is determined by a line minimization. The process continues until the gradient becomes flatter than a predefined cut-off value. A disadvantage of this method is that many small steps may be performed when proceeding down a long narrow valley. The SD method also often oscillates around the real minimum energy path because a subsequent step will be perpendicular to the previous step and the energy can be further lowered by following the gradient component along the previous search direction.

2.1.2. Conjugate Gradient

The Conjugate Gradient (CG) algorithm takes the gradient information of the current and the previous step to construct a search direction which is "conjugate" to the previous search direction. The search direction is given by:

$$d_i = -g_i + \beta_i d_{i-1}$$

For the determination of β , several possibilities are available such as the Fletcher-Reeves, the Polak-Ribiere or the Hestenes-Stiefel approaches.¹⁷⁴ For the first step, $d_0 = -g_0$. Each subsequent direction is a combination of the gradient at the current position and the previous search direction. The CG algorithm is more efficient than SD, where subsequent steps are made orthogonal to the previous search vectors. For a quadratic energy surface, this will converge to the minimum in a number of steps equal to the number of variables. However, in real world problems, the functions are not exactly quadratic and the algorithm takes more steps. The CG algorithm is very efficient at moderate to close distances from a minimum but has slow convergence when very close to an energy minimum.

2.1.3. Newton Raphson

The Newton Raphson (NR) method uses both the gradient and the second derivative (H) of the potential energy surface.¹⁷⁶ In the NR method, the displacement vector Δr is given by:

$$\Delta r = -H^{-1}g$$

However, for a realistic potential energy surface, there is the possibility to reach other stationary points, such as transition state, when starting from a position not close to the minimum. Thus, the expression is modified to be:

$$\Delta r = -\lambda H^{-1}g$$

where λ is a scalar quantity determined by a line search along the search direction to find the one-dimensional minimum and the procedure becomes iterative like the CG method. The key step of the NR method is the inversion of the Hessian matrix H , which may vary slowly between consequent steps in large systems. It is therefore undesirable to invert the H at every step of the optimization. This is avoided by Quasi-Newton method, where Hessian matrix H does not need to be computed in every step and is updated by analyzing successive gradient vectors instead. One very widely used Quasi-Newton method is the BFGS method,¹⁷⁷ where the Hessian matrix H is initialized by performing an exact inversion of the second derivatives and is then subsequently updated for a number of cycles.

The most appropriate algorithm or combination of algorithms for a given problem depends on the size of the system, number of variables and the memory requirement. Most minimisation algorithms can go downhill or uphill on the PES and locate the minimum or maximum, respectively, that is near to the starting point, which is likely to be a local energy minimum, thus we require a means of generating different starting points to locate more than one local minimum. In this thesis, both Conjugate Gradient and Quasi-Newton algorithms are used during the energy minimisations.

2.2. Global Optimization Methods

The above described local optimization methods are deterministic schemes that approach the next local minimum from a starting point constructively, since the local information obtained for a given configuration, like the energy and forces, uniquely guides the system to the next local minimum. In order to find all isomers and particularly the global minimum, a search algorithm is required that not only scans the local environment but samples the whole PES. Since local information is not enough to locate the global minimum of the system, stochastic methods are required that provide some recipe to systematically sample the huge configurational space. An ostensibly

“simple” method that runs through all local minima quickly becomes unfeasible due to the computational cost associated with the huge number of possible structures. Due to the exponential growth of the number of local minima with system size global optimization is a difficult task and no known algorithm guarantees that one can locate the global minimum for anything but the most simple systems. One key feature of any search algorithm is the way new structures are generated, which can be called a trial move corresponding to a jump of the system in the configurational space. A simple trial move is to randomly displace the atomic positions. After such a jump, a criterion is required which decides whether this new structure is accepted and the search should continue from there, or if it should rather be discarded. Such an acceptance criterion is typically based upon the total energy since it is usually the quantity to optimize. As already stated in the Introduction chapter, several global optimization algorithms exist, such as simulated annealing or genetic algorithms. Here we discuss one other algorithm, the Monte Carlo Basin Hopping method, which we have used in this work.

2.2.1. Monte Carlo Basin-Hopping

Basin Hopping algorithms¹⁷⁸ are one of the popular global optimization techniques based on the Monte Carlo method. With the basin-hopping scheme, Wales et al.¹⁷⁹ identified all known global minima of Lennard-Jones(LJ)-clusters containing up to 110 atoms and additionally new ones. The Monte Carlo algorithm is based on the idea of repeated random sampling in order to calculate results for a specific problem. Although it does not guarantee the correct result, statistically it should converge towards the right result. The basic idea of Basin hopping method is to generate a new structure and relax it at every step, where the existence of the relaxation is the main difference with respect to the pure Monte Carlo method. Each relaxation locates one of many local minima, of which the lowest energy one found correspond to a candidate for the global minimum. Like any other algorithm, the Basin Hopping algorithm does not guarantee to locate the global minimum of the system since the number of possible configurations increases exponentially when the system size increases. However, The Basin Hopping effectively simplifies the PES so that the probability to find the global minimum increases. The energies of global and local minimum are unchanged, but the other points are transformed by:

$$\tilde{E}(X) = \min\{E(X)\}$$

where $\tilde{E}$ is the transformed energy, X is the nuclear coordinates and the *min* indicates the local structural relaxation. The resulting steps are mapping any given configuration space to the nearest local minimum and thus the PES is converted into a set of interpenetrating staircases with steps corresponding basins of attraction (see Figure 36). The transformed done PES has no transition state regions, which accelerates the minimization by the (i) removal of the barriers to a lower energy minima and (ii) the increased possibility of the inter-basin hopping from and to any point on the PES.

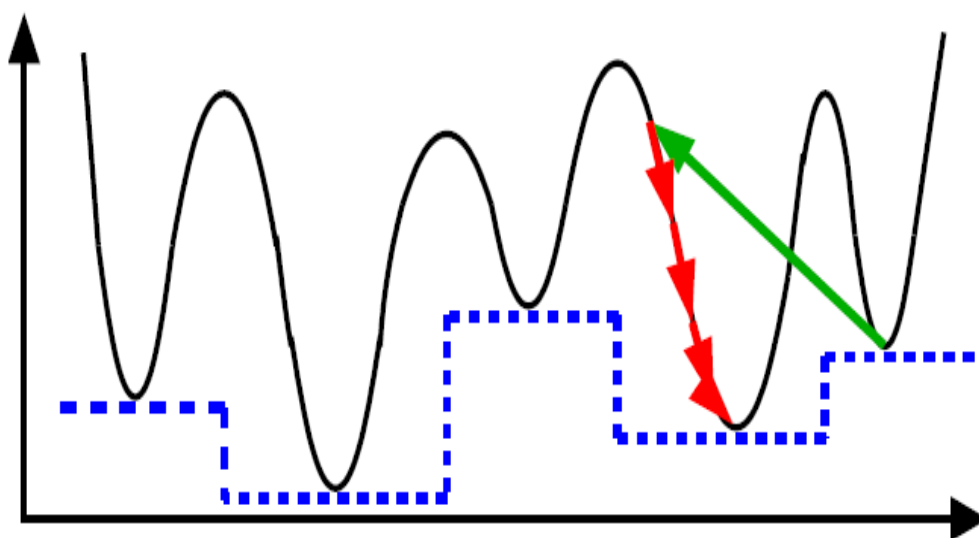


Figure 36. Schematic diagram of a one-dimensional PES, in which the original energy (solid line) is transformed onto the $\tilde{E}$ (dashed line). The green arrow indicates a random move performed on a local minimum, which is followed by a local structural minimization (red arrows).

The simple Metropolis Monte Carlo¹⁸⁰ walk is the general method used for the random moves on the simplified PES with only the temperature as a variable. According to this method, a random move has applied to the system in each step, and accepted if a random number N is less than the metropolis criterion

$$N \leq e^{-\frac{\Delta E}{k_b T}}$$

where ΔE is the energy difference between the structures, k_b is the Boltzmann constant, and T is the fictitious temperature variable that decides how high in energy structures will be accepted. Thus the probability of acceptance of a higher energy structure can be controlled with the T parameter, and a lower energy structure will be always accepted. A random move followed by a relaxation is called a step in Basin hopping and in order to search the global minima structures, these steps are repeated. Figure 37 shows a

schematic diagram of a Basin Hopping run. To increase the probability to find the global minimum, multiple runs starting from different initial structures are often used.

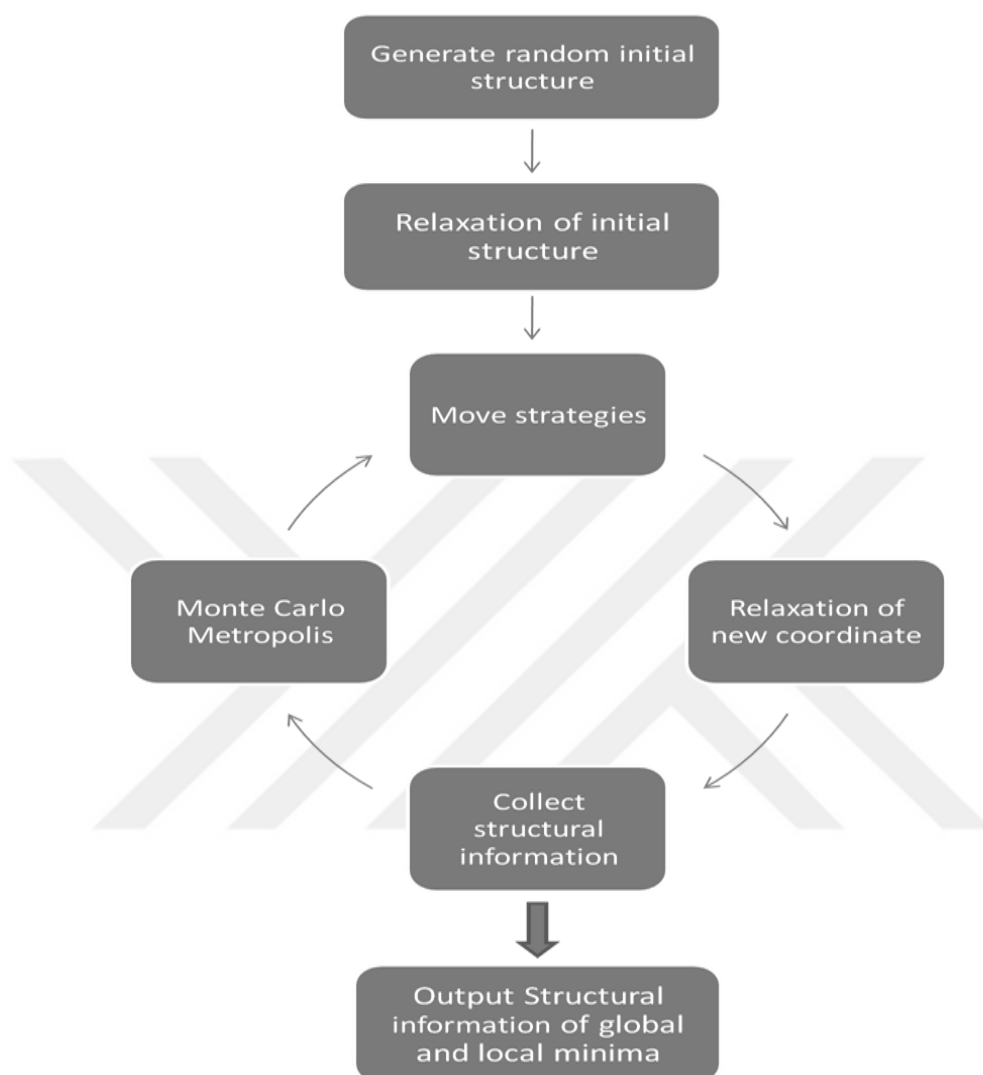


Figure 37. A schematic diagram of a Basin Hopping run.

3. Force Fields

Over the last few decades atomistic simulation, in which we are only concerned with atoms, rather than electrons and sub-atomic particles, has developed significantly with the widespread use of computers. Correspondingly the field has evolved from one that was initially concerned with reproducing experimental numbers, to one where predictions are being made, and insight is being offered.

For ionic materials, these simulation methods are based on the use of Born Model employing force fields to describe the interaction between atoms. Such simulations are

relatively less time consuming than calculations using quantum mechanical methods and allow modelling of large scale systems containing $10^4 \sim 10^6$ atoms. As a result, they have been widely applied to identify the geometrical structures and properties for ionic materials.

The starting point for the majority simulation techniques is the calculation of the energy. In most formulations of the Born Model, the interaction energy of an N-body system can be written as an expansion of the coordinates ($r_1, r_2, \dots, r_n$) in the following way:

$$\phi_{tot} = \sum_{i=1}^N \sum_{j>i}^N \phi_2(r_i, r_j) + \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j}^N \phi_3(r_i, r_j, r_k) + \dots$$

For broad range of systems and applications there does not exist a universal set of analytical functions that manage to approximate ϕ_{tot} well. Therefore the functional form of the force-field has to be chosen with care since it often has implications for the results. Consequently, even for one and the same class of systems more forms are in use in the literature. A few examples of popular potentials in use for the non-electrostatic part of pair interaction energies are the Lennard-Jones potential, the Buckingham potential, and the Morse potential.

In the simplest force-field models the total interaction (ϕ_{tot}) is approximated by neglecting higher order interactions ($\phi_3 + \dots$), i.e. only the interactions between all pairs of atoms in the system are considered. For example, for a binary system consisting of Zn and O atoms described by a 2-body potential the total interaction would consist of a sum of Zn-Zn, Zn-O, and O-O types of interactions. These two-body terms can be further decomposed into the long range electrostatic or Coulombic interactions, where the energy is calculated using the Ewald summation, and short range dispersive forces, i.e. non-Coulombic terms including overlap repulsion and van der Waals attraction between electron charge clouds.

3.1. Coulomb interaction

When considering ionic materials, the Coulomb interaction is by far the dominant term and can represent, typically, up to 90% of the total energy. It is given by Coulomb's law as:

$$U_{ij}^{coulomb} = \sum_{i < j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Where the q_i and q_j are the charges on atoms i and j respectively, r_{ij} is the distance between atoms i and j , and ϵ_0 is the permittivity of the free space. Despite having the simplest form, Coulomb interaction is in fact the most complicated potential to evaluate for periodic systems. For a finite system of charges, this expression can be evaluated directly, however for a periodic (infinite) system, the expression does not converge and numerical tricks must be applied to evaluate the energy because it has an infinite amount of charge and the energy of interaction is undefined. To overcome this problem Ewald summation method¹⁸¹ is applied. In the method of Ewald summation, a Gaussian function is added to each point charge. The mean value of this Gaussian function is the value of the original point charge but with the opposite sign. The new system now can be evaluated in real space, which converges quickly since the overall amount of charge in the system are reduced by the addition of the Gaussian functions. To calculate the true energy a second set of the Gaussian functions of the opposite sign of the first ones are added, which cancels out the first set of Gaussian functions. The second set converges slowly in real space, however since they are Gaussian functions, they are evaluated easily in reciprocal space. Effectively, the Ewald method splits the conditionally convergent series into two convergent series, one in real space and the other in reciprocal space, each of which converges rapidly.

3.2. Electronic Polarizability

The Born model discussed above is formulated treating ions as point charges. However, for oxides, ions and defects will polarize other ions in the lattice. Polarizability relates to the tendency of the electron cloud of an atom to be distorted from its original shape by the presence of an electric field. One simple way to include the electronic polarizability of the atoms is to use the core-shell model,¹⁸² which represents the polarisable ion as a massless shell connected to a core containing all the mass, where the total charge of the ion is the sum of the charges of both core and shell. The position of the core represents the location of the ion in the lattice and the position of the shell shows the electronic polarizability. The core and shell interact with each other by a harmonic spring where

the equilibrium distance between them is set to 0, as shown in Figure 38, and the spring constant (K) and the charge of the shell (Y) determine the polarizability of the ion as:

$$\alpha_p = \frac{Y^2}{4\pi\epsilon_0 K}$$

Both K and Y can be obtained by fitting empirically to reproduce experimental properties. In shell model, the short range forces are assumed to act between the shells while the long range electrostatic forces act between all shells and cores, except between them for the same atom.

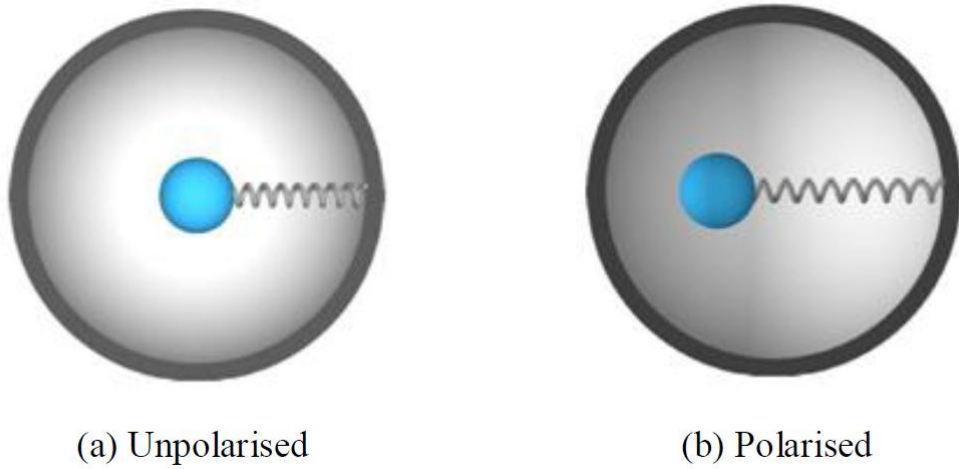


Figure 38. Schematic representation of the core-shell model. Blue sphere represents the core while the grey circle represents for the shell.

3.3. Interatomic Potential functions

The non-electrostatic short range interactions are usually expressed as:

$$U^{short-range}(r_1, \dots, r_N) = \sum_{A,B} U_{AB}(r_A, r_B) + \sum_{A,B,C} U_{ABC}(r_A, r_B, r_C) + \dots$$

where U_{AB} refers to the two-body interactions, U_{ABC} three-body interactions, and so on. This expression combines a number of interactions, containing covalent interaction, electronic polarizability, and non bonded interactions such as repulsion and van der Waals attraction. The two-body potential functions act between neighbouring charge clouds and gives the most contribution to the short-range interaction. Figure 39 displays a typical two-body short range interaction curve with interatomic distance. The short range potentials are usually handled by analytical functions which have both an attractive and a repulsive term. The repulsive term describes the Pauli repulsion due to

the overlap of the closed shell electron configurations, while the attractive term arises at close interatomic separations due to an induced-dipole interaction and covalent effects. There exist a very wide range of different potential forms, in which the famous Lennard-Jones, Buckingham and Morse potentials are just a few examples. The choice of which potentials to be used depends on a number of factors, including the atomic species in the system, the computational capacity and the nature of the energy landscape.

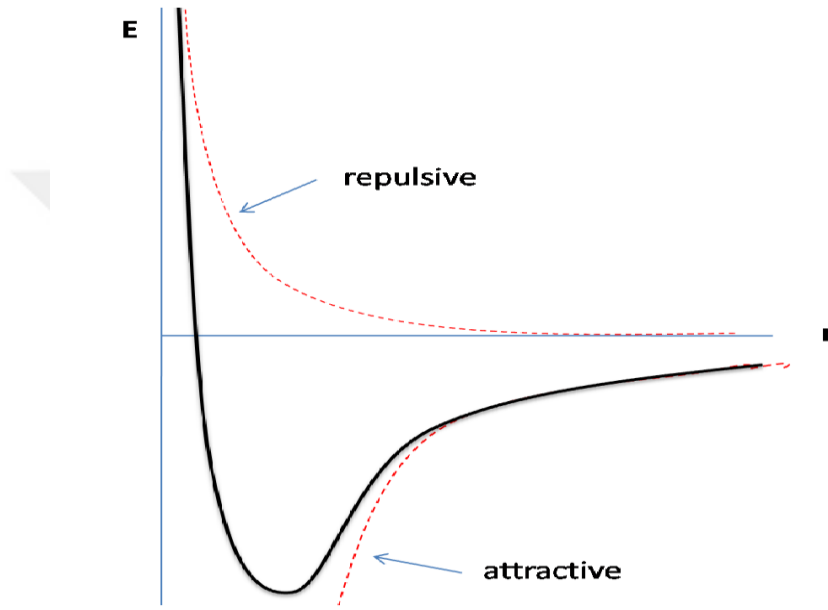


Figure 39. The non-Coulombic interaction including the attractive and repulsive components of ion separation.

3.3.1. Buckingham Potential

For ionic solids, the Buckingham potential¹⁸³ is one of the most widely used functional forms for the short range two-body potential.¹⁸⁴ It can be written as:

$$U_{ij}^{Buck} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

Where A_{ij} , ρ_{ij} and C_{ij} are constants and r_{ij} is the interatomic distance between the ions i and j . A_{ij} and ρ_{ij} are related to the number of electrons and the electron density respectively. The first term stand for the Pauli repulsion interaction and the second term stand for the van der Waals interactions.

3.3.1. Lennard-Jones Potential

The Lennard-Jones potential¹⁸⁵ is another very common potential with its simple form:

$$U_{ij}^{LJ} = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^6}$$

with $A = 4\epsilon\sigma^{12}$ and $B = 4\epsilon\sigma^6$, where ϵ is the depth of the potential well and σ is the finite distance where the inter-particle potential is 0. The repulsive first term is dependent on r^{-12} and thus acts at close range, while the attractive second term becomes dominant at longer range. Although there exist more accurate potentials, the Lennard-Jones potential is used extensively in computational simulations due to its computational simplicity.

4. Electronic Structure Calculations

4.1. Many-Body Schrodinger Equation

A theory for a stationary system of nuclei and interacting electrons is intrinsically quantum-mechanical, and is based on solving the time-independent Schrodinger equation of the form:

$$H\Psi(R; r) = E\Psi(R; r)$$

where H is the Hamiltonian of the system, containing the kinetic and potential energy operators; E is the energy of the system; Ψ is the wavefunction of the system; $[R]$ are the positions of the nuclei, and $[r]$ are the variables that describe the coordinates of the electrons. The potential energy term arising from the repulsion from two electrons at r_i , r_j is:

$$\frac{e^2}{|r_i - r_j|}$$

where e is the electronic charge. The potential term arising from the attraction of an electron at r and a nucleus at R can be written as:

$$\frac{Ze^2}{|R - r|}$$

where Z is the charge of the nucleus. The potential energy term for the repulsion of two nuclei can be written similarly:

$$\frac{Z_i Z_j e^2}{|R_i - R_j|}$$

For the kinetic energy of an electron the energy term will be:

$$\frac{\hbar^2}{2m_e} \nabla_r^2$$

Practically, it can be assumed that the nuclei move slower than the electrons, so that φ has only dependence on the electronic degrees of freedom. This is called the Born-Oppenheimer approximation.¹⁸⁶ Its validity comes from the huge mass difference between nuclei and electrons, making the former behave like classical particles. So the term for the kinetic energy of the nuclei can be omitted and taken into account as a classical contribution. In this case the Hamiltonian of the system becomes in atomic units:

$$H = - \sum_i -\frac{1}{2} \nabla_{r_i}^2 - \sum_{iI} \frac{Z_I}{|R_I - r_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

The last term in the previous equation is a constant and the electronic Hamiltonian can be written as:

$$H_e = - \sum_i -\frac{1}{2} \nabla_{r_i}^2 - \sum_{iI} \frac{Z_I}{|R_I - r_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}$$

Even with the proposed Born-Oppenheimer approximation, solving for $\Psi(r)$ remains a difficult task, due to the many body nature of interactions. Each electron is affected by the motion of other electrons in the system, which is called correlation. Furthermore, two electrons of the same spin can change their positions, in which case Ψ must change sign.

4.2. Density Functional Theory

The many-body Schrodinger equation is practically impossible to solve for many electron systems. Therefore one should apply approximate methods to solve the problem. Density Functional Theory (DFT) provides a general framework to deal with the ground-state energy of the electrons in many atom/electron systems. DFT is based upon two theorems, proved by Hohenberg and Kohn,¹⁸⁷ and a computational scheme proposed by Kohn and Sham.¹⁸⁸ The first theorem states that the electronic structure of the ground state of a system is uniquely determined by the ground state electronic

density, $\rho_0(r)$. The second theorem states a variational criterion for the determination of $\rho_0(r)$ and E_0 starting from an arbitrary function $\rho(r)$ constrained by the normalization condition:

$$\begin{aligned}\int dr \rho(r) &= N \\ E[\rho] &\geq E[\rho_0] \\ E[\rho_0] &= E_0\end{aligned}$$

where N is the total number of the electrons of the system. E_0 can be found by minimizing the functional $E[\rho]$ with respect to arbitrary infinitesimal changes in the form of the function $\rho(r)$. Kohn and Sham¹⁸⁸ that the ground-state density of the original interacting system is equal to that of some chosen non-interacting system. This leads to independent-particle equations for the non-interacting system that can be soluble, if all the difficult many-body terms are incorporated into an exchange-correlation functional of the density. For such a system the kinetic energy is defined as:

$$T_S = -\frac{1}{2} \sum_i \nabla_i^2$$

This kinetic energy term forms part of the Hamiltonian operator that does not contain electron-electron interactions:

$$H_S = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V_S(r_i)$$

where $V_S(r)$ is an effective local potential. So the ground-state wavefunction associated with this Hamiltonian can be represented by a Slater determinant of the form:

$$\Psi_S = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \varphi_1(x_2) & \dots & \varphi_1(x_N) \\ \varphi_2(x_1) & \varphi_2(x_2) & \dots & \varphi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(x_1) & \varphi_N(x_2) & \dots & \varphi_N(x_N) \end{vmatrix}$$

where the orbitals φ_i are termed Kohn-Sham orbitals. In this case the non-interacting kinetic energy is not equal to the interacting system's. Kohn and Sham accounted for that difference by defining the functional:

$$F[\rho(r)] = T_S[\rho(r)] + J[\rho(r)] + E_{XC}[\rho(r)]$$

where $J[\rho(r)]$ stems for the classical Coulomb integral of the electron-electron term and $E_{XC}[\rho(r)]$ is the exchange-correlation energy defined as:

$$E_{XC}[\rho] = (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_C[\rho] + E_{ncl}[\rho]$$

The remaining part of the true kinetic energy, T_C is added to the non-classical electrostatic contributions, E_{ncl} . So everything that is unknown is contained in the exchange-correlation energy, which are the non-classical effects of self-interaction correction, exchange, correlation and a portion of the true kinetic energy. Thus, the total energy of the system can be expressed as:

$$E[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho]$$

In this expression, the only term for which no explicit form can be given is E_{XC} . If it were known, the exact ground-state energy could be found by solving the Kohn-Sham equations for independent particles. For an approximate form of E_{XC} , the Kohn-Sham method provides a practical approach to calculating ground-state properties.

4.3. Exchange-Correlation Functional

The important quantity in the Kohn-Sham method is the exchange-correlation energy, which is expressed as a functional of the density, $E_{XC}[\rho]$. In order for a DFT calculation to provide reasonable results an accurate approximation to exchange-correlation functional is necessary. The first approximation to be suggested was the Local Density Approximation (LDA).¹⁸⁸ The idea is to have an approximate the exchange-correlation of the system by using the properties of homogeneous electron gas:

$$E_{XC}^{LDA}[\rho] = \int dr \epsilon_{XC}(r, \rho(r))$$

where $\epsilon_{XC}[\rho]$ is the exchange-correlation energy per particle of a uniform electron gas with the same density of the system.

Although LDA works surprisingly better than predicted since it is a crude approximation, it is insufficient for the systems having inhomogeneous density. In this sense the next approximation was made by the extension of exchange correlation energy in terms of the density.¹⁸⁹ In this approach only the density and its first derivative is included and called Generalized Gradient Approximation (GGA):

$$E_{XC}^{GGA}[\rho] = \int dr f(\rho(r), \nabla \rho(r))$$

For choosing function $f(\rho(r), \nabla \rho(r))$ there is no unique way so that there exists many of different GGA potentials. In general the GGA results are better than the LDA results, but it is not always the case. Thus it is necessary to compare the results to have a more

accurate result. In this study, two of the widely used GGA potentials, PW91¹⁹⁰ and PBE¹⁹¹ was used in addition to some LDA calculations.

4.4. Plane Waves

Solving the Kohn-Sham equations in real space is a difficult job. Instead some different basis sets are used to expand Kohn-Sham orbitals, such as pseudoatomic orbitals, plane waves etc. Plane waves are a good choice for basis sets in periodic systems, due their convenient representation and manipulation in reciprocal space with Fourier transformations. For periodic systems the reciprocal unit cell is called Brillouin zone and the infinitely many vectors spanning this space are called k-vectors. Since observables should be calculated by integrating over the Brillouin zone one should take as many k-vectors as necessary in a numeric calculation to get accurate results, which is called k-point sampling. According to Bloch' Theorem,¹⁹² the wavefunction in a periodic system can be described by the product of a cell-periodic function, $u(r, k)$, and a plane wave:

$$\phi(r) = u(r, k)e^{ik \cdot r}$$

As any periodic function can be expanded in terms of plane waves, $u(r, k)$ can be written as:

$$u(r, k) = \frac{1}{\sqrt{\Omega}} \sum_G c_i(k, G)e^{iG \cdot r}$$

where Ω is the volume of the unit cell and $c_i(k, G)$ are the expansion coefficients. So the wavefunction will become:

$$\phi(r) = \phi_i(r, k) = \frac{1}{\sqrt{\Omega}} \sum_G c_i(k, G)e^{i(k+G) \cdot r}$$

By this way the Kohn-Sham equations are transformed from a set of differential equations into a set of algebraic equations. The expansion requires infinitely many G vectors which is impossible to calculate. However this expansion can be truncated at some point, where for large G values, plane waves become negligible. This cut-off is called kinetic energy cut-off and denoted by E_{cut} .

4.5. Projector Augmented Wave Method

Finite plane wave expansions are insufficient in describing the strong oscillations of the wave functions near the nucleus and needs huge number of plane waves for convergence and accuracy. Therefore some approximations are used. One of them is the pseudopotential method, which considers only the valence electrons and holds the core electrons to behave as in a free atom. In the pseudopotential approach, the Pauli repulsion of the core electrons is described by an effective potential that expels the valence electrons from the core region, causing the wave functions to be smooth. However, all the information about the charge density and wavefunctions near the nucleus is lost.¹⁹³ Another type of approximation is the augmented wave method. In this method basis functions are composed out of atom-like partial waves in the atomic regions and the bonding is appropriated by a set of functions. The space is divided by atom-centered spheres and an interstitial region for the bonds. The projector augmented wave (PAW) method is an extension of augmented wave methods and the pseudopotential approach, combining them into a unified electronic structure method. In PAW method, space is considered as two but linked regions; interstitial and augmented regions. There is a transformation operator defined to transform highly oscillating all-electron wavefunctions to numerically convenient pseudowavefunctions. The transformation operator is chosen in such a way that it only acts on the augmentation region. In the augmentation region, the wavefunction can be expanded in terms of the solutions for the isolated atom. These solutions are called all-electron partial waves. In the interstitial region the solutions can be found by simply pseudopotential methods. At the end an all-electron wave function can be defined by combining these solutions by defined translation operator and projector operators.

4.6. Self Consistent Cycle

DFT calculations work within Kohn-Sham equations in a self-consistent manner. The calculations start with an initial guess for the charge density. By this density Kohn-Sham Hamiltonian is constructed and solved for Kohn-Sham eigenvalues and orbitals. By solved Kohn-Sham orbitals new charge density is constructed and compared with starting density. If they are not consistent the procedure repeats itself until the self consistency is achieved. This can be called electronic cycle and the tolerance for the

convergence is given as a parameter in the calculations. For faster convergence in an electronic cycle, instead of using directly output density as an input in following step, some mixing schemes are used. For our calculations we used Broyden mixing scheme,¹⁹⁴ which mixes the output density with previous input density to get the subsequent input density. After the convergence for electronic cycles, quantum-mechanical forces can be calculated on the atoms by Hellmann-Feynman Theorem.¹⁹⁵ To get the equilibrium positions for the atoms in the system, atoms are moved along these forces (following one of the local optimisation methods detailed above) and then convergence of the electronic cycles is repeated to obtain new forces. This process is repeated until the forces drop below a threshold, at which point the optimization of the geometry is complete.



CHAPTER III Comparison of free space and surface-supported ZnO nanoclusters

1. Introduction

Nanoscale and nanostructured materials (generally referred to here as nanomaterials), have increased surface area to volume ratios and show improved and/or novel properties due to quantum size and surface effects due to the immense reduction in size relative to the bulk. Nanomaterials, are highly topical due to their unusual properties, which are often tunable by size and/or dimension to fit a wide range of different criteria required by different applications. Semiconducting clusters and nanoparticles are one of the simplest well known examples of such materials. With the ongoing development of nanoscience, device performance and efficiency is likely to thus greatly benefit from utilising materials with nanoscale dimensions. For device applications nanomaterials are likely to be employed by first depositing them onto stable supports. As the binding interaction between a cluster and a supporting system in equilibrium is typically quite strong (of the order 1 eV), the significant effect of the support should be included in the consideration of the structure and properties of supported nanomaterials. In this paper, we focus on one example of such an interaction, zinc oxide nanoclusters supported on surfaces of silver.

Zinc oxide (ZnO) is an important and a heavily researched semiconducting oxide compound which, due to its remarkable optical and electronic properties, is already widely used and has great promise in a range of new device applications (e.g. gas sensors, optoelectronic devices, and photocatalysis). In the extreme case, nanoclusters consist of only a few ZnO units. Experimentally, a large variety of low-dimensional structures of ZnO have been synthesized as ultrathin films, nanowires, nanotubes, nanocages, nanoparticles, *etc.* The atomic configurations of the smaller nanostructures, however, are not clear from experiment, especially for very small sizes of a few nanometers across, due to the limitations of the experimental techniques. Therefore, theoretical studies are expected to close the knowledge gap by searching the configurational energy landscape of these nanosystems and supplying reliable data

based on electronic structure calculations. Although free space $(\text{ZnO})_n$ nanoclusters have been modelled,^{196,197,198,199,200} for realistic device applications it is important to understand how the properties of such nanoclusters change with the effect of a support.

The work presented in this chapter considers ZnO clusters on Ag; a common noble metal support. Silver surfaces have extensively been studied both experimentally and computationally.^{201,202} Silver crystallises exhibiting three important surfaces of differing morphology: (111), the most stable in the form of a triangular lattice (see Figure 40a), (100), having four-fold surface symmetry (Figure 40b), and (110), exhibiting a linear pattern of corrugation (Figure 40c). In general the possible adsorption locations on these surfaces are the symmetry unique sites: on-top (T), above a single metal atom, bridge site (B), between two metal atoms, and hollow site (H), where higher coordination is possible (see Fig. 40).

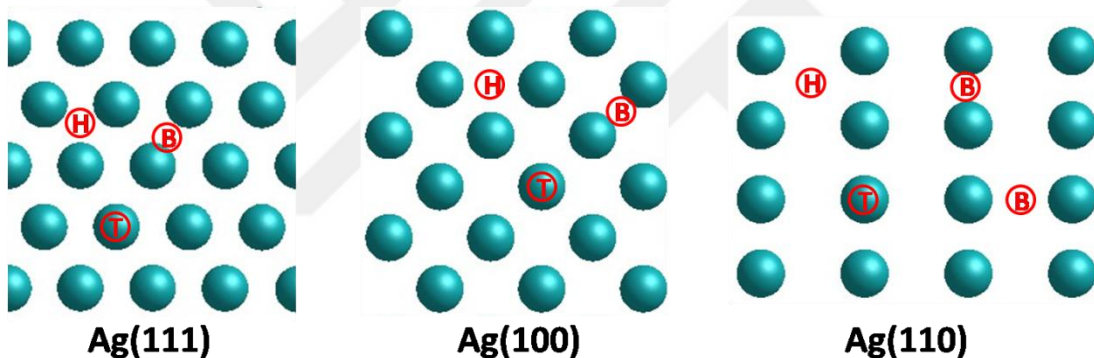


Figure 40. Top view of Ag(111), Ag(100) and Ag(110) surfaces. The symmetry unique sites hollow: (H), bridge (B) and on-top (T) sites are indicated with letters.

Investigating how small nanoclusters adsorb on surfaces can provide valuable insight into the very initial stages of thin film growth. In contrast to abundant literature on straightforward oxidation processes at metal surfaces,^{203, 204} there are only few theoretical studies of the very initial stages of growing a metal oxide on a surface of an alternative metal. This scarcity of reports, perhaps, arises from an additional complexity of the atom, monomer or cluster deposition, which results in many possible adsorption geometries. Although previous studies mainly focused on the opposite process of metal nanocluster adsorption on an oxide surface,^{205,206,207,208} there are some examples where ZnO monomers were investigated on Ag(111),²⁰⁹ MgO(001)²¹⁰ and graphite²¹¹ surfaces. In the opposite limit of ZnO thin films. Firstly, Freeman et al.¹²³ predicted for free-

standing thin films of ZnO that the layered phase would be more stable than the wurtzite phase up to a 36 layer thickness. Thin films exhibiting the layered phase were experimentally confirmed up to a few monolayers on Ag(111)¹²⁵ and Pd(111)¹²⁶ surfaces. To understand the effect of the surface, Bristowe et al. studied the Ag/ZnO interfaces²¹² and the initial growth of ZnO on Ag(111) surface²⁰⁹ up to three units of ZnO using density functional theory (DFT). In this study it was predicted that ZnO dimers and trimers form linear chains of alternating Zn and O atoms parallel to the surface.

In this study, we have systematically searched for the global minimum structures of (ZnO)_n nanoclusters on Ag(111) surface for the sizes $n = 1-16, 20$ and 24 , by Monte Carlo Basin Hopping method using interatomic potentials (IPs). The best candidate structures found by these searches were then refined by DFT calculations. In the next section we briefly explain the methods we used throughout this study. In the third section we start with a summary of what is known for free space ZnO clusters, and after that we concentrate on the adhesion to of ZnO clusters to the Ag(111) surface modelled with IPs, followed by a comparison with adhesion to Ag surfaces of different morphologies. The last section focuses on the results refined by *ab initio* DFT calculations.

2. Methodology

Throughout this study we have modelled the ZnO nanocluster adhesion to the Ag surfaces with two complementary approaches to the definition of their energy, used in exploration of their energy landscapes: IPs and DFT (DFT). Due to the high computational cost of the *ab-initio* DFT method, IPs have been employed as the energy definition during the search of the configurational energy landscape. Then a selection of the best candidate structures was refined by using DFT.

2.1 Models

In both IP and DFT approaches, periodic boundary conditions were imposed to model the Ag-supported ZnO nanoclusters. A more appropriate free space (or gas phase)

model was used for bare ZnO nanoclusters in the IP calculations. In the plane-wave DFT calculations periodic boundary conditions were still necessary for the refinements because of the inherent limitations of the method. In these calculations, sufficiently large supercells were thus constructed to eliminate the spurious interactions between the nanocluster and its periodic images.

Silver surface models were built following a bulk optimization with DFT. The lattice constant of the Ag bulk unit cell was found to be 4.15 Å, which is very close to a previous theoretical result²¹³ of 4.17 Å, and slightly higher than the experimental value²¹⁴ of 4.09 Å. Ag(111), Ag(100) and Ag(110) surfaces were created using four-layer slabs cut from bulk as; the three top layers have been relaxed while the bottom layer of silver slab was kept fixed. As for bare clusters, the large surface supercells of Ag the support were chosen to keep supported ZnO clusters ≥ 1 nm apart, in particular, an $(8 \times 4\sqrt{3})$ Ag supercell was used for $(\text{ZnO})_n$ cluster sizes $n < 14$, and a $(10 \times 6\sqrt{3})$ Ag supercell for larger cluster sizes. During the search of the configurational energy landscape, which demands a large number of calculations to be performed for random positions of Zn and O atoms on the surface, a two-layer Ag slab was used and the Ag atoms kept fixed at their ZnO-free surface positions calculated from a four-layer slab calculation for simplicity. However, in the DFT calculations, for modelling the supported nanoclusters, three-layer Ag slabs were used with only the bottom layer kept fixed.

2.2 Global Optimisation Approach

In our study of the energy landscape of supported and free-space ZnO nanoclusters, we employ the Monte Carlo Basin Hopping (MCBH) method.²¹⁵ This method is one of the most successful strategies of global optimization for clusters, and has previously been used to predict the ground state structures of Lennard-Jones clusters containing up to 110 atoms.²¹⁶ A recent implementation of this approach in the Knowledge-Led Master Controller (KLMC)²¹⁷ code utilizes local minimization routines of the General Utility Lattice Program (GULP),²¹⁸ which allowed us to use different methods, or analytical forms of IPs. We have performed a search over energy landscapes of $(\text{ZnO})_n$ nanoclusters for a range of sizes between $n = 1$ and 16, and a larger sized clusters with $n = 24$. To find the global minimum (GM) and the low energy local minimum (LM)

structures a two-stage procedure was used. First, the global optimization was applied separately to free-space and Ag-supported ZnO nanoclusters. As a second stage, an additional randomized scan is employed, in which multiple quenches are performed on the candidate cluster structures (found by the free space global optimization) placed initially at random positions and in random orientations above the Ag support, to find the best location for these structures on the surface. Next, randomized scan results were compared with the global optimization results for Ag-supported ZnO nanoclusters, to examine the effect of the support in the global optimization stage.

2.3 Energy Definition

Classical IPs were used for the energy definition during the global optimization stage. The IP set included ZnO IPs developed by Whitmore *et al.*²¹⁹ to study ZnO surface structures and custom-parameterized IPs for the Ag–Zn and Ag–O interactions.²²⁰ In the latter case, we fitted parameters of Buckingham IPs for Ag–O and Ag–Zn to reproduce the geometries and energies from a series of periodic DFT calculations on a (ZnO)₆ cluster interacting with a four-layer thick Ag(111) slab. In particular, the previously known drum structure of (ZnO)₆ was chosen and placed on the Ag(111) surface, and the best adsorption site was found to be on-top position (see Figure 41). Next, the adsorption energies were calculated by moving the cluster towards and away from the surface by 0.1 Å displacements as shown in Figure 41. All of the parameters of the IPs are given in Table 6.

Key low-energy structures for each size found at the global optimization stage have been refined on an energy landscape defined at a DFT level of theory. Throughout, we employed the PW91 generalized gradient approximation exchange-correlation density functional²²¹ as implemented in the VASP code.²²² The projector augmented wave approach^{223,224} was used to describe the effect of core electrons on the valence states. Valence states were taken as $d^{10}s^2$, s^2p^4 and $d^{10}s^1$ for Zn, O and Ag atoms respectively. One-electron valence states were expanded in a plane wave basis up to a kinetic energy cutoff of 400 eV, where the total energy is converged to within 0.03 eV. Due to the spatial extent of the system, calculations were done only at the Γ point in reciprocal space. As the bottom layer of the Ag slab was fixed, the remaining atomic positions

were optimized until the forces on the atoms became less than 0.02 eV/Å. These criteria were necessitated by the large volume of calculations, carried out on a large unit cell and were found to satisfy a minimum requirement of conserving the cluster energetic stability ranking and essential structural features found when using more stringent convergence criteria.

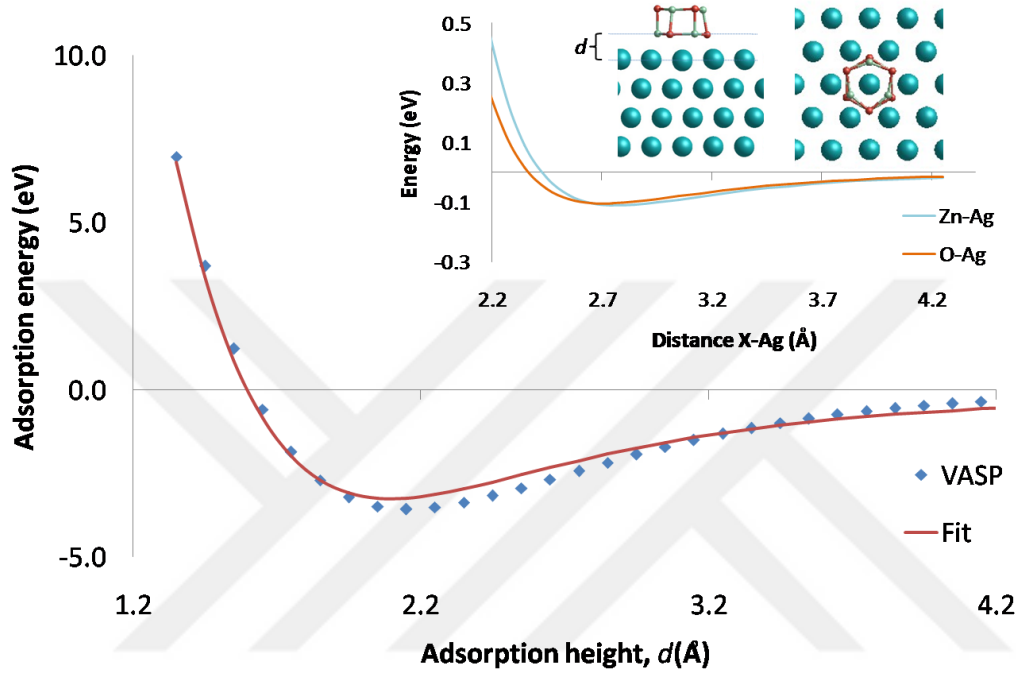


Figure 41. DFT calculated adsorption energy for a $(\text{ZnO})_6$ nanocluster on the Ag(111) surface as a function of the adsorption height. Inset shows the graphical forms of the fitted Ag-O and Ag-Zn Buckingham potentials.

In this chapter, we report binding energies of the nanoclusters calculated as $E_b = (E_n - nE_1)/n$, where E_n is the total energy of the size n nanocluster, and E_1 is the energy of a single ZnO unit. For the supported nanoclusters, we have subtracted the energy of the surface from E_n and the stabilization energy was defined for a nanocluster as $E_{\text{stabilization}} = E_n^{\text{on surface}} - E_n^{\text{free space}}$. It should also be noted that the clusters may have different orientations on the surface, which also changes their stabilization energies. Here, in all cases we have reported the lowest energy orientation found for each cluster, but we also have given examples of other orientations for some of the global minima structures.

Table 6. Parameters for IPs used in this study.

Buckingham potentials	Range (Å)	A (eV)	ρ (Å)	C (eV Å ⁶)
Zn core–O shell	0.0–2.2	592.342818	0.352159	12.896893
Zn core–O shell	3.1–3.3	157.297013	0.429673	5.815914
Zn core–O shell	3.6–12.0	912.517869	0.078935	11.723055
O shell–O shell	0.0–12.0	23674.698081	0.226404	33.476469
Ag core–O shell	0.0–12.0	13930	0.2301	83.4652
Ag core–Zn core	0.0–12.0	19068	0.2295	99.2348
Polynomial potentials	Range (Å)	C ₀ (eV)	C ₁ (eV Å)	C ₂ (eV Å ²)
Zn core–O shell	2.2–3.1	111.901725	–158.72704	89.657363
Zn core–O shell	3.3–3.6	64102.354057	–93216.170229	54188.8077
	Range (Å)	C ₃ (eV Å ³)	C ₄ (eV Å ⁴)	C ₅ (eV Å ⁵)
Zn core–O shell (cont.)	2.2–3.1	–24.98635	3.399631	–0.177932
Zn core–O shell (cont.)	3.3–3.6	–15741.070904	2284.873362	–132.581025
Spring potential	Range (Å)	k ² (?)	k ⁴ (?)	
O core–O shell	0.0–0.6	55.518883	31506.808344	
L–J potential	Range (Å)	A (eV Å ¹²)	C (eV Å ⁶)	
Zn core–O shell	0.0–2.2	316.435204	0.000000	
EAM potential	A (eV)	x (eV)	p	q
Ag core	0.1028	1.178	10.928	3.139
Ion charges	charge (–e)			
Zn core	2.000000			
O core	1.754415			
O shell	–3.754415			
Ag core	0.000000			

2.3 Nomenclature

Here the nomenclature used by Al-Sunaidi *et al*¹⁹⁹ is refined to cover new structures that become stable on the support. Al-Sunaidi *et al.* used a nomenclature for nanoclusters consisting of a number and a letter; na, nb, nc, ... etc., where “n” refers to the number of ZnO units in the nanocluster, and the small letter “a” refers to the structure found with the lowest energy of formation at that nanocluster size with the rigid ion IP model. This lower-case letter changes alphabetically with each next lowest-energy structure. The same ordering was also followed with capital letters, corresponding to where Al-Sunaidi *et al.* refined their results with a IP model using shells, which is an improvement to the rigid ion IP model as it can account for electronic polarization effects on the oxygen anion. Our addition to the nomenclature extends it to define newly found nanoclusters, which were mostly found by global optimization in the presence of an Ag-support. The newly found nanoclusters were denoted with three characters such as: npN, nqN or ncN. Here, as before, “n” refers to the number of ZnO units in the nanocluster. “N” is a number corresponding to the energetic ranking (1 being the most stable) of the cluster of class “p”, “q” or “c”. The letter “p” stands for planar 2D-type nanoclusters. These planar cluster isomers are not reported after n=7 nanoclusters in free-space, because their energies are much higher than the bubble-type clusters. The letter “q” is used for the clusters having structures containing both planar and bubble-like parts. In rare cases, the letter “c” was used to denote the newly found bubble-type clusters within the range of lowest energy structures for the corresponding size “n”.

3. Results and Discussion

Our global optimization study yielded many possible low energy structures for (ZnO)_n nanoclusters both in free-space and on Ag support. On a comparison with the earlier study of local minimum (LM) ZnO nanoclusters by Al-Sunaidi *et al.*¹⁹⁹ it is observed that the low-energy LM free-space nanoclusters were readily reproduced by KLMC with high efficiency in their range/diversity and energy ordering. In this section we first discuss what is known so far generally about free-space ZnO nanoclusters. Then we move to our results on the ZnO nanoclusters in the presence of the Ag(111) surface for

different sized $(\text{ZnO})_n$ clusters between $n = 1$ to 16, followed by the investigation of the effect of the surface morphology by introducing Ag(110) and Ag(100) surfaces for several cluster sizes. In the final sections, we continue our discussion with the corresponding results obtained at a higher DFT level of theory.

3.1. Free Space Clusters

According to their common structural features, the ZnO nanoclusters we find can be divided into families which we refer to as: sticks, rings, fused-rings, tubes, spheroids (or bubbles). Sticks are composed of one atom thick 1D chains of alternating Zn and O atoms, which can form rings by bending and connecting their ends. The fusion of multiple rings can result in planar 2D clusters. The bending of 2D fused-ring patchworks in the third dimension can result in the creation of 3D tubes, if the ends are left open, or spheroids/bubbles, if completely closed. Multilayer spheroids, or nested bubbles found for larger clusters sizes than considered herein, are often referred to as onions in the literature. The coordination number of atoms in these clusters depends both on the dimensionality of the structure and the position of the constituent ion in the structure (e.g. whether it is at an internal or an external site). Typically, the coordination number is two for 1D clusters, three for 2D clusters and four for 3D nanostructures for the internal ions, while it is decreased by 1 in each case for the external ions. According to previous studies of ZnO nanoclusters in free space²²⁵, ring structures are stable up to $(\text{ZnO})_7$ where an energetically preferential switch to bubble clusters then occurs. Bulklike wurtzite or other polymorph structures related to zinc blende or rocksalt phases were not found stable for small sized nanoclusters. However, it is estimated²²⁶ that the crossover from bubble structures to bulk-like structures will take place at an approximate cluster size of $(\text{ZnO})_{120}$.

3.2. IP Based Global Optimization Results for ZnO Nanoclusters on the Ag(111) Surface

3.2.1 $(\text{ZnO})_{1-4}$

Before moving larger nanoclusters, we started our calculations with the smallest possible clusters to gain insight into the very initial stages of growth of ZnO

nanoclusters on Ag. Due to the simplicity of these small systems we could exhaustively construct models by hand to look at patterns of ZnO atom matchings with the Ag surface. For a single unit of ZnO, the only non-fragmented structure is a simple Zn-O dimer. The most energetically favourable absorption site for the monomer was found to be with both the Zn and O atoms near to hollow sites on the Ag surface. Upon adsorption, for this dimer to align parallel with the Ag(111) surface and with atoms located on hollow sites the interatomic distance between Zn and O would need to be reduced by 0.038 Å, which increases the internal energy of the dimer by ~ 0.05 eV. However, our calculations predict that the dimer rotates, with the O atom 2.00 Å and the Zn atom 2.08 Å above the uppermost Ag plane and thus maintains its free space 1.701 Å Zn-O interatomic distance. Upon a closer inspection, the Zn atom is displaced 0.04 Å from the hollow site z-axis away from the O atom, the O atom is displaced 0.08 Å from the hollow site z-axis towards the Zn atom, whereas the shell of the O atom is polarized away from the Zn atom by 0.04 Å from the hollow site z-axis. The energy of the dimer in free-space is -30.86 eV/ZnO, which, upon exothermic adsorption onto the support, is lowered by a further 1.01 eV/ZnO.

On adsorption, a second ZnO monomer, would adsorb onto an equivalent position, if the interaction between the two monomers is ignored. By construction, assuming now they do interact, this will be one of the nearest vacant hollow sites to where the first monomer is adsorbed. Note that a simple linear extension of the first monomer (as an alternating Zn-O-Zn-O stick) would result in the second monomer occupying an energetically unfavorable top-site (directly above a silver atom). Even after carefully constructing various (ZnO)₂ sticks with atoms constrained to be at hollow axes, after optimization these hand-prepared sticks becomes buckled and relax by up to 3.27 eV/ZnO, with each eventually becoming a simple (ZnO)₂ ring on the surface. The (ZnO)₂ ring can be considered as being a flat rhombus (see Figure 42). When adsorbed on the Ag surface it has one of its Zn-O-Zn triangles above an Ag top site with the adjacent O atom on or near a neighboring hollow site. From the side view in Figure 42, it can also be seen that this ring is tilted: the O atom on the hollow site stabilizes at 2.05 Å above the Ag surface plane while the O atom within the triangle above the top site is 2.44 Å above the surface. The global optimization search for this system found not only the (ZnO)₂ ring structure but also a buckled stick, which bends about the

internal O atoms while the internal Zn atoms remain in linear O-Zn-O configurations. Note that, unlike the ring, the buckled stick is not stable in free space. On the Ag support, the four-membered ring is more stable than the buckled stick by 2.10 eV/ZnO.

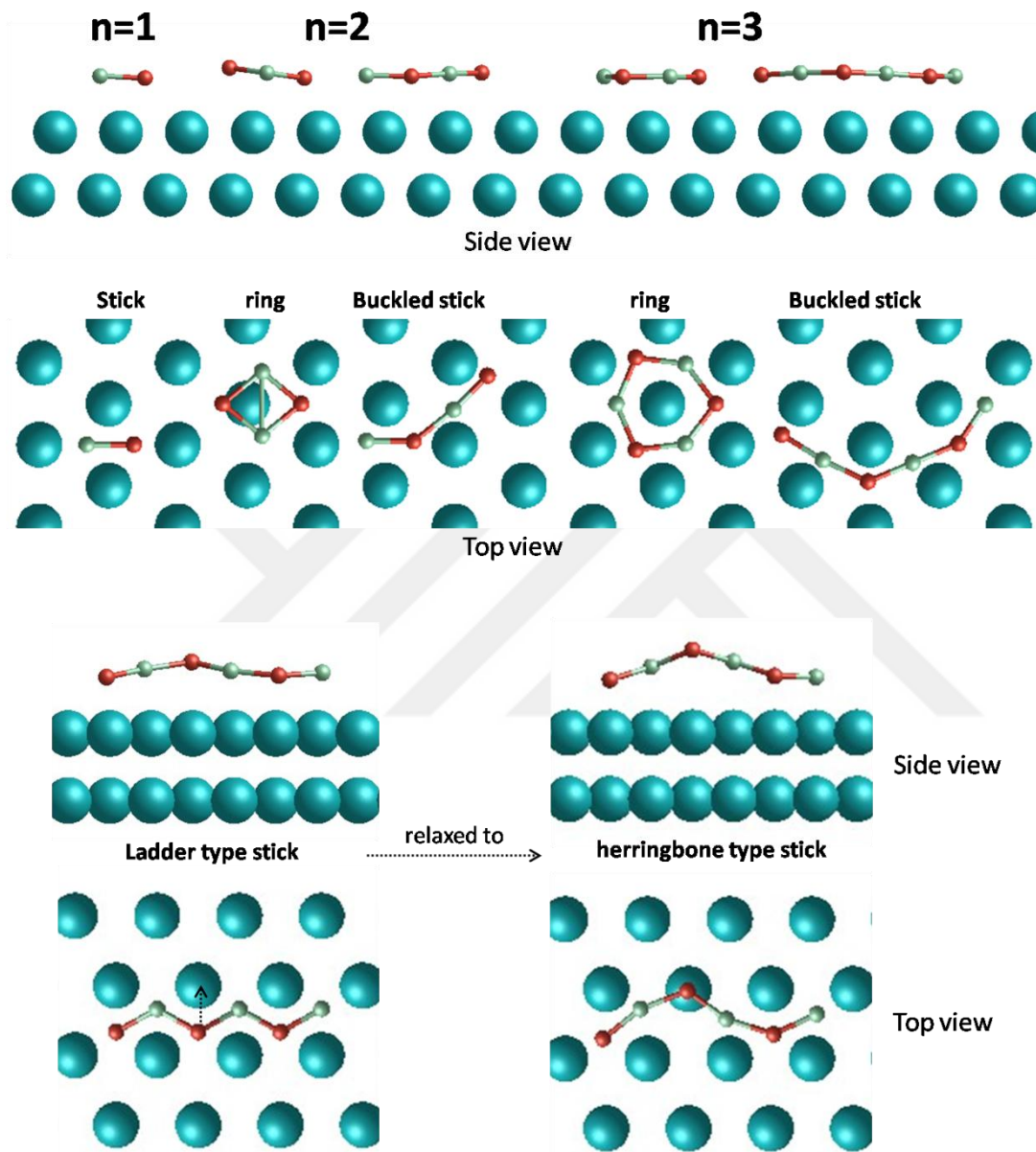


Figure 42. $(\text{ZnO})_n$ cluster structures on the Ag(111) support for the sizes $n = 1-3$.

In principle, the number of possible configurations is expected to rise as the cluster size increases. Like the $n = 2$ case, $n = 1$ sticks can be brought together to form longer sticks and even a six-membered ring for $(\text{ZnO})_3$. By careful consideration of many structures, only the ring was found to be stable for $(\text{ZnO})_3$ and relaxed by 0.54 eV/ZnO with atoms

displacing slightly from initially perfect hollow sites. Most other initially stick-like structures relaxed by 3.3-5.3 eV/ZnO and became the ring apart from the “ladder type” buckled stick, which relaxed by 1.17 eV/ZnO and become a “herringbone type” buckled stick. As shown in Figure 42, in this latter case the middle oxygen atom of the “ladder type” stick moved from hollow site to an on-top site, while the Zn atoms tend to approach a linear configuration (the O-Zn-O angles widen to 161.1° and 163.3°). For the (ZnO)₃ ring on surface, all of the Zn-O interatomic distances were found to be the same (1.804 Å), with the structure bending around O atoms considerably more than at the Zn atoms (O-Zn-O angles: 134.4°, Zn-O-Zn angles: 105.6°). Upon adsorption, Zn-O interatomic distances in the ring reduced only by 0.001 Å while the angles reduced by only 0.1°, which implies the internal interactions are much more decisive for the structure. Global optimization for $n = 3$ found both the ring and herringbone stick on the surface, but also uncovered another buckled stick, which is slightly more favorable than the herringbone type buckled stick by 0.04 eV/ZnO. In the latter buckled stick, Zn atoms are in an almost linear configuration, with the bending angles around the middle Zn atom of 178.1° and of 173.1° around the other Zn atom, whereas at the oxygen atoms the bending is more pronounced (131.7°, 148.8°). As for $n=2$ stick, both (ZnO)₃ sticks are not stable in free space but are stabilized by the support. However, the (ZnO)₃ ring is more stable than the sticks by 2.4 eV/ZnO on the Ag(111) surface.

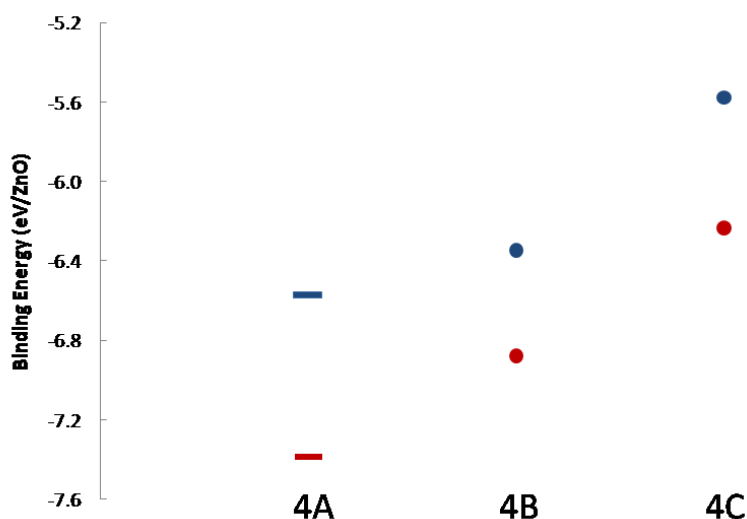


Figure 43. Energy ordering of (ZnO)₄ low-energy nanoclusters on the Ag(111) surface (red). Blue colored symbols are corresponding energies in free space. 2D structures are represented by sticks while 3D cluster structures are represented by filled circles.

For $n = 4$, three low-energy structures were found on the Ag(111) surface by global optimization, which correspond to the lowest energy structures 4A, 4B and 4C in free space (Figure 44). The energy ordering does not change in the supported case as can be seen in Figure 43, however the stabilization energies differ for each structure. The 2D 4A structure is stabilized by 0.82 eV/ZnO, whereas this stabilization is significantly smaller for the 3D-cluster structures 4B and 4C, 0.53 and 0.66 eV/ZnO respectively. In Figure 44, it can be seen that the mid-point of the eight-membered ring (4A structure) is in the middle between a hollow and an on-top position. However, the centres of the four-membered ring and a distorted six-membered ring, the contacting parts to the support of the 4B and 4C structures respectively, are on an on-top position. We note that this ring-surface adsorption configuration was also found for the $n = 3$ six-membered ring (see Figure 42). The centre of the ring was on the on-top position where all atoms are located at all of the surrounding hollow sites with small displacements. The adsorption height (taken as the average distance of the first contacting atoms of the cluster from the surface plane) was found to be 2.11 Å for this configuration. This distance is very close to the adsorption height of a single dimer, where both atoms are in hollow positions. However, the adsorption heights of the four-membered ring ($n = 2$) and of the eight-membered ring ($n = 4$) were found to be significantly greater, 2.25 and 2.30 Å, respectively. This difference is probably due to the poorer surface matching in $n = 2$ and $n = 4$ than in the $n = 1$ and $n = 3$ cases, as the stabilization energies also follow the same ranking. For the eight-membered ring, two oxygen atoms are close to on-top positions, and the other two oxygen atoms are closer to the hollow sites, while the Zn atoms are further from symmetric positions on the surface. As we check the distances from the surface plane for all of the individual atoms of the ring and stick structures $n = 2$ to $n = 4$, we observe that the hollow positioned atoms are always closest to the surface, and the distances are very similar for the closest atoms (~ 2.05 Å). However, the adsorption heights of the 3D-cluster structures 4B and 4C are found to be lower than that of 4A, 2.18 Å and 2.06 Å respectively, while their binding energies are considerably higher. This is possibly due to the structures of the clusters having a good match with hollow sites, but having relatively fewer surface contacting atoms.

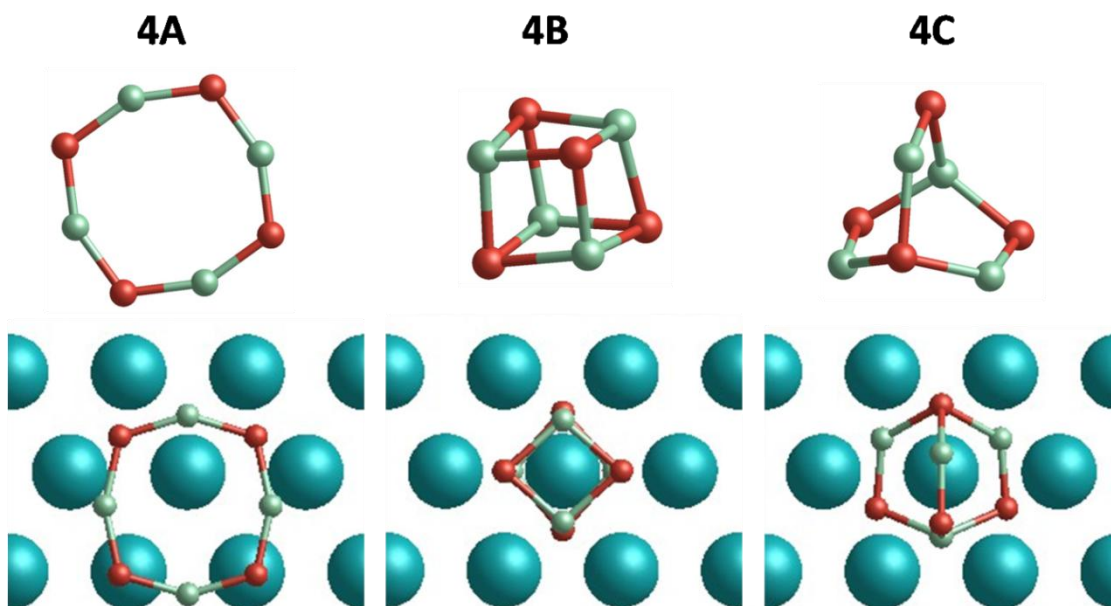


Figure 44. Nanocluster structures of $(\text{ZnO})_4$ both in free space (above) and on the Ag(111) support (below).

3.2.2 $(\text{ZnO})_{5-6}$

Ten clusters were found by global optimization on the Ag(111) support for the size $n = 5$. The energy ordering of these structures is given in Figure 46. The free space global minimum, 5A, which is a ten-membered 2D ring structure, does not change its energetic ranking in the Ag-supported case. The stabilization energy of this cluster on the Ag support is 0.84 eV/ZnO. The second lowest-energy Ag-supported structure is found to be 5p1, which is a distorted double ring (Figure 45). In free space, 5p1 is found to be the third lowest energy after 5A and the 3D cluster, 5B. The 5p1 structure is stabilized by the support by 0.95 eV/ZnO whereas 5B structure only stabilized by 0.59 eV/ZnO. This higher stabilization can be probably attributed to the number of atoms contacting with the surface. Whereas for a 2D structure all the atoms are close to the surface, 3D clusters only have a relatively small surface contact area. The next seven lowest energy structures on the Ag(111) surface are all 3D cluster structures and follow almost exactly the same ordering as in free space, with very similar surface stabilization energies of about 0.6 eV/ZnO. The only energy ranking change occurred between the 5C and 5D clusters, which have the same structural configuration but with atom types exchanged (*i.e.* $\text{Zn} \leftrightarrow \text{O}$). They both have very similar energies both in free space

(0.004 eV/ZnO difference) and on the Ag support (0.010 eV/ZnO difference) and they both make contact with the surface with their six-membered ring parts, where the ring is slightly distorted and positioned at an on-top surface site. This small stability switch can be attributed to these distorted rings where the oxygen and zinc distances to the surface differ slightly. The last structure found on the surface was another 2D structure, which can be roughly described as a distorted 5H cluster, with a Zn-O tail. The stabilization energy for the 5H structure is found to be 0.75 eV/ZnO. For the size $n = 5$, the separation of the 2D and 3D cluster types becomes clearer, as the stabilization energies of 2D and 3D cluster types form two distinct groups (Figure 46).

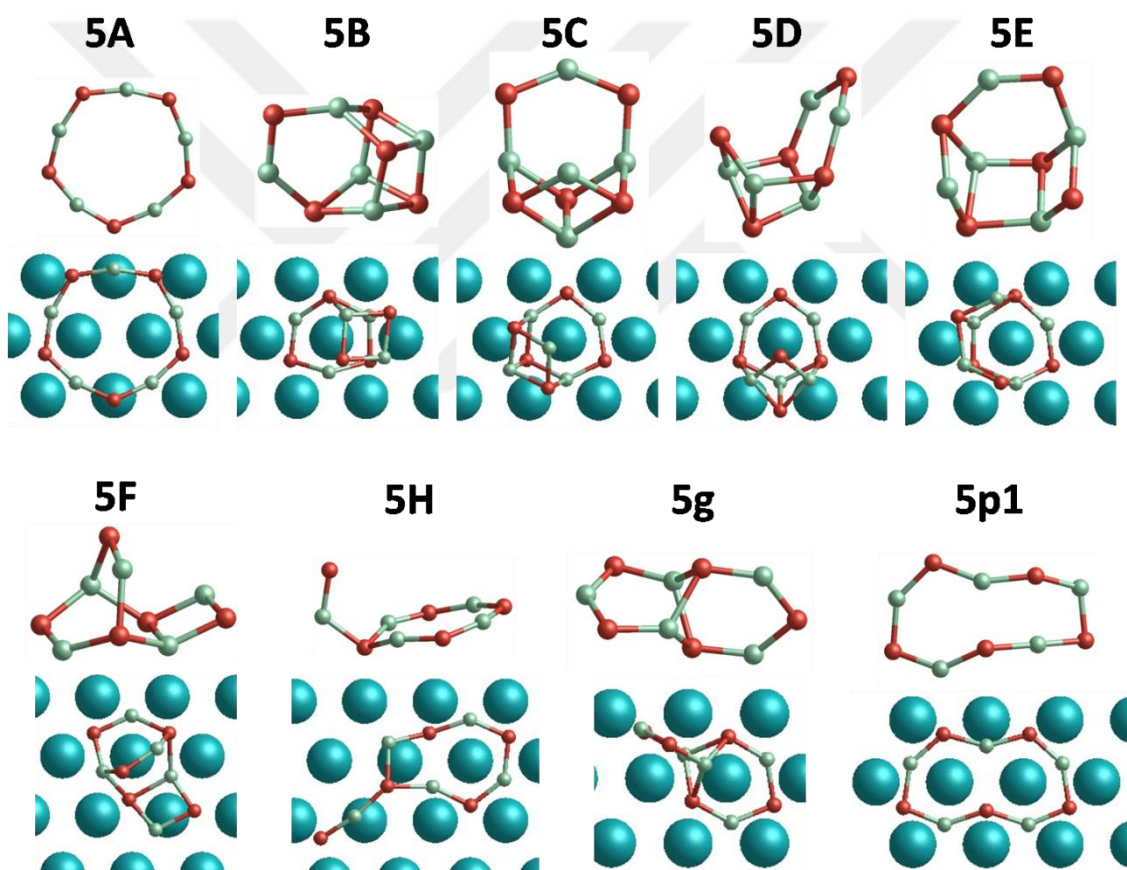


Figure 45. Structures of $(\text{ZnO})_5$ clusters in free space (above) and on the Ag(111) support (below).

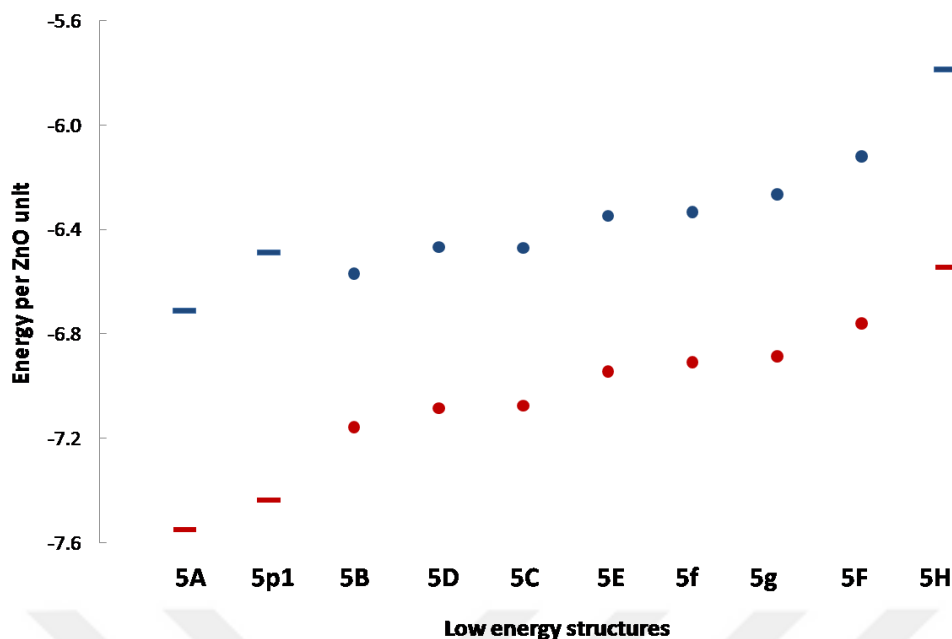


Figure 46. Energetic stability ordering of $(\text{ZnO})_5$ nanoclusters on the Ag(111) surface (red). Blue colored symbols are corresponding energies in free space. 2D structures are represented by bars, while 3D cluster structures are represented by filled circles.

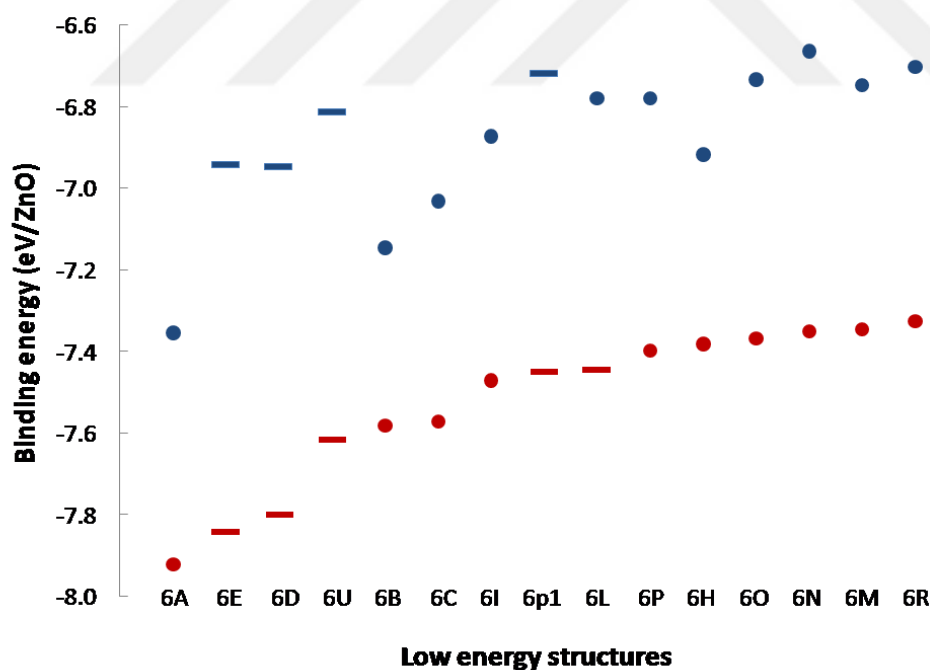


Figure 47. Energetic stability ordering of $(\text{ZnO})_6$ nanoclusters on the Ag(111) surface (red). Blue colored symbols are the corresponding energies in free-space. 2D structures are represented by bars while 3D cluster structures are represented by filled circles.

For $n = 6$, the global minimum structure in free space, 6A, which is a drum-like hexagonal prism, retained its number one energy ranking when absorbed on the Ag(111) support. It is adsorbed with one hexagonal face in an on-top position on the surface, and its stabilization energy was found to be 0.57 eV/ZnO. The next lowest energy cluster, 6B, was found to be ranked 5th when supported. The third lowest free-space energy cluster, 6C, is ranked sixth on the Ag support. The 6C cluster binds to the surface by a six-membered ring, while the 6B by a part of a distorted six-membered ring, in which only four of the atoms make contact with the surface. The three 2D structures, 6E, 6D and 6U, achieve a better rank when supported than either 6B or 6C. The stabilization energies for 6E, 6D and 6U are 0.90, 0.85 and 0.80 eV/ZnO whereas for 6B and 6C they are 0.44 and 0.54 eV/ZnO, respectively. 6D and 6E clusters also switch their ranking on the support. The 6D structure is a ring, which, unlike the smaller $n = 2, 3, 4$ and 5 clusters, is not the global minimum on the Ag support. The 6E structure can be seen as joined six-membered rings, which are connected with a four-membered ring. The four-membered ring of 6E is at an on-top position on the Ag surface, while the six-membered rings adjust to match the neighboring on-top positions. The larger ring of 6D structure centers on a hollow site, with three oxygen atoms directly above Ag atoms. Thus the planarity of the ring is distorted because the on-top oxygen atoms move 0.30 Å away from the surface, while oxygen atoms in the hollow position move 0.25 Å closer to the surface. Similar distortions can be also seen for the supported 6U structure, which consists of an eight- and a six-membered ring. These orientation differences due to the surface matching and the related distortions can explain the difference in the stabilization energy of these three 2D clusters.

It should also be noted that for the 2D clusters, one single cluster configuration on the support can correspond to different but closely related free-space clusters, which are also close in formation energies. In such cases, we have chosen the corresponding free space cluster using a reverse process, i.e. relaxing the supported cluster again in free space. The first example of such a phenomenon emerges at size $n = 6$ (where 2D clusters start to form as multiple rings) for the 6E cluster on the support, which also corresponds to 6F and 6G structures, i.e. all three structures converged to the same structure on the support. In free space, multiple rings do not stay planar, and the rings get tilted where the rings are connected (where atoms have coordination number of

three instead of two) due to the polarization effects (when we switch off the shell model, the clusters all became planar again). However, on the support planarity is enhanced (e.g. the maximum difference in atomic z-coordinate, Δ_z , for 6E on the support is 0.07 Å).

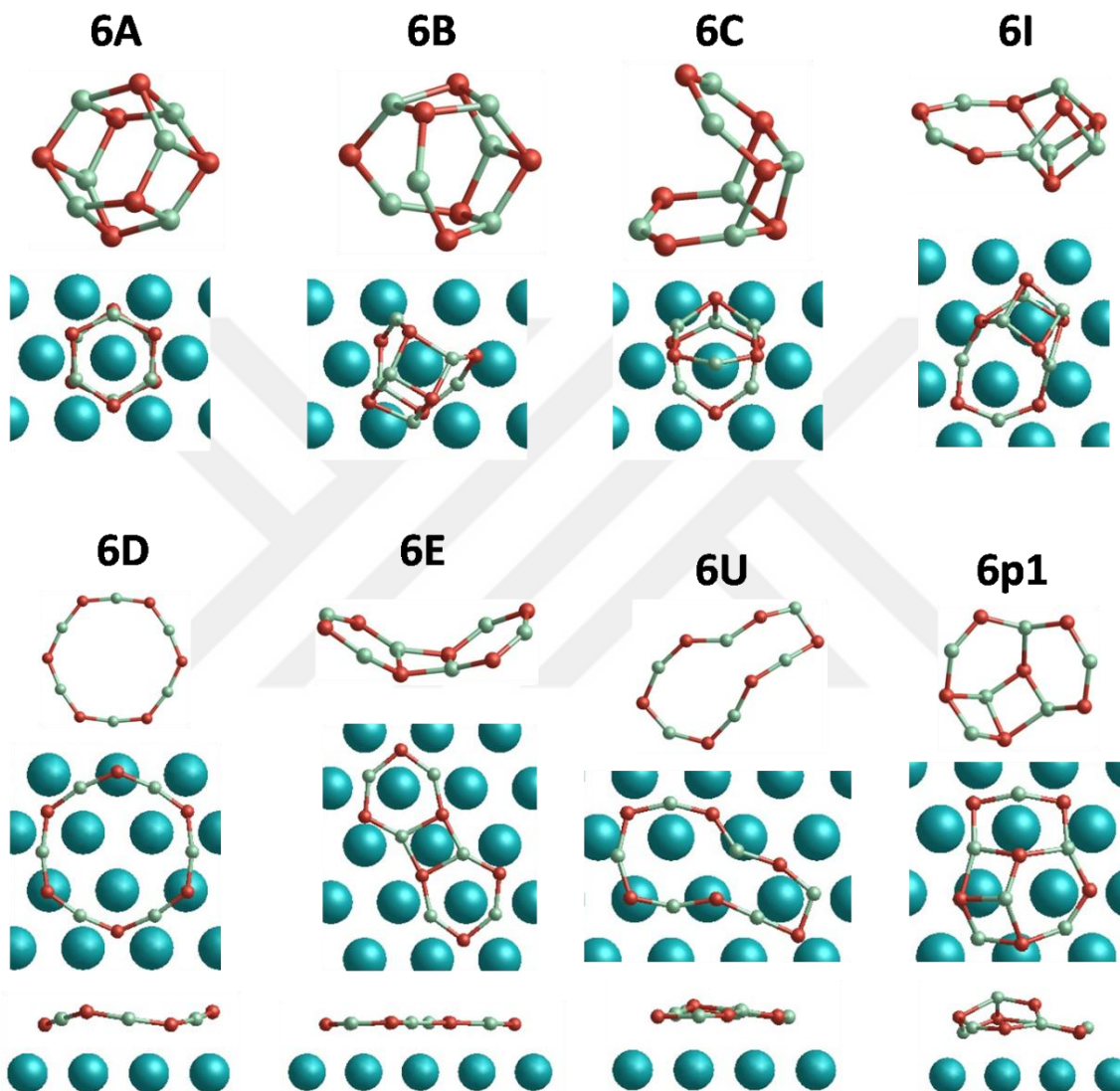


Figure 48. Low energy structures of $(\text{ZnO})_6$ in free space and on the Ag(111) support. Side views of 2D clusters are also given.

It should be noted that there is another low-energy orientation for the global minimum structure, 6A, in which the cluster binds to the surface via a four-membered ring in an on-top position instead of a six-membered ring. This orientation is 0.17 eV/ZnO higher in energy than that of the lowest energy orientation of 6A. This would make its rank 4

as the 2D structures 6D and 6E are less stable than the global minimum only by 0.07 and 0.12 eV/ZnO, respectively.

In general, for sizes $n = 5$ and 6, the lowest energy orientations for most of the structures were found to be those that minimize the on-top interactions of the contacting atoms as much as possible. The 3D type clusters tend to bind to the support by their six-membered ring faces, and the stabilization energy increases with a better surface-cluster matching. For the 2D clusters, it becomes more difficult for the adjacent rings to occupy better positions because of the lattice mismatch, and the structures which fit the surface better also stabilize more.

3.2.3 (ZnO)₇₋₈

For the size $n = 7$, the global minimum structure in free space, 7A, was found to be the fifth lowest energy structure on the Ag support, while four 2D structures which are not in the first ten lowest energy clusters in free space are significantly stabilized on the surface. The stabilization energies for these 2D structures were found to be 0.85 ± 0.03 eV/ZnO whereas the stabilization energy for the 3D cluster 7A is 0.50 eV/ZnO as the number of the contact atoms in 2D structures is higher. The large energy difference of 7A relative to the 2D structures result in this ranking change and the 7A is not global minimum anymore. The next lowest energy structure found on the surface is also another 2D structure with the stabilization energy 0.79 eV/ZnO. The low energy metastable 3D cluster structures in free space align with a similar ordering on the surface with the stabilization energies of 0.48 ± 0.03 eV/ZnO. Among these structures, 7E acquires the lowest energy on the surface, most probably because of a better orientation, where it binds to the surface via a six-membered ring again in a on-top position. In Figure 49, a clear separation of the stabilization energies of 2D structures and the 3D clusters can be seen, starting from $n = 7$ it holds for higher sizes. At size $n = 7$, clusters composed of both 2D and 3D parts form another class, which are distinguished in the energy graphs by the use of triangles. Not surprisingly, the stabilization energies of these quasi-2D structures lie between those of the 2D and 3D structures.

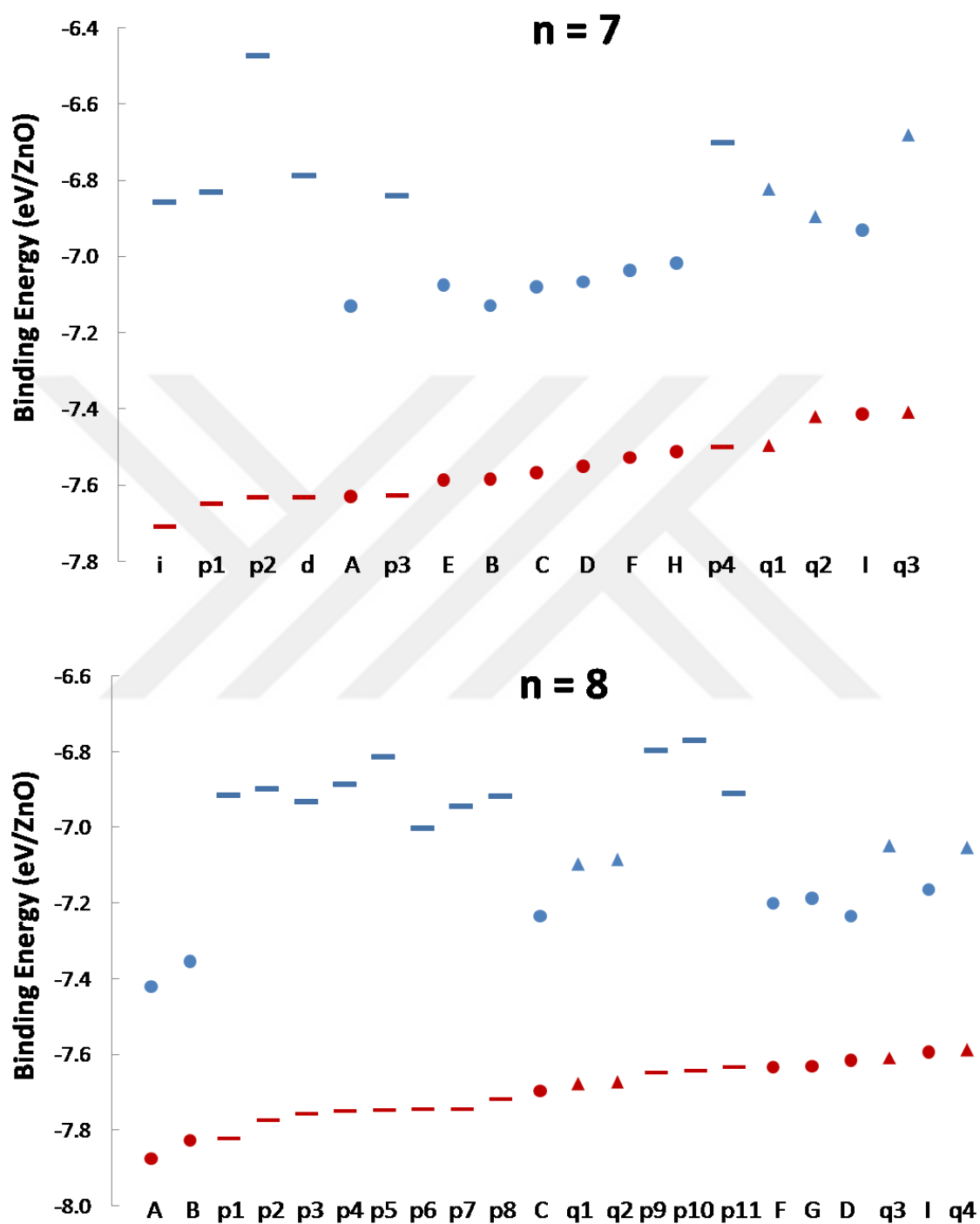
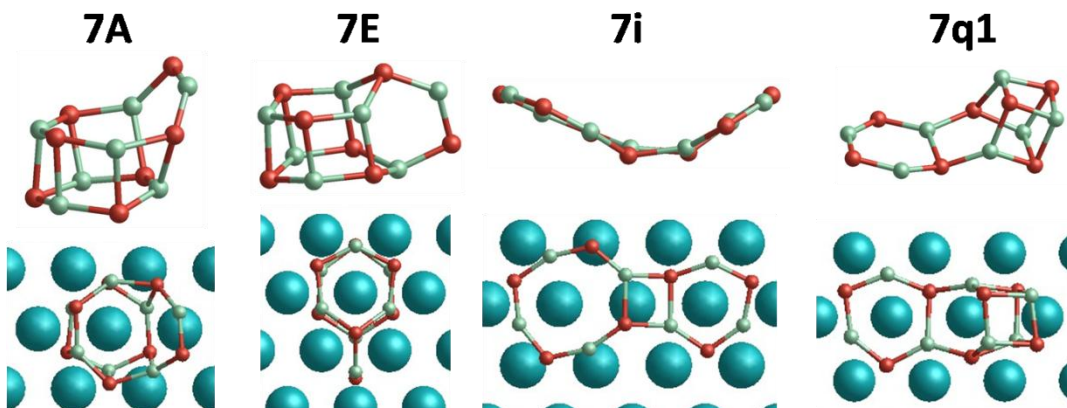
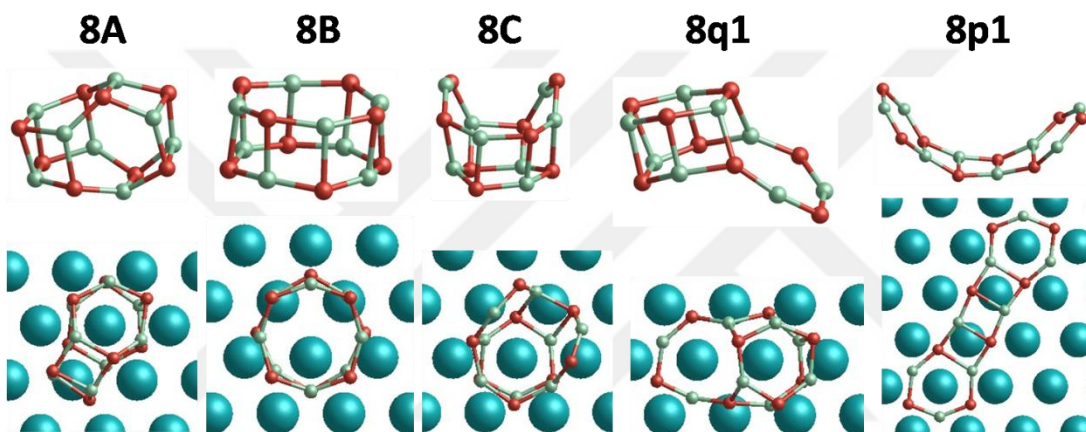


Figure 49. Energy ordering of $(\text{ZnO})_7$ and $(\text{ZnO})_8$ nanoclusters on the Ag(111) surface (red). Blue colored symbols are corresponding energies of clusters in free space. 2D structures are represented by bars while 3D cluster structures are represented by filled circles. Triangles represent the clusters having both 3D and 2D parts.

Figure 50. Structures of $(\text{ZnO})_7$ clusters in free space and on support.Figure 51. Structures of $(\text{ZnO})_8$ clusters in free space and on the Ag(111) support.

For size $n = 8$, the global minimum and the second lowest energy structure, 8A and 8B, retain their ranking in the supported case. The stabilization energies for these two structures are 0.45 and 0.47 eV/ZnO, respectively. However, the third lowest energy structure in free space, 8C, was found to be 11th on support, whereas eight new supported 2D structures fill the gap between 8B and 8C, which are not found among the fifty lowest energy cluster isomers during global optimization in free space. The stabilization energy of 8C, 0.46 eV/ZnO, is almost the same as that of 8A or 8B, whereas the 2D structures have stabilization energies of 0.84 ± 0.09 eV/ZnO. The lowest energy supported 2D structure has almost the same energy as 8B on the support with only a very small energy difference of 0.005 eV/ZnO. All of the 2D structures are also found to be lower in energy than the 8A structure in other possible orientations to the most stable one reported. Examples of the so-called quasi-2D class of clusters are also found in the first fifteen structures on the support for size $n = 8$. Although such

structures can be generated by free-space global optimization, there are still many more 3D clusters than quasi-2D structures which are lower in energy in free-space. The average stabilization energies for these three types of clusters on the surface: 2D, quasi-2D and 3D, are found to be 0.84, 0.57 and 0.45 eV/ZnO, respectively.

3.2.4 (ZnO)₉₋₁₀

For the size $n = 9$, again the two lowest energy clusters, 9A and 9B in free space found to be have the same 1st and 2nd ranking on the support with corresponding stabilization energies of 0.42 and 0.39 eV/ZnO. The third lowest energy cluster was found to be 9G, with a higher stabilization energy of 0.53 eV/ZnO, which is the highest stabilization energy found among all 3D clusters for $n = 9$. This is probably due to its structure which can fit to the Ag surface via two adjacent six-membered rings at on-top sites while having the largest number of surface-contact atoms among 3D clusters. The 2D structures were not found in a global optimization in free space, which is also the case for all cluster sizes higher than $n = 9$. However, global optimization in the presence of a support still results in low-energy 2D structures, mixed with 3D cluster structures. For $n = 9$, rank 4 to 8 structures were found to be 2D apart from the 7th, which is quasi-2D. For $n = 9$ size, the average stabilization energies are 0.45 and 0.85 eV/ZnO for 3D and 2D structures, respectively.

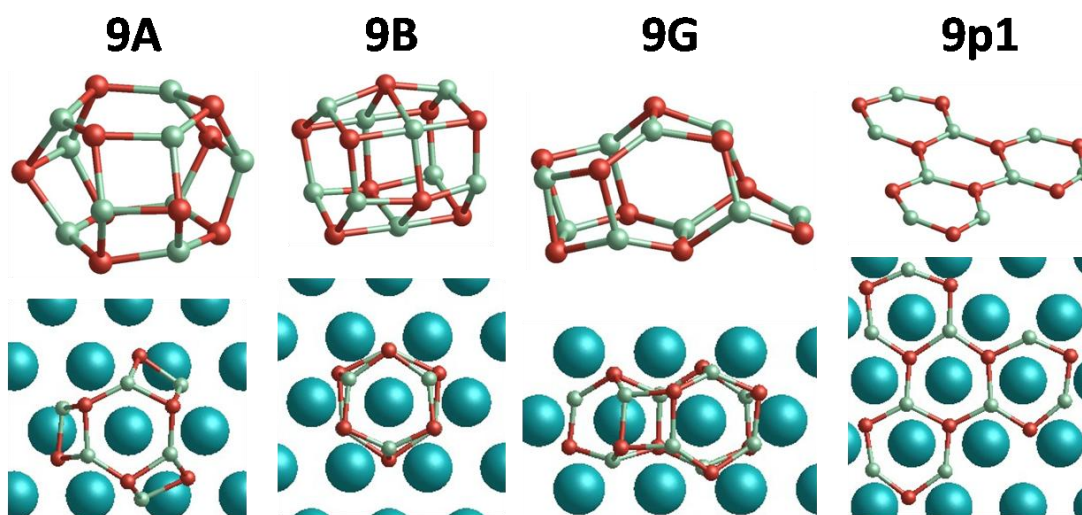


Figure 52. Structures of (ZnO)₉ clusters both in free space and on the Ag(111) support.

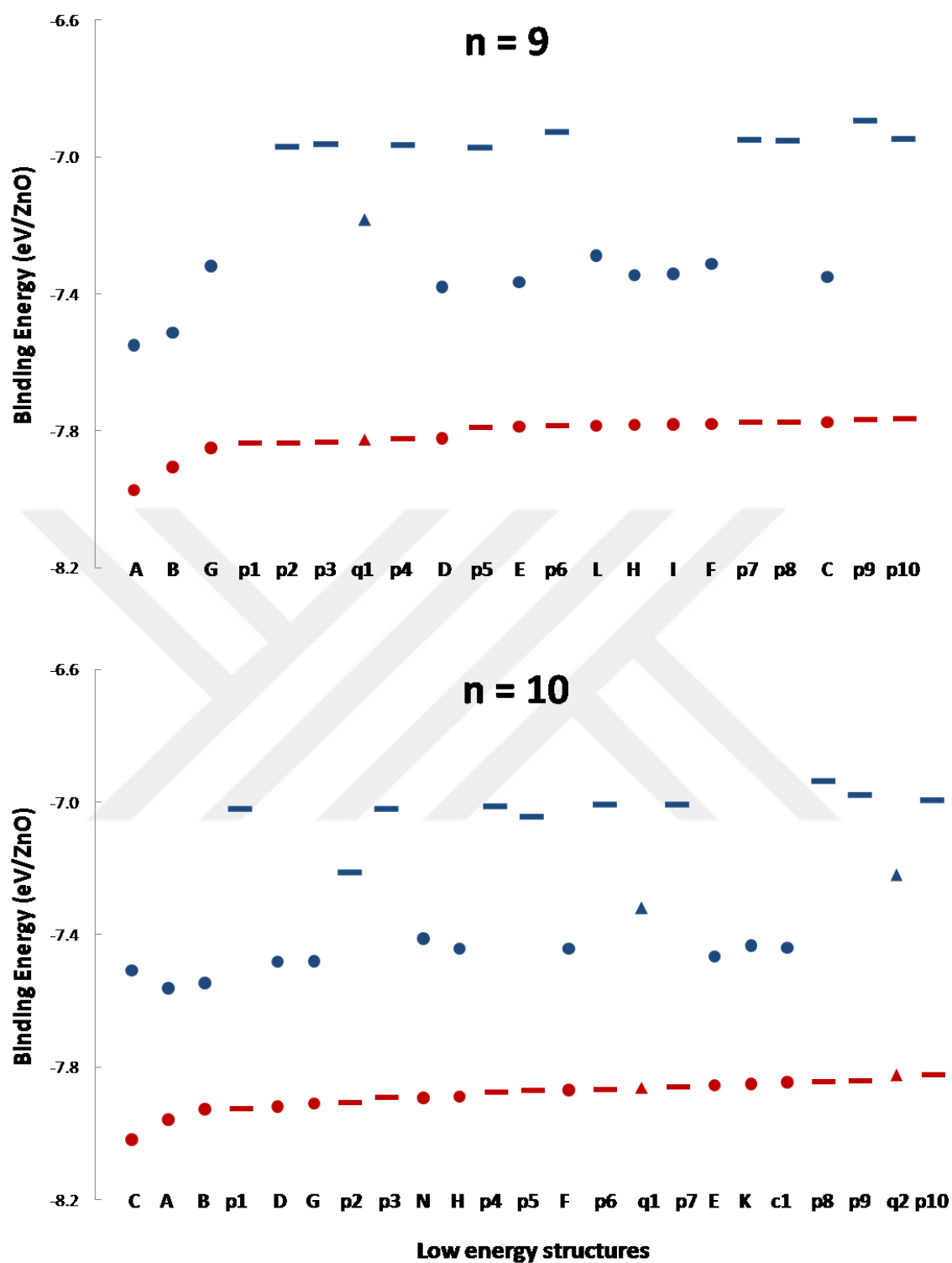


Figure 53. Energetic ordering of $(\text{ZnO})_9$ and $(\text{ZnO})_{10}$ nanoclusters on the Ag(111) surface (red). Blue colored symbols are corresponding energies in free space. 2D structures are represented by bars whereas 3D cluster structures are represented by filled circles. Triangles represent the clusters having both 3D and 2D parts.

For size $n = 10$, the third lowest energy structure in free space, 10C, was found to be the global minimum on the Ag support. Like the case 9G, 10C adsorbs by two adjacent six-membered rings enclosing two neighboring surface silver atoms, whereas the 10A and 10B structures interface via only one six-membered ring enclosing one surface silver atom. The fourth ranked cluster on the surface was found to be a 2D structure consisting of two four-membered, three six-membered and one eight-membered ring. Note that in the Figure 53 the free space energy of the 10p2 cluster is significantly lower than that of the other 2D structures and has the stabilization energy of 0.69 eV/ZnO. This is because in free space, this structure bends in such a way that it results in a new bond being formed between two rings. If we force the cluster to stay planar, its energy becomes similar to the energies of other 2D structures. All of the 2D structures are have fused ring structures from size $n = 9$, which usually consist of four-, six- and eight-membered rings, although rarely ten- or twelve-membered rings also occur. The orientation on the surface is mainly determined by the six-membered rings, where they fit on-top positions on the surface, followed by the same tendency for four-membered rings. The average stabilization energies found to be 0.85 and 0.43 eV/ZnO for 2D and 3D structures, respectively.

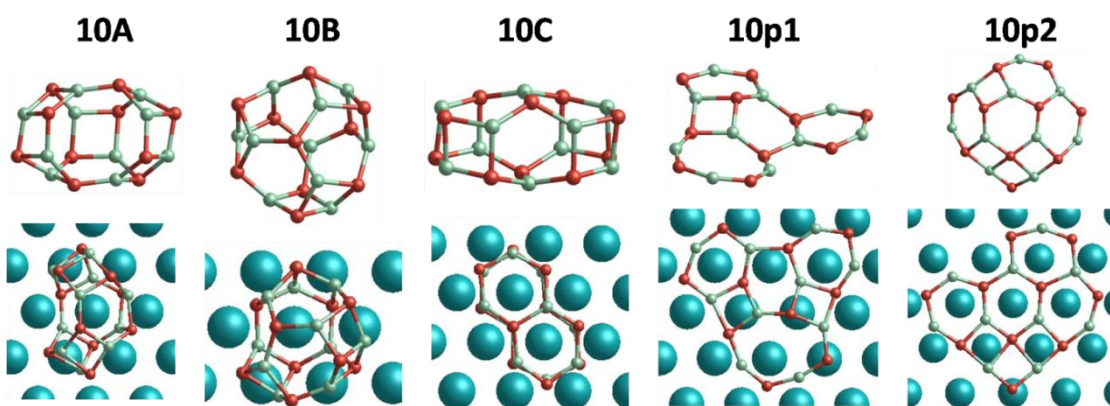


Figure 54. Structures of $(\text{ZnO})_{10}$ clusters in free space and on the Ag support.

3.2.5 $(\text{ZnO})_{11-16}$

For sizes $n = 11$ to 16, all the global minima free-space structures nA were found to be the lowest energy structures also on the Ag surface. The stabilization energies of 2D, quasi-2D and 3D structures follow the same trends as those of smaller sized clusters, in that they are much higher for 2D than 3D structures and the energies of quasi-2D

structures are in the middle. The lowest-energy free space 2D structures, when on the surface, were found to be second for $n = 11$ and 12, and fifth and fourth for $n = 13$ and 14 respectively. The low energy structures for $n = 13$ and 14 exhibit a mixture of 2D and 3D clusters, while at size $n = 15$ an energetic separation occurs, where all the 2D clusters are found to be higher in energy than almost all the 3D cluster structures. The same situation also happens for $n = 16$. However, the energy differences between the lowest energy 2D and 3D clusters (see Figure 55) do not increase as the cluster size increases from $n = 11$ to $n = 16$; found to be 0.05, 0.12, 0.03, 0.09, 0.10, and 0.06 eV/ZnO respectively. Apart from the most stable 3D clusters, nA , there are also energy ranking changes among the 3D clusters on the surface, according to how they match the surface, following the trends seen above for smaller sizes. In general, the clusters adsorbing to the surface by two adjacent six-membered ring faces (11C, 11D, 12C, 13D, 13F, 14E, 15B, 16D) or other size adjacent rings (11F, 11c5, 12I, 13E, 13J) are stabilized more, while clusters adsorbed only by a single six-membered ring (11B, 11E, 13B, 13C, 14B, 15c4, 16B) or a single eight-membered ring (12B, 16C) are stabilized less. The higher surface stabilization of the six-membered rings can be also seen for the most stable 3D clusters shown in Figure 56. Similarly, 2D clusters match the surface as much as possible via hexagonal rings. However, there is a mismatch between a uniform hexagonal ZnO patchwork and the Ag(111) surface. Furthermore, the clusters consisting of only six-membered rings are generally not stable in free space and relax to alternative 2D structures, including four- and eight-membered rings. One exception is for size $n = 9$, for which has the most stable 2D cluster on the surface (the D_{3h} symmetric structure: 9p1) is also the most stable 2D cluster in free space. We have also considered fused chains of six-membered rings. For such chains, all the rings collapsed into four-membered rings except from those at the ends. In a chain of rings, all the corner atoms on one side are O atoms while on the other side are Zn atoms. Most of the 2D structures are found to be buckled in free space due to energy-lowering polarization of the oxygen anions, while they become planar with the effect of support.

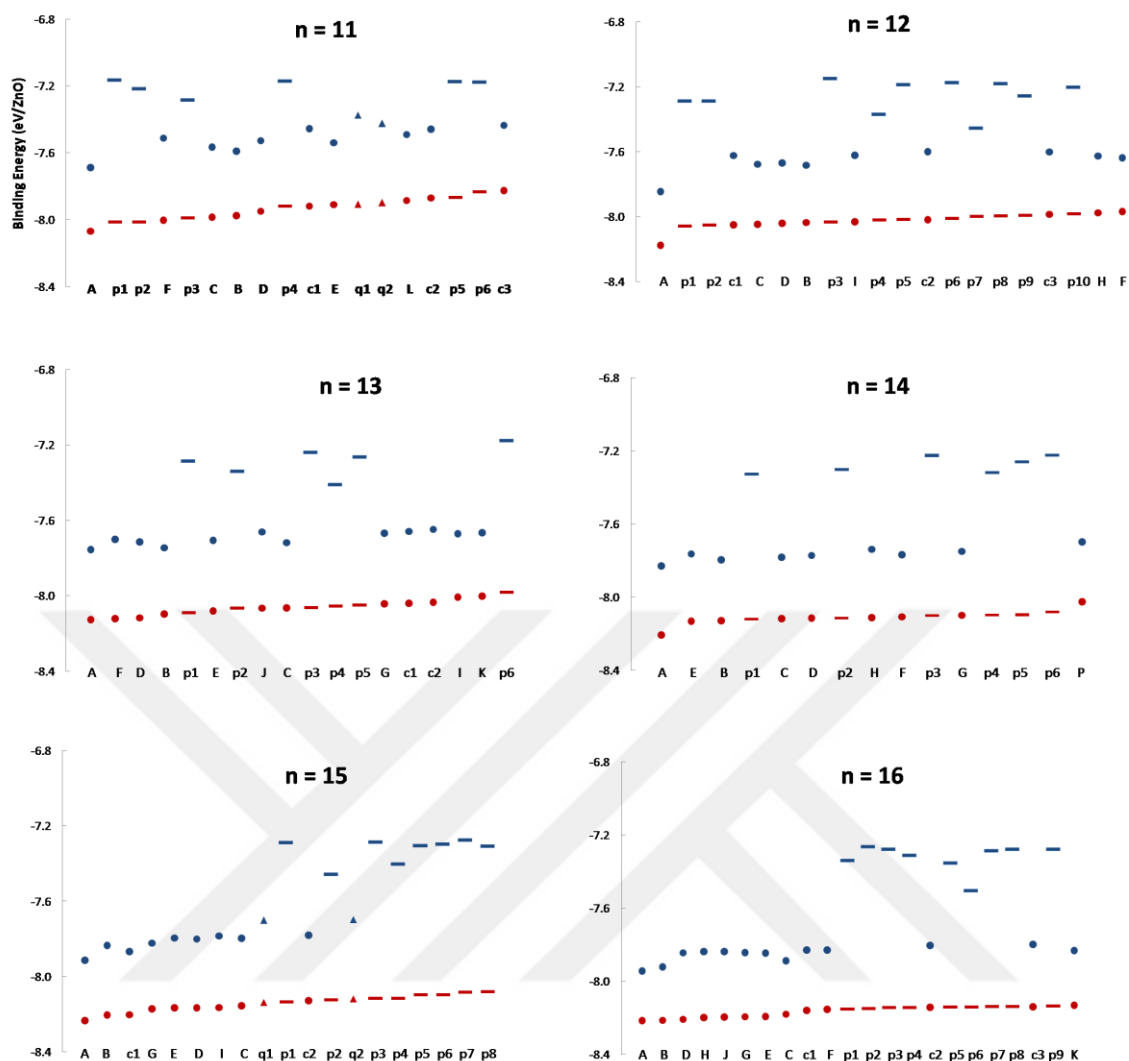


Figure 55. Energetic ordering of $(\text{ZnO})_{11}$ - $(\text{ZnO})_{16}$ nanoclusters on the $\text{Ag}(111)$ surface (red). Blue colored symbols are the corresponding energies in free space. 2D structures are represented by bars whereas 3D cluster structures are represented by filled circles. Triangles represent the clusters having both 3D and 2D parts.

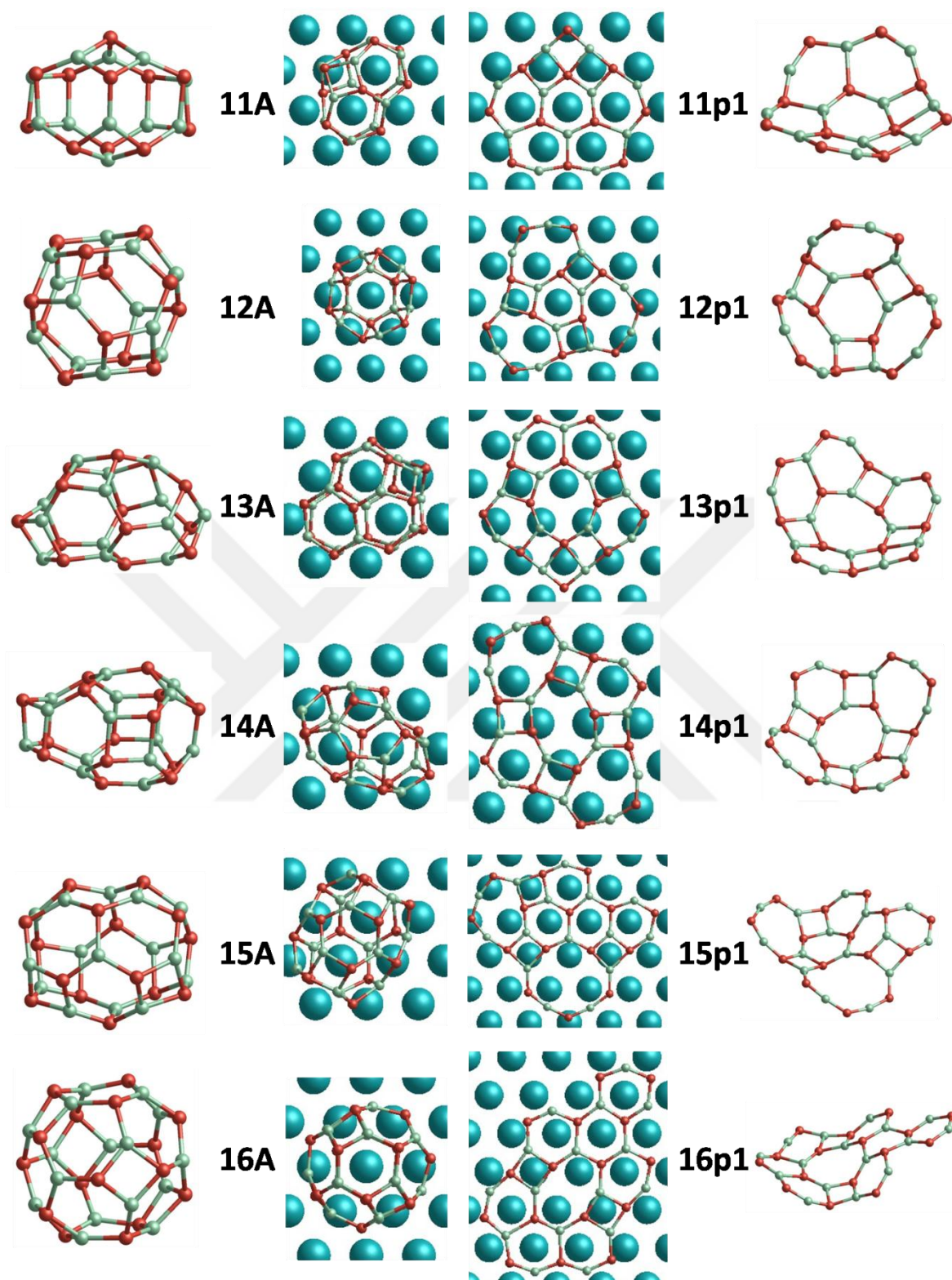


Figure 56. Structures of lowest energy 2D and 3D $(\text{ZnO})_{11-16}$ clusters in free space and on the $\text{Ag}(111)$ support.

3.2.6 (ZnO)₂₀, (ZnO)₂₄ and (ZnO)₂₀-based sub-monolayers

As the cluster size increases, a lower proportion of the outer surface of the low-energy free-space 3D clusters becomes available for contact with the silver surface. Therefore the ranking changes between 3D and 2D clusters become more pronounced on the surface. For (ZnO)₂₀, the free space GM structure, 20A, was found to be ranked 19th on the surface, with fifteen 3D and three 2D supported clusters found to be more stable. Similarly, the 20C cluster, which also does not include a large adsorption face, decreased by fifteen ranking positions when on the Ag surface, whereas the 20D cluster, which adsorbs via a face consisting of five adjacent six-membered rings (see Figure 57), becomes the lowest energy structure on the Ag surface. The 20D structure is stabilized by 0.37 eV/ZnO on the surface, whereas structures 20A and 20C are stabilized by 0.25 and 0.29 eV/ZnO, respectively. The 20B and 20E clusters were found to be the second and the third lowest energy structures on the surface with 0.34 eV/ZnO stabilization energies. Among these structures, 20D can be seen as a double layered ellipsoidal structure. 20B and 20E are also ellipsoidal in form, whereas 20A and 20C are more spherical. Both these latter pairs of clusters are adsorbed via their fused six-membered rings, however, the 20B and 20E exhibit flatter faces. Global optimization also generated new bubble-like clusters, which are mainly ellipsoidal, with stabilization energies of about 0.33 eV/ZnO. The 2D clusters were found as 14th, 17th and 18th lowest energy structures, with stabilization energies of about 0.87 eV/ZnO. The energy difference between the lowest energy 2D and 3D clusters (20p1 and 20D) on the surface was found to be 0.07 eV/ZnO. As shown in Figure 60, the 20p1, 20p2 and 20p3 structures mainly consist of six-membered rings.

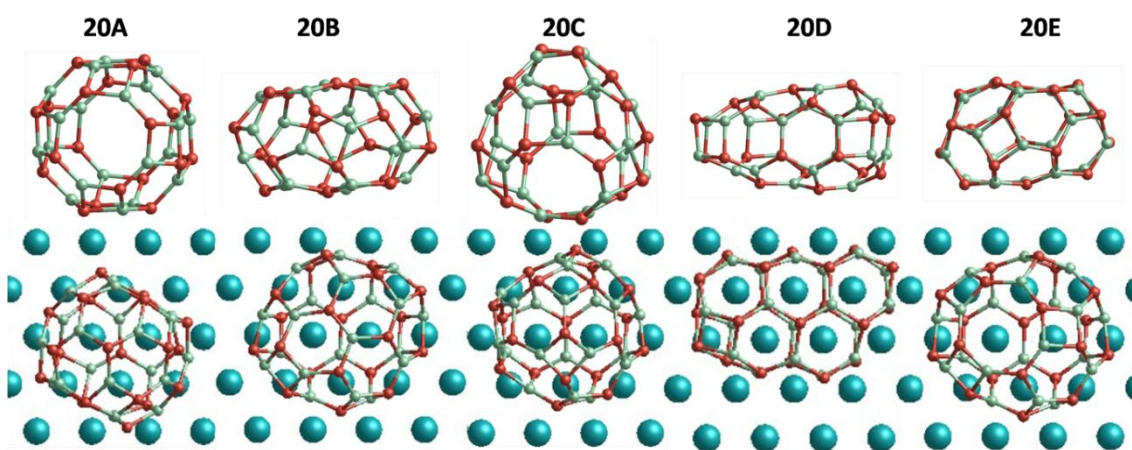


Figure 57. Structures of (ZnO)₂₀ in free space and on support.

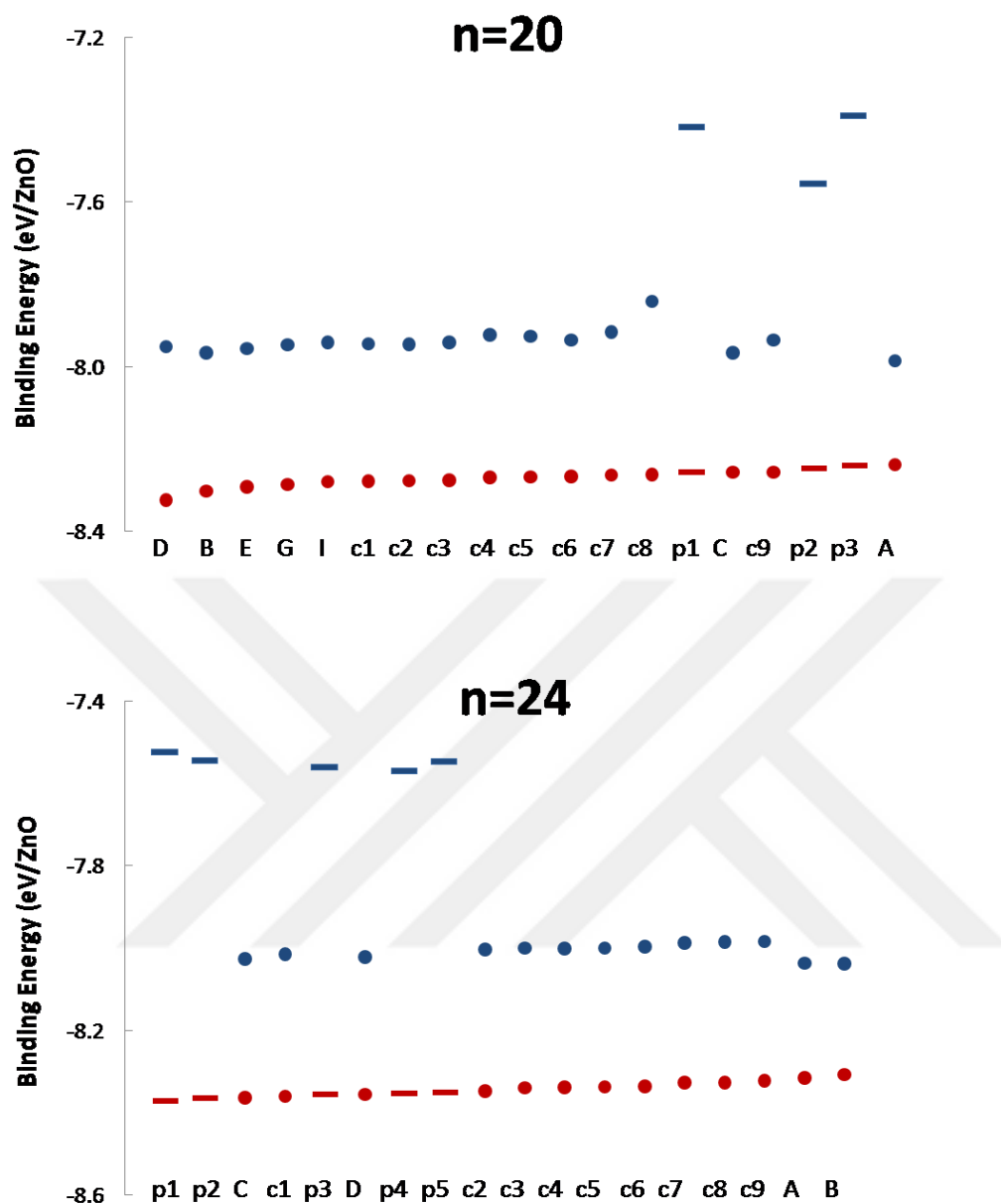


Figure 58. Energetic ordering of $(\text{ZnO})_{20}$ (above) and $(\text{ZnO})_{24}$ (below) nanoclusters on the Ag(111) surface (red). Blue coloured symbols are corresponding energies in free space. 2D structures are represented by bars whereas 3D cluster structures are represented by filled circles.

For the size $n = 24$, again the energetic ranking of the 2 lowest energy free space clusters increases drastically when on the surface. Cluster 24A becomes the 17th most stable supported structure and 24B becomes 18th with the stabilization energies of 0.28 and 0.27 eV/ZnO, respectively. All other 3D clusters are stabilized by 0.33-0.34 eV/ZnO. Like in the case of $(\text{ZnO})_{20}$, all the lower energy supported 3D clusters, except 24A and 24B, were found to adopt an ellipsoid bubble morphology. The lowest energy 3D cluster, 24C, can be seen as an inflated two layered structure, which has faces

formed by adjacent hexagonal rings. For $(\text{ZnO})_{24}$, planar 2D structures are slightly more stable on the surface than the supported ellipsoidal bubbles in general, the former having 0.80-0.85 eV/ZnO stabilization energies. 2D 24p1 and 24p2 structures become 1st and 2nd lowest energy structures on the surface, which are only 0.008 and 0.001 eV/ZnO more stable than the 3rd lowest energy structure on the surface, the 3D 24C structure, respectively. We note that global optimization also generated three other low energy closely related supported 2D structures (24p3, 24p4, 24p5). All the supported 2D structures were found to have a hexagonal core, which is surrounded by other sized rings as can be seen in Figure 59.



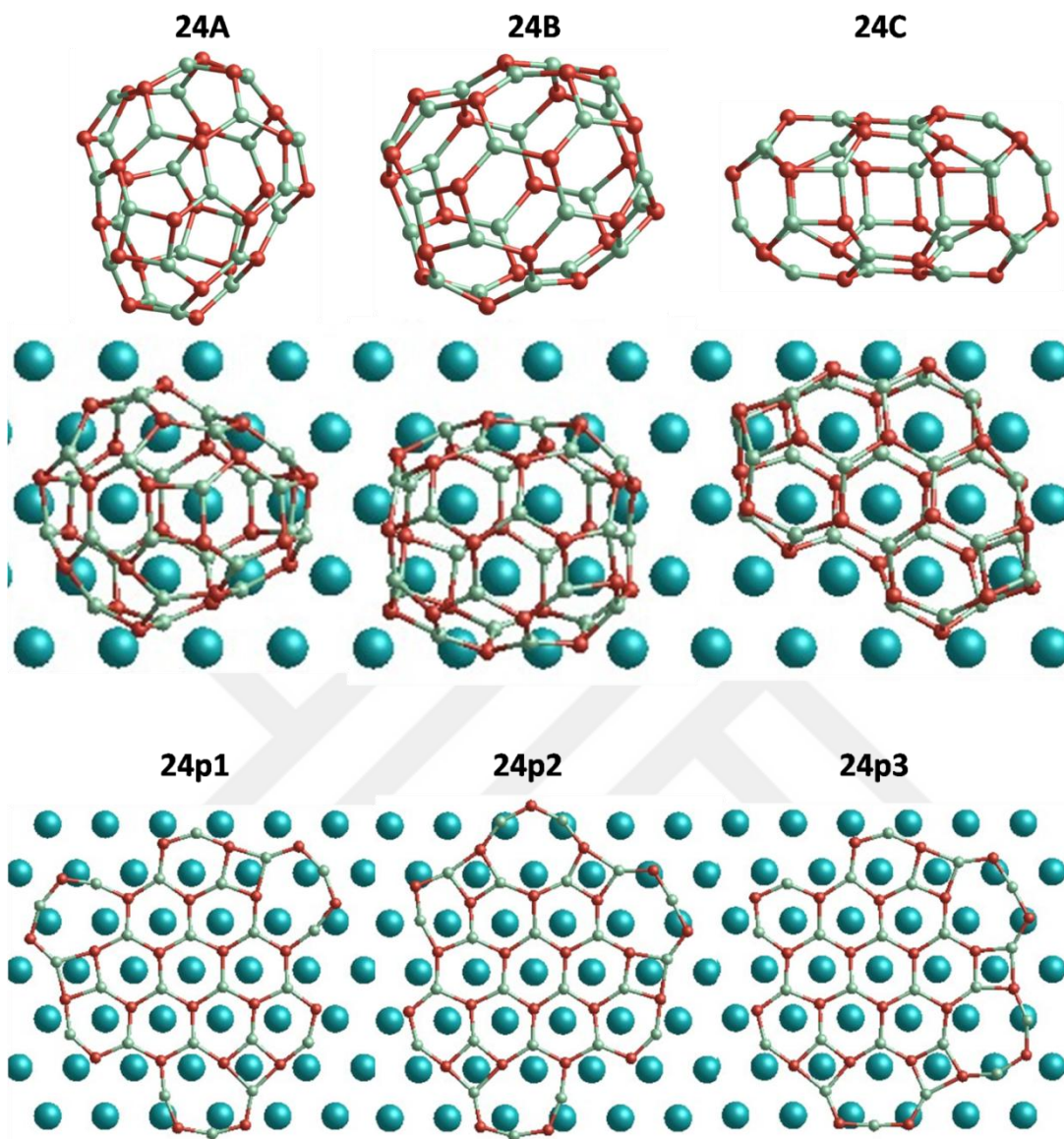


Figure 59. $(\text{ZnO})_{24}$ structures: (a) 3D clusters in free space and on support, (b) 2D clusters on support.

In addition to assessin the influence of a realistic support on the most energetically favoured cluster isomers, one of the aims of this work in this chapter was to examine the initial stages of ZnO monolayer monolayer formation. Towards this objective, a global optimization search was also performed for $(\text{ZnO})_{20}$ using a considerably smaller unit cell, which allowed for periodical 2D sub-monolayer structures to occur. Figure 60 shows the most energetically stable two structures obtained from this search. Due to the additional bonds formed for the periodic structures, the 2D layers were found to be significantly lower in energy than the global minimum for the isolated supported

(ZnO)₂₀ cluster, 20D. The hexagonal layered structure, ML2, was found to be 0.39 eV/ZnO more stable than 20D, while ML1, a symmetric structure consisting of differently sized rings, was found to be 0.45 eV/ZnO more stable. Due to the rectangular periodicity of the surface and the lattice mismatch, the ML2 structure distorted significantly. When we remove the periodicity and place these structures within the larger unit cell (i.e. make them into isolated supported 2D clusters), ML1 and ML2 become 0.23 and 0.30 eV/ZnO higher in energy than the 20D structure, and also higher in energy than all of the considered structures in Figure 58. It should also be noted that ML1 is also higher in energy than other 2D structures in free space by about 0.1 eV/ZnO while ML2 is 0.1 eV/ZnO higher still.

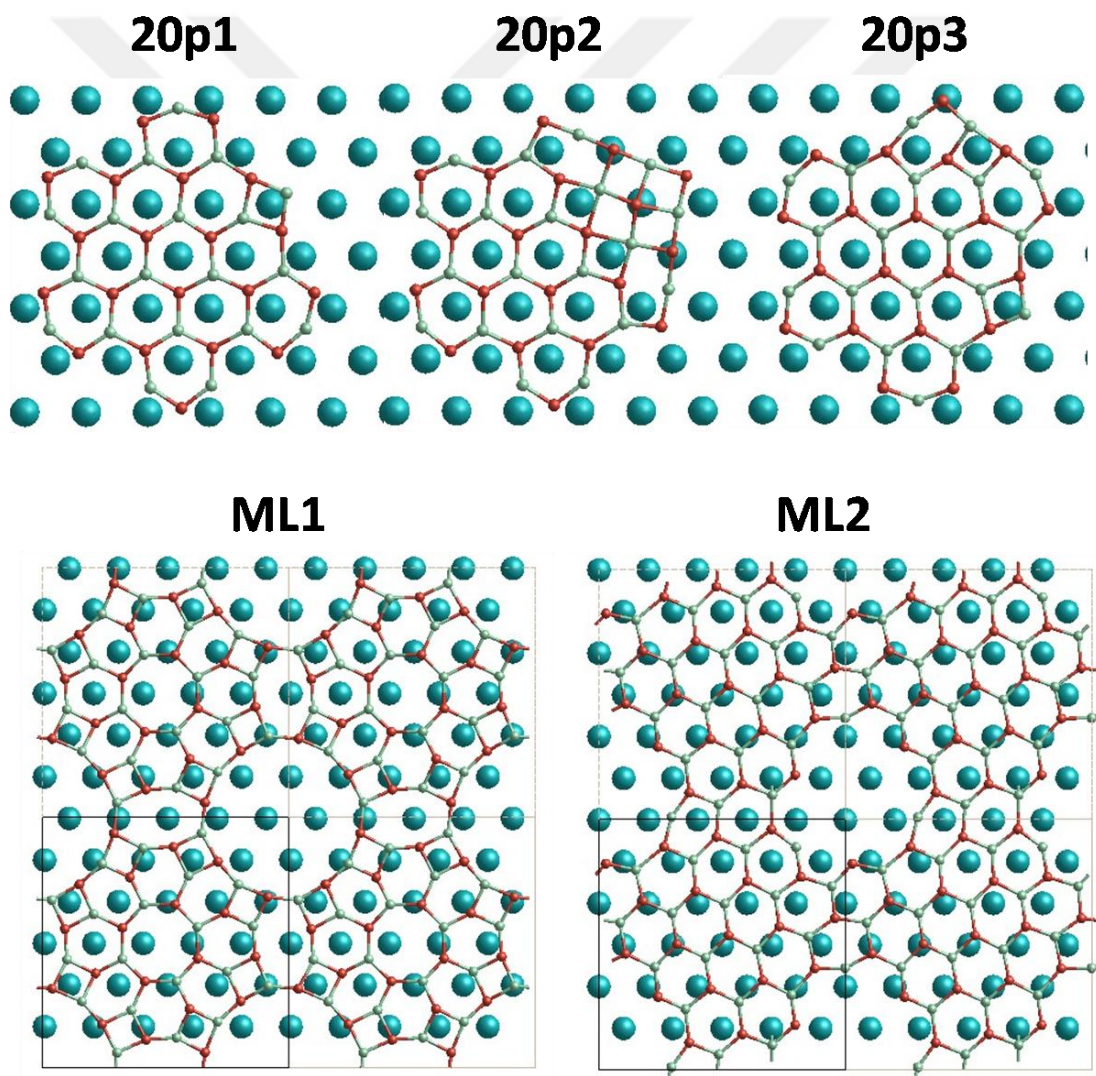


Figure 60. Top views of (ZnO)₂₀-based sub-monolayer structures on the Ag(111) surface.

3.2.7 General overview

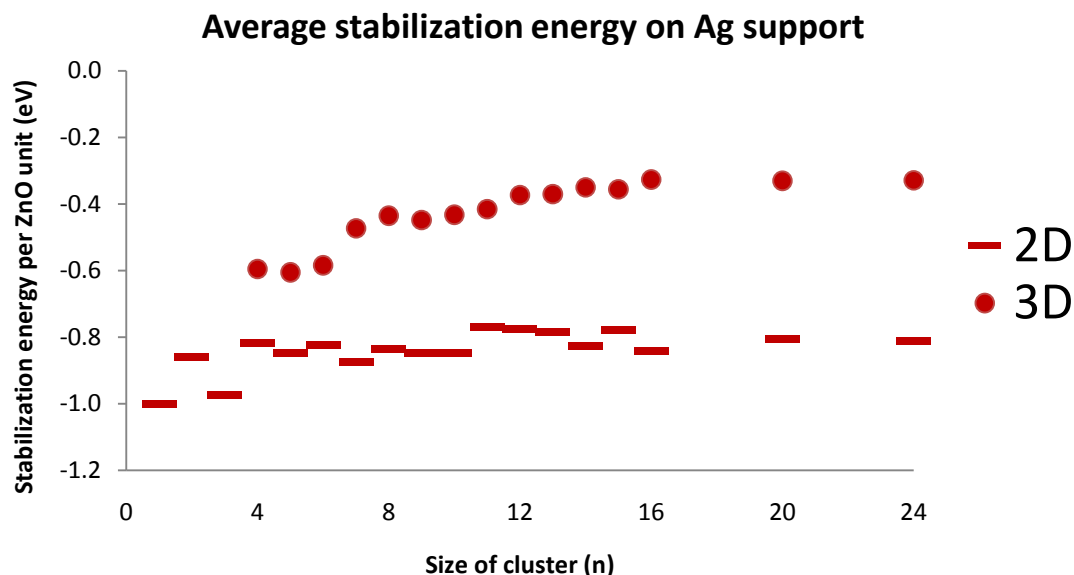


Figure 61. Average stabilization energies for 3D and 2D structures on Ag support.

In Figure 61, the average stabilization energies for 3D and 2D structures on the Ag(111) support are given. For 2D structures, the stabilization energy typically remains constant as the size increases. The single stick and the hexagonal ring are stabilized slightly more because their structure and small size allow for all their atoms to match relatively well with the surface. With increasing size the mismatch between the atom spacing in fused-ring 2D structures and the favourable hollow sites on the Ag(111) surface increases. For 3D clusters, since the fraction of atoms in contact with the surface decreases as the size increases, the stabilization energy is expected to decrease accordingly. However, as the bubbles grow with the increasing size, flatter ellipsoidal bubbles become more stable on the surface, which helps preserve the fraction of atoms binding to the surface, and the stabilization energy becomes constant with increasing cluster size. Because average values are taken over all the clusters of each size, deviations are expected due to some cluster structures matching the surface better than the others. Figure 62 shows the binding energies of the best 2D and 3D clusters both in free space and on the surface. In free space, after the size $n = 5$, 3D clusters become more stable than 2D structures, and the energy difference increases as the size increases. However, in the supported cluster

case, 2D structures compete with 3D clusters up to the considered size $n = 24$. Due to relatively lower energies of 2D structures in free space (see Figure 62), most of the 2D structures are not typically found in global optimization runs in free space (at least not in the set of low energy structures) after the cluster size $n = 8$, however, they were produced by the supported-cluster global optimization runs. Quasi-2D structures, which have both 2D and 3D parts, are also infrequently found in free-space global optimizations but more so than 2D clusters as they tend have energetic stabilities between 3D and 2D cluster types in free space.

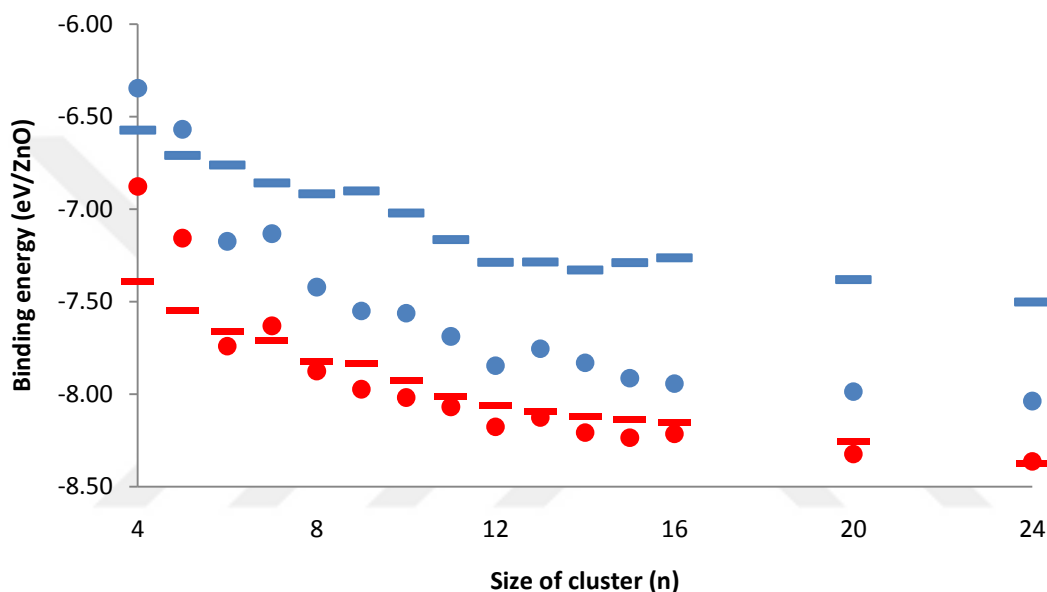


Figure 62. Energies of best 2D (dashes) and 3D structures (filled circles) in free space (blue) and on support (red) with increasing size.

In Figure 63, the second order energy difference: $\Delta E_2 = (2E_n - E_{n-1} - E_{n+1})/n$ of the clusters with increasing size is plotted. The former gives a measure of the increment in energetic stability with monomer addition (often referred to as the nucleation energy). the second order energy difference provides a measure of energetic stability with respect to clusters of a similar size. Pronounced peaks in this measure tend to indicate unusually stable or unstable cluster structures. It can be seen from figure 63 that there is less variation in ΔE_2 on the surface, apart from size $n = 3$, a six-membered ring. The high stability of six-membered ring also leads to the tendency of 3D clusters to align with respect to the surface by a six-membered ring side whenever possible. The drum structure 6A and the sodalite (SOD) cage of 12A are the other structures with low ΔE_2 values for both free space and supported clusters. The drum structure and the sodalite

cage are also the only structures that have the lower energy per formula unit than any cluster with one additional formula unit. The sodalite cage is also 0.12 eV/ZnO more stable than the second lowest energy structure of the same size, also indicating its special stability.

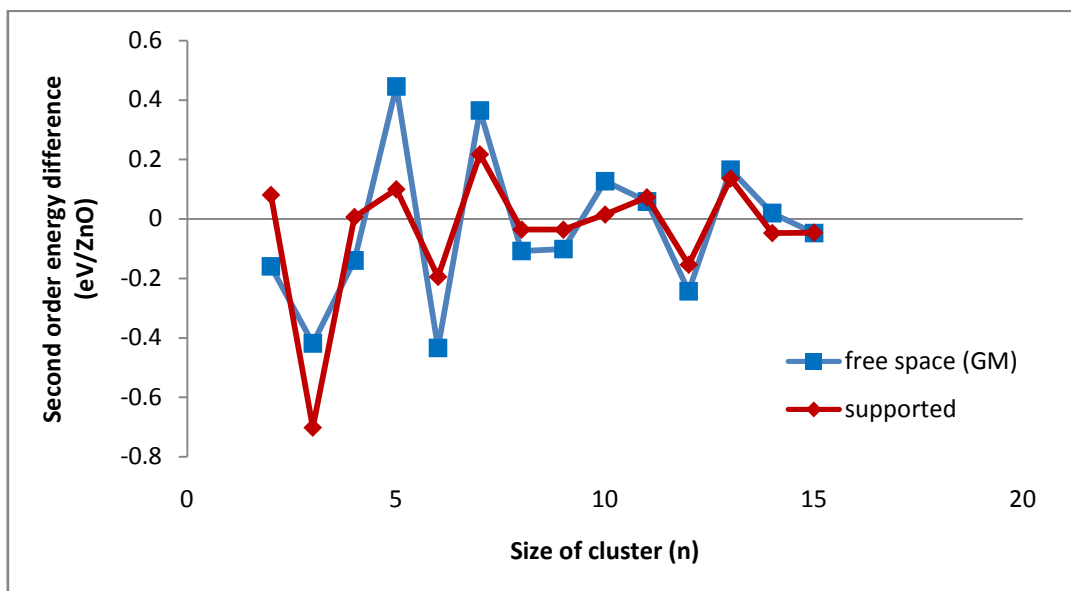


Figure 63 Second order energy difference for lowest energy free space and Ag(111)-supported clusters with respect to increasing cluster size.

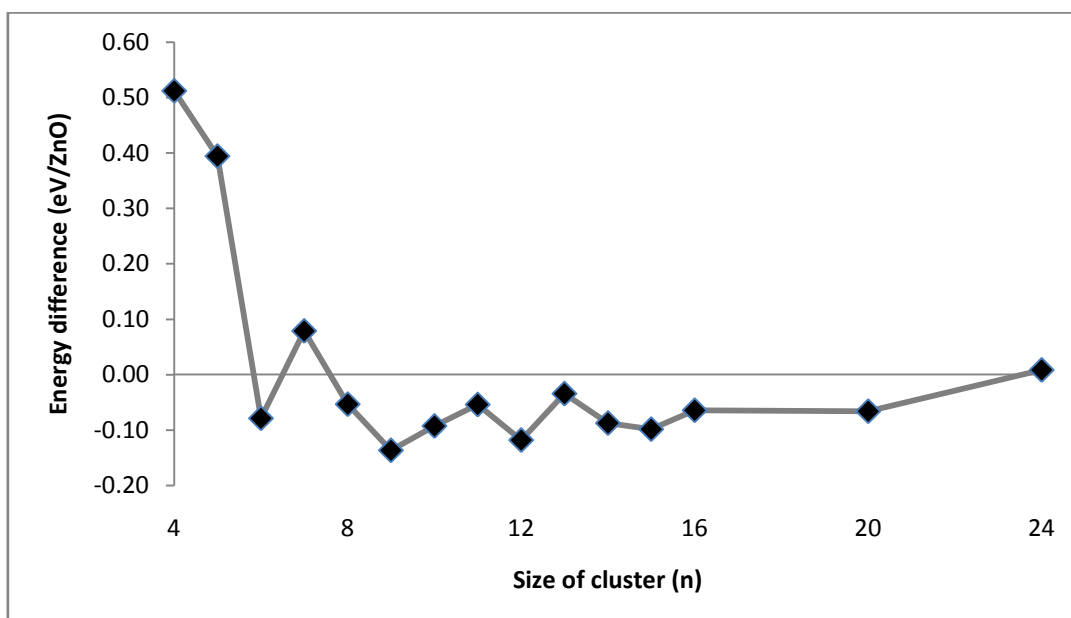


Figure 64. Energy difference between the lowest energy 2D and 3D clusters on support with respect to the cluster size. Positive values are where the 2D clusters are more stable than 3D clusters.

Figure 64 shows the energy differences between the lowest energy 3D and 2D clusters on the Ag(111) support for each cluster size. According to the graph, in the small size range the $n = 4, 5$ and 7 , 2D structures are energetically preferred over the correspondingly sized 3D clusters. For cluster sizes $n > 7$, 3D clusters start to have higher stabilities, however this difference slightly decrease as the size increases, and the 2D clusters stay within 0.1 eV/ZnO up to the considered size $n = 24$, where the 2D structures become more stable again. In the size range considered, the highest stability excesses for the 3D structures are for the sizes $n = 9, 12$ and 15 . If we consider approaching a monolayer within periodic boundary conditions, where extra bonds will form for 2D structures, we may expect a complete monolayer growth. Indeed, our preliminary global optimization results for cluster sizes $n = 12\text{-}16$ using a smaller unit cell, which allows the 2D structures to see their periodic image, unsurprisingly showed that nanosheet structures, which are periodic in two dimensions, become lower in energy per ZnO unit than the global minimum clusters. These nanosheets mainly consist of fused four- and six-membered rings with larger “holes”. Together with the known high relative stability of the six-membered ring on the Ag(111) support, it would be no surprise that a uniform monolayer formation of six-membered rings would be the structure of the most energetically favoured first monolayer coverage of ZnO on the Ag(111) surface.

3.3. Effect of different surfaces; Ag(100) and Ag(110)

To study the effect of the surface morphology on the cluster adsorption, Ag(100) and Ag(110) surfaces were also studied for the selected support cluster sizes of $n = 6, 7, 8, 12, 13$, and 16 . The Ag(111) surface has a hexagonal surface periodicity, while the Ag(100) surface has 4-fold symmetry and the Ag(110) exhibits a bumpy surface, where some extent of underlying second layer silver atoms are exposed at the surface.

For $(\text{ZnO})_6$, $(\text{ZnO})_7$, and $(\text{ZnO})_8$, the global minima were found to be the same on all three considered Ag surfaces. However, for other low-energy cluster isomers for these sizes the energetic ranking varies due to the different surface morphologies giving rise to different stabilization energies upon adsorption. The global minimum of $(\text{ZnO})_6$, the drum structure (6A), is stabilized slightly less on the Ag(100) and Ag(110) surfaces, by 0.48 and 0.50 eV/ZnO respectively, than on Ag(111) surface, where on adsorption the stabilization was 0.57 eV/ZnO . In general, 2D structures appear to be

affected more by the surface morphology. For example the second and third lowest energy $(\text{ZnO})_6$ structures on Ag(111), 6E and 6D, stabilize by 0.10 and 0.02 eV/ZnO less on Ag(100) and by 0.16 and 0.12 eV/ZnO less on Ag(110) surface, respectively. On Ag(100), 6D and 6E switch ranking and 6D becomes lower in energy, as the six-membered rings of the 6E structure do not match the periodicity of this surface as well as that of Ag(111), in which all the atoms on the rings find hollow positions (see Figure 66). In contrast, the stabilization of the 6D structure was found to be very similar on Ag(100) and Ag(111) surfaces. While the planarity of 6D is distorted on Ag(111) as half of the O atoms overlap the on-top positions, it is preserved on Ag(100), where only two Zn atoms match the hollow positions. On the rougher Ag (110) surface, the planarity of both 6D and 6E structures is distorted, and they are stabilized less than on the other surfaces. Another 3D cluster fitting the rough Ag(110) surface well, 6B, surpasses both 6D and 6E with respect to stability and becomes the second lowest energy structure. Similarly 6H and 6I structures also fit the surface rows on Ag(110) and thus are stabilized more than in the Ag(111) case (see Figure 65). We also note one 2D cluster, 6U, which stabilizes more on the Ag(110) surface than on the other surfaces, where the chains of atoms of the cluster fit well to the surface rows.

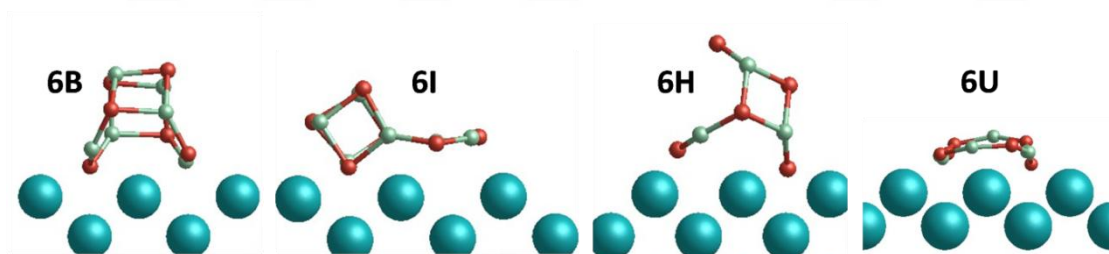


Figure 65. Side views of 6B, 6I, 6H, and 6U clusters on Ag(110) surface.

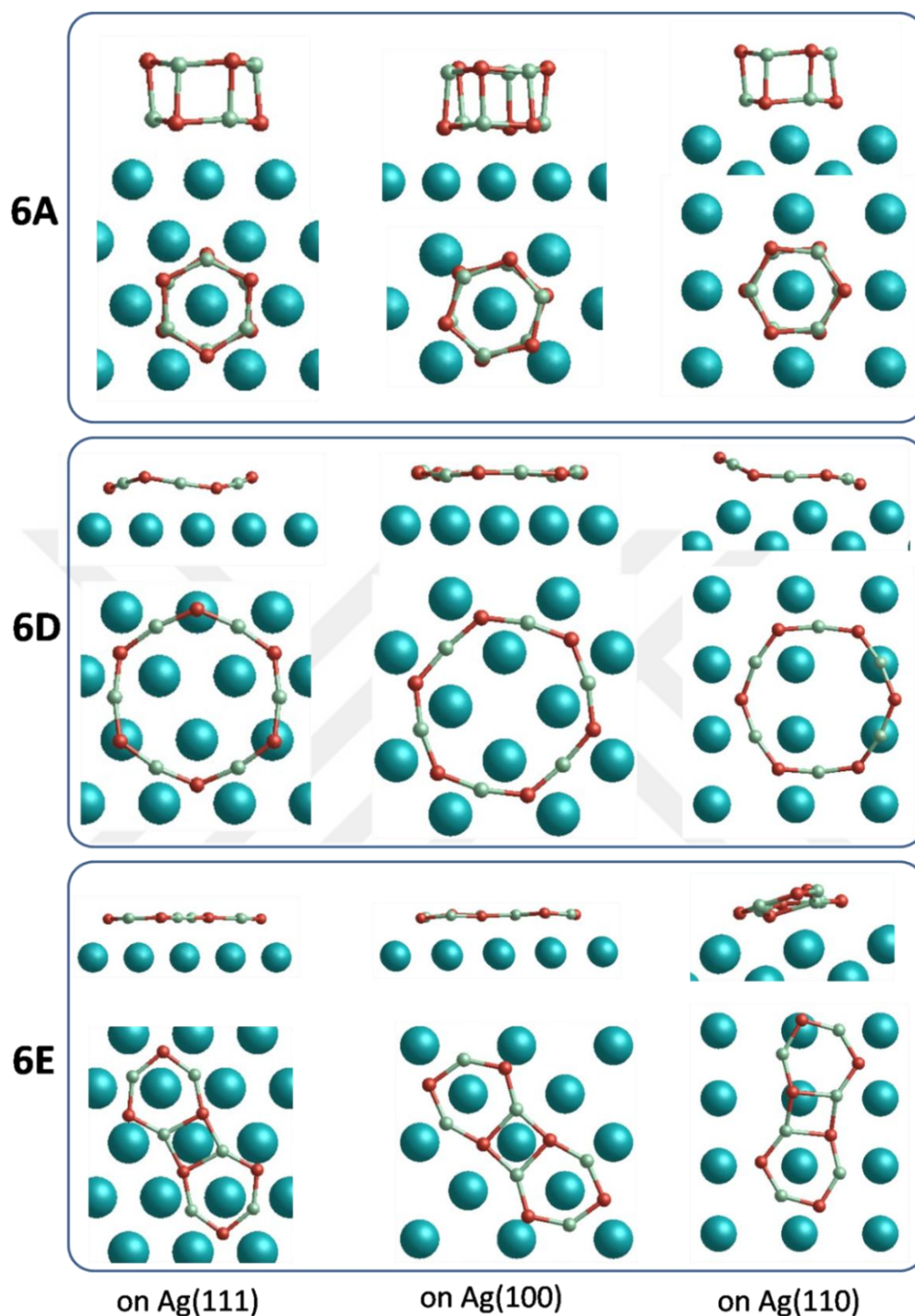


Figure 66. Top and side views of 6A, 6D and 6E clusters on Ag(111), Ag(100) and Ag(110) surfaces.

For size $n = 7$, the 2D 7i structure was found to be the global minimum on all three surfaces, however the stabilization energies on Ag(100) and Ag(110) was found to be 0.06 and 0.05 eV/ZnO less than on Ag(111). On the Ag(111) surface, five out of six lowest-energy structures found were 2D structures, however due to a weaker stabilization of 2D clusters, only three remain in the list of six lowest energy structures on Ag(100) and only two respectively remain for the Ag(110) surface. For 3D clusters, even more stabilization was observed on Ag(110) surface because of the edges of the cluster fitting the rough surface structure as in the (ZnO)₆ case. On Ag(100), 7B is the only 3D cluster, which is stabilized more than on the Ag(111) surface. In the 7B case on the Ag(100) surface, the two closest atoms to the surface are situated in hollow positions, while the six-membered ring at the interface between the cluster and the surface is stabilized around an on-top site.

For (ZnO)₈, all types of clusters except for 8p4 are stabilized least on the Ag(100) surface. In general, this effect is most pronounced for 2D clusters with the 3D clusters being affected the least. As shown in Figure 68, 8p4 exhibits a one-layered rocksalt template, which has a four-fold symmetry like the Ag(100) surface, and its energetic ranking was found to be increased from 16th on the Ag(111) surface to 9th on the Ag(100) surface. On the Ag(100) surface, the edge atoms of 8p4 coincide with the hollow positions, and the cluster planarity is distorted as the internal atoms move outward from the surface. 8p4 stabilizes even more on the Ag(110) surface, where the rows of the rocksalt template follow the rough surface by assuming a zigzag shape, however, its energetic ranking increased to only 11th. On the Ag(110) surface, the 3D (ZnO)₈ clusters, which fit the surface rows, are stabilized even more, and their energetic rankings are changed drastically, while other clusters are affected less and stabilized slightly less than on Ag(111). For example 8C and 8D clusters have 0.10 and 0.07 eV/ZnO higher stabilization energies on Ag(110) than on the Ag(111) surface, and this extra stabilization changes their energetic ranking so that 8C becomes the second lowest energy structure and 8D becomes more stable than 10 structures that are more stable on Ag(111).

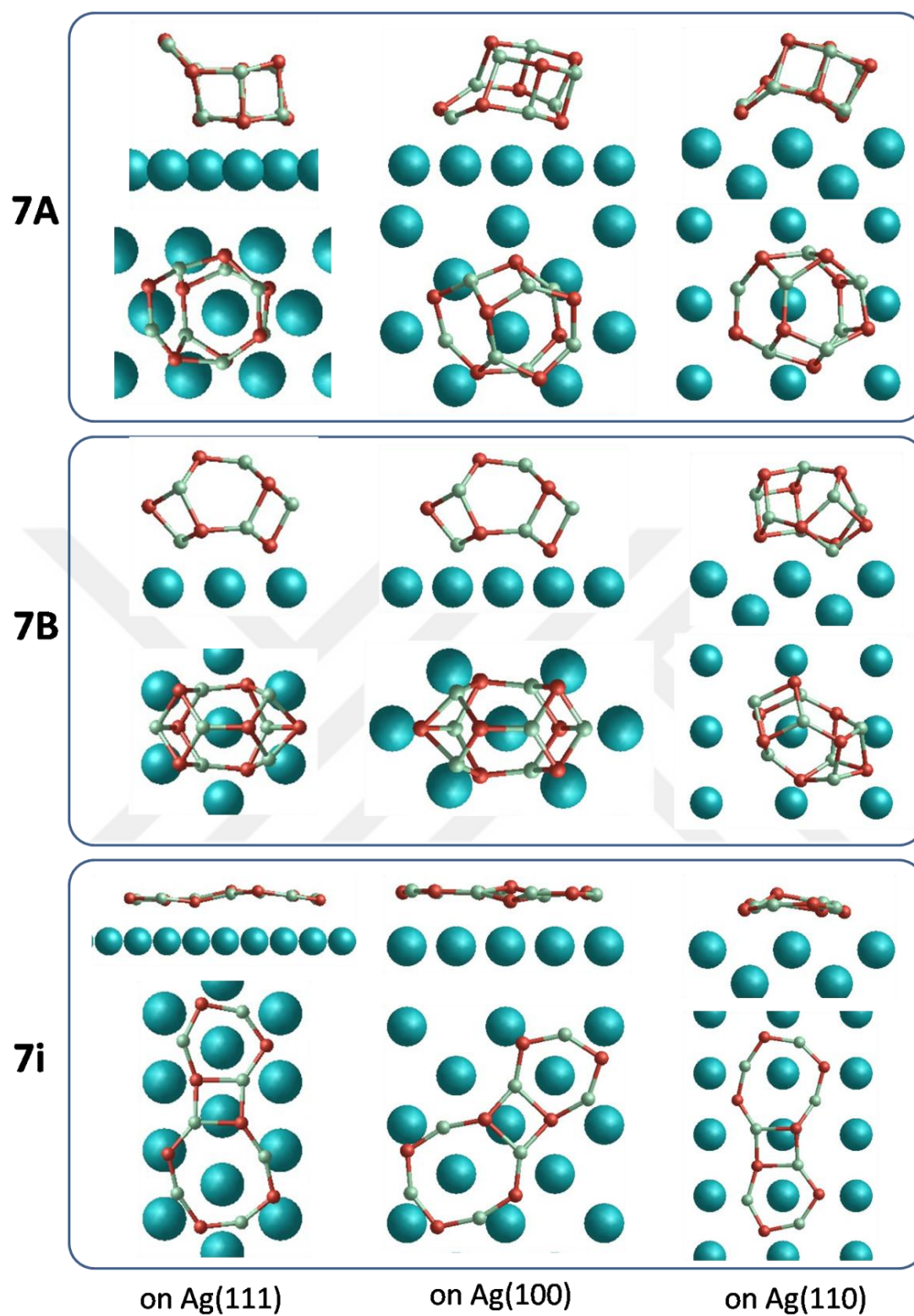


Figure 67. Top and side views of 7A, 7B and 7i clusters on Ag(111), Ag(100) and Ag(110) surfaces.

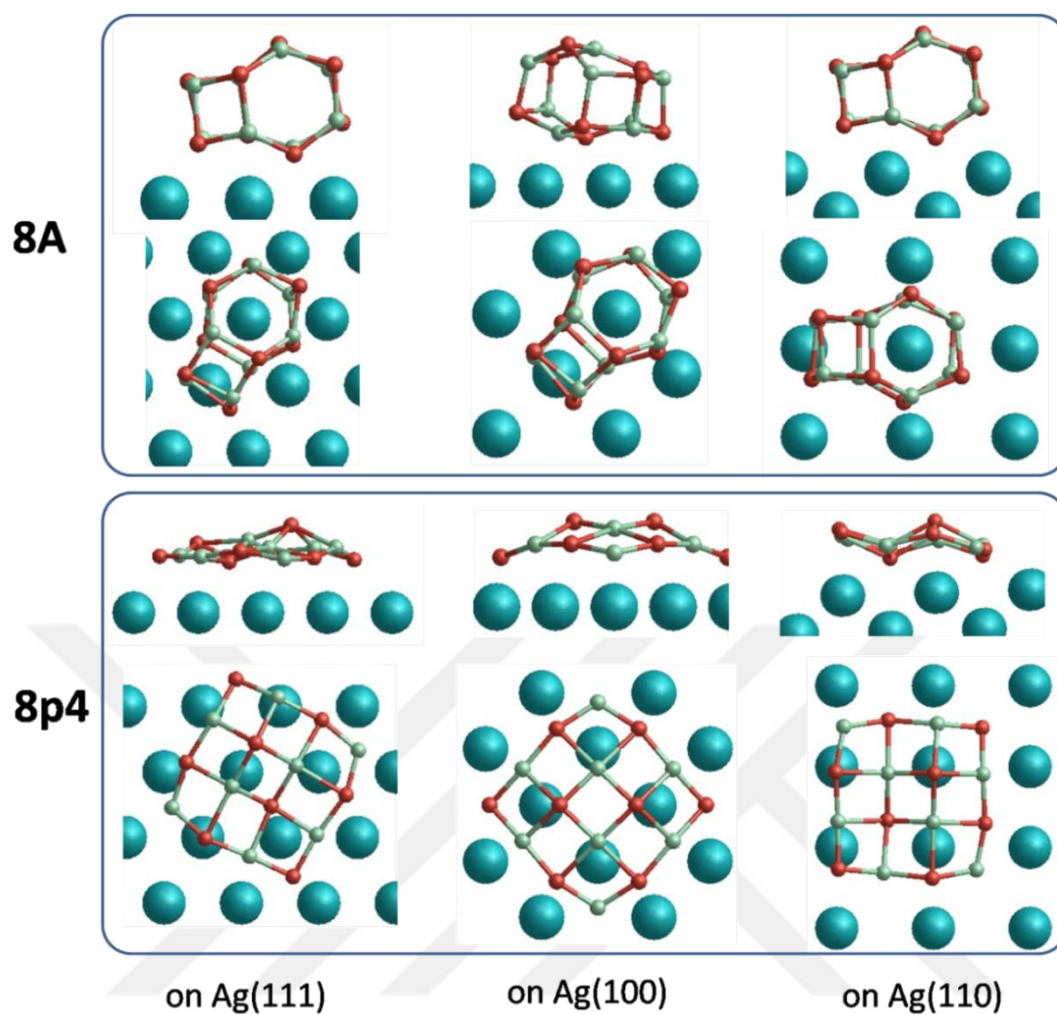


Figure 68. Top and side views of 8A and 8p4 clusters on Ag(111), Ag(100) and Ag(110) surfaces.

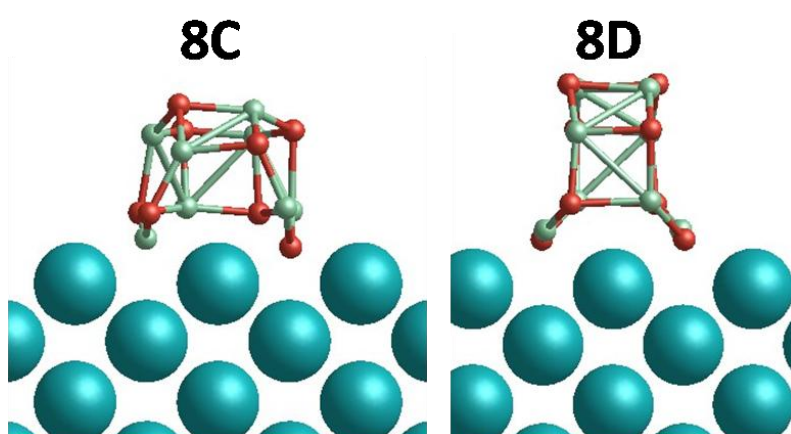


Figure 69. Side views of 8C and 8D clusters on the Ag(110) surface.

As the cluster size increases, the difference in the stabilization energies on different surfaces of Ag does not change significantly both for 3D and 2D cluster types (see Figure 70). However, the ranking of 2D clusters drops drastically on Ag(100) and on Ag(110) surfaces for the larger sizes, $(\text{ZnO})_{12}$ and $(\text{ZnO})_{13}$, because of the relative stabilities of 3D clusters relative to 2D ones increases in free space with increasing size. Thus, for the largest size we considered, $(\text{ZnO})_{16}$, all of the 2D clusters are higher in energy than the 3D clusters on Ag(100) and on Ag(110) surfaces.

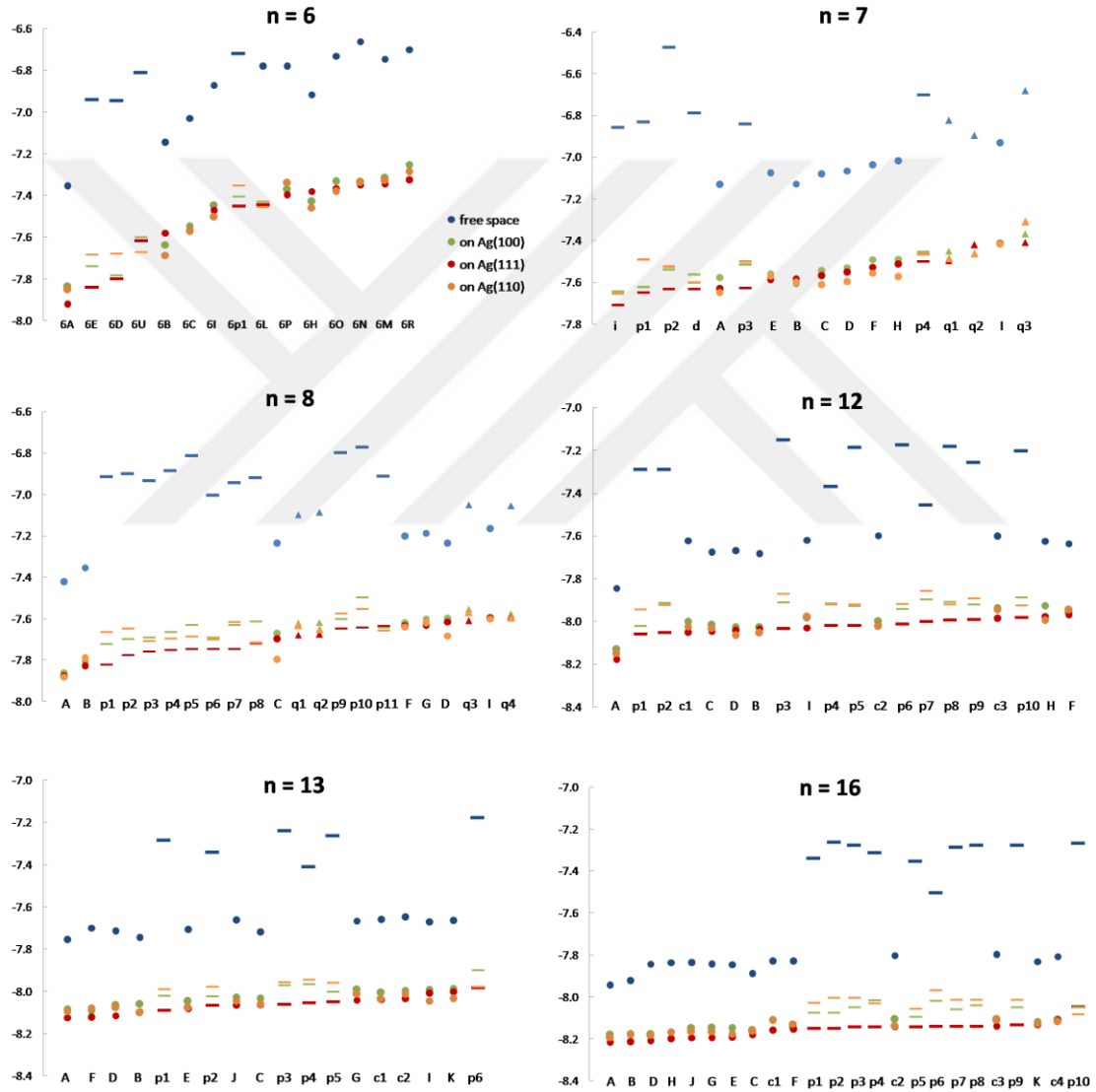


Figure 70. Binding energies of low-energy clusters for the selected sizes both in free space and on different Ag surfaces.

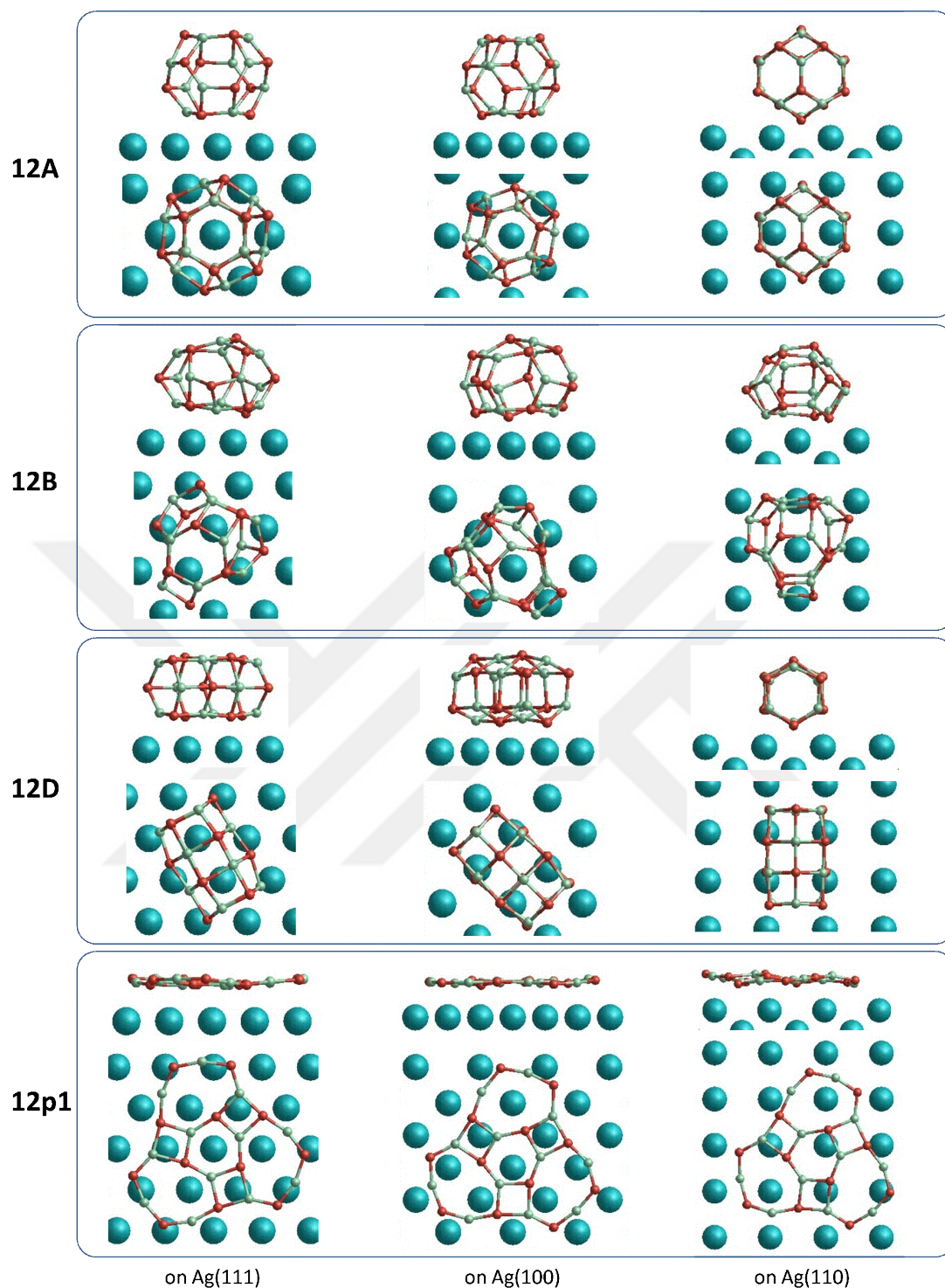


Figure 71. Top and side views of 12A, 12B, 12D, and 12p1 clusters on Ag(111), Ag(100) and Ag(110) surfaces.

For $(\text{ZnO})_{12}$, the highlighted sodalite cage, 12A, remained the global minimum by far for all surfaces due to its pronounced high stability in free space. 12A was stabilized more on the Ag(111) surface, on which it is adsorbed via a six-membered ring matching the hexagonal surface periodicity, and stabilized least (+0.05 eV/ZnO) on Ag(100),

where the contact atoms of the hexagonal face of 12A do not match the surface hollow positions. On the Ag(110) surface, the stabilization energy the 12A cluster also decreases by 0.03 eV/ZnO with respect to that on Ag(111) due to a similar structural mismatch. The lowest energy 2D cluster on Ag(111), 12p1, deteriorates to 4th rank on Ag(100) and 11th on Ag(110), whereas the 3D clusters 12D and 12B become 2nd and 3rd, respectively, on both surfaces. 12D is a barrel, which can be seen as a folded 2D rock-salt sheet, and it fits well on the surface rows on the Ag(110) surface.

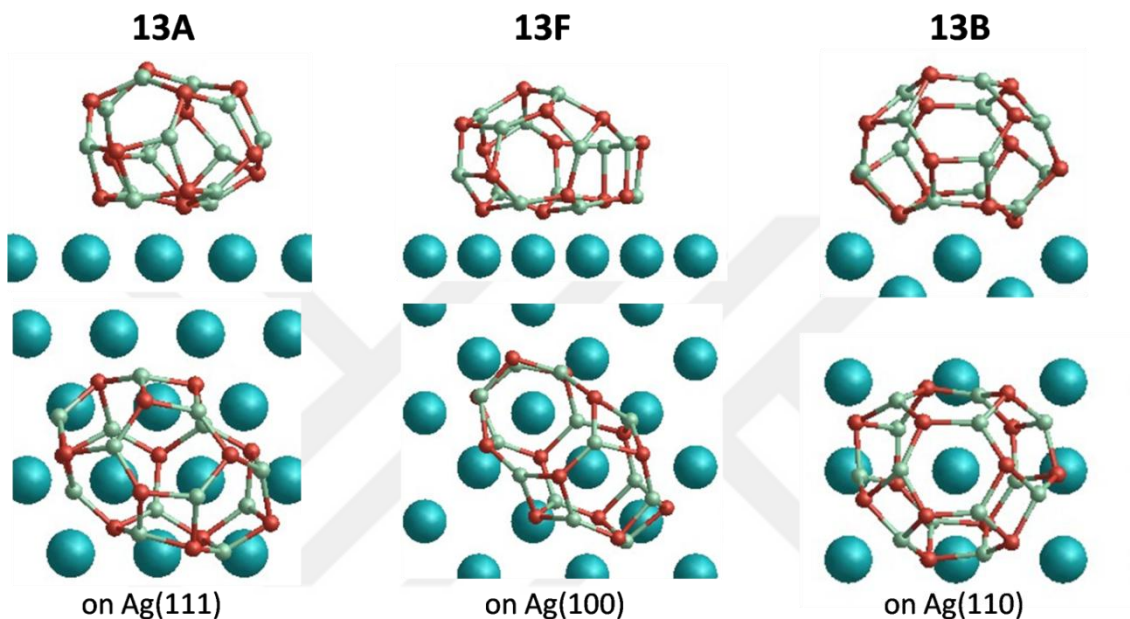


Figure 72. Top and side views of 13A on Ag(111), 13F on Ag(100) and, 13B on Ag(110) surfaces.

For $(\text{ZnO})_{13}$, 13p1, the lowest energy 2D cluster on the Ag(111) surface, decreases its ranking to become 9th and 13th on the Ag(100) and Ag(110) surfaces, respectively. The four lowest energy 3D clusters on the Ag(111) surface, 13A, 13F, 13D, and 13B, are maintained as being the first four ranked clusters on both Ag(100) and Ag(110) surfaces. Interestingly, however, the global minima structures on Ag(100) and on Ag(110) change and becomes 13F and 13B respectively. The 13F fits well to the Ag(100) surface morphology where two adjacent six-membered rings match the surface Ag atoms, and the 13B structure matches the corrugated Ag(110) surface well by enclosing a part of a Ag surface row.

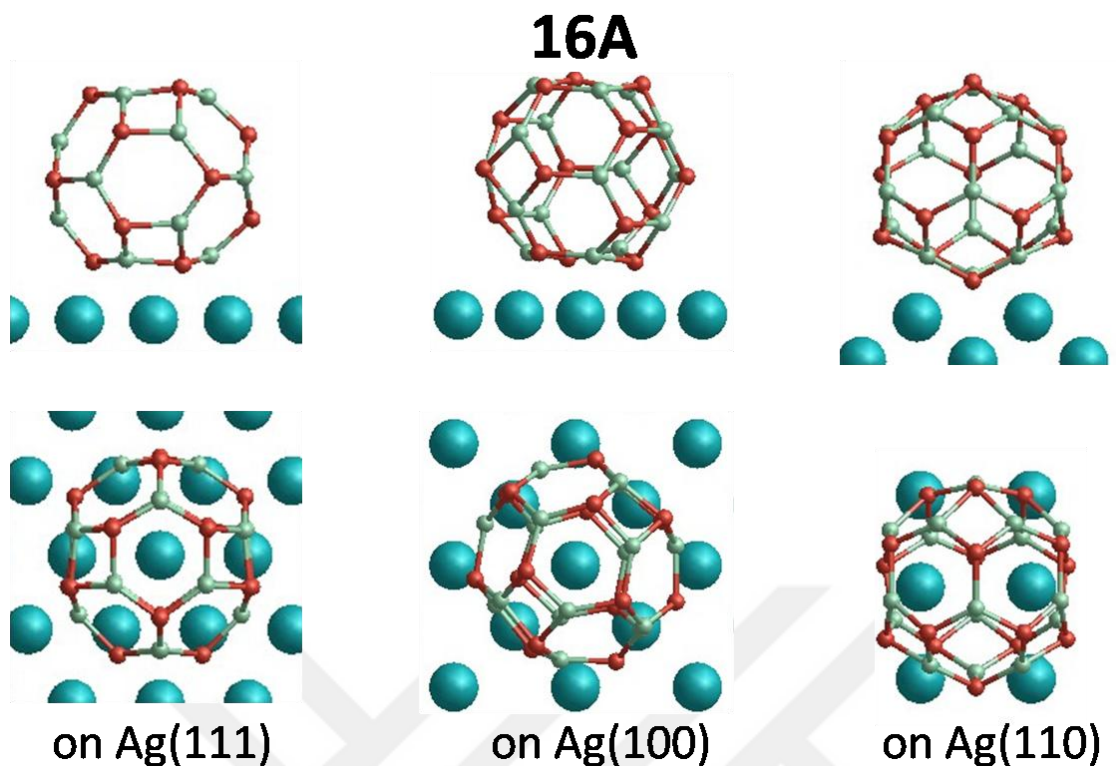


Figure 73. Top and side views of 16A cluster on Ag(111), Ag(100) and Ag(110) surfaces.

For size $n = 16$, 16A was found to be the global minimum on all surfaces, which, much like 12A, is symmetrical cage and follows similar stabilization trends. As the cluster size increased, 3D clusters show fewer “handles” and edges to fit to the Ag(110) surface, thus like on Ag(100), all the 3D clusters on Ag(110) are found less stabilized than on Ag(111). Similarly, as the size increases, 2D islands stabilize less on Ag(100) and Ag(110) surfaces than on Ag(111). The only case where we observed more stabilization for 2D clusters on Ag(100) or Ag(110) surfaces were for the rock-salt sheets like 8p4. For such structures (e.g. 13p6 and 16p10 – see Figure 74) and the relative stabilization increase is especially large for the Ag(110) surface, where these clusters assume a zigzag shape matching the surface corrugation of the Ag(110) surface. Nevertheless, the rock-salt sheets do not compete energetically with 3D clusters. Although being stabilized much more than the 3D clusters, all 2D clusters are significantly less stable for $n = 16$ on Ag(100) and Ag(110), and even more 3D clusters than on Ag(111) become more stable than most of the 2D structures (e.g. 16c2, 16K, 16c3, and 16c4).

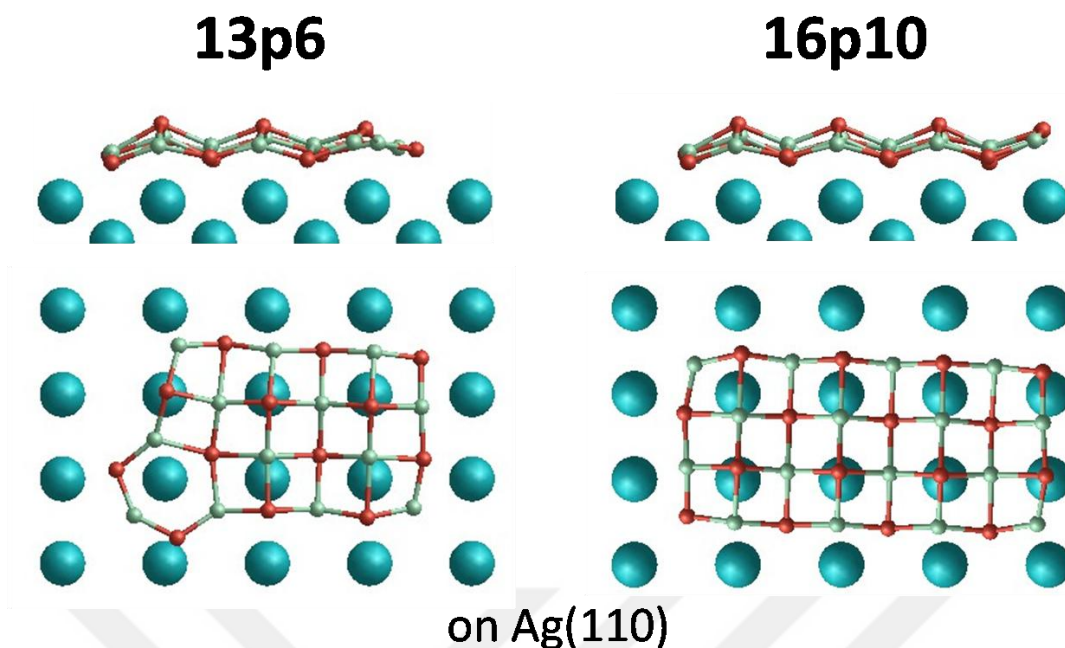


Figure 74. Top and side views of 13p6 and 16p10 clusters on the Ag(110) surface.

cluster size	on Ag(100)		on Ag(110)	
	2D clusters	3D clusters	2D clusters	3D clusters
n = 6	0.04 eV/ZnO	0.02 eV/ZnO	0.06 eV/ZnO	0.00 eV/ZnO
n = 7	0.05 eV/ZnO	0.02 eV/ZnO	0.03 eV/ZnO	-0.02 eV/ZnO
n = 8	0.06 eV/ZnO	0.02 eV/ZnO	0.05 eV/ZnO	0.02 eV/ZnO
n = 12	0.09 eV/ZnO	0.03 eV/ZnO	0.11 eV/ZnO	0.01 eV/ZnO
n = 13	0.07 eV/ZnO	0.03 eV/ZnO	0.08 eV/ZnO	0.01 eV/ZnO
n = 16	0.07 eV/ZnO	0.03 eV/ZnO	0.10 eV/ZnO	0.02 eV/ZnO

Table 7. The average change of stabilization energy for 2D and 3D clusters on the Ag(100) and Ag(110) surfaces relative to that on the Ag(111) surface.

In conclusion, our investigation of ZnO nanocluster adhesion to surfaces of different morphologies using selected cluster sizes strongly indicates that the Ag(111) support stabilizes all types of ZnO clusters more than the Ag(100) and Ag(110) surfaces (see also table 7). In general, 2D clusters are stabilized significantly more than the 3D ones on all different surface morphologies, mainly because they have larger contact areas with the surface. However, to energetically compete with the 3D clusters on the surface, 2D clusters need to overcome the high 2D *versus* 3D energy differences in free space, which increase with cluster size. Although, as on Ag(111), 2D clusters are stabilized

significantly more than 3D clusters on Ag(100) and on Ag(110), the differences in the degree of stabilization for these two cluster families becomes smaller on Ag(100) and on Ag(110) surfaces. The decrease in the stabilization energies on the Ag(100) surface relative to that for Ag(111) is less pronounced for the for 2D clusters, although they are still more affected than 3D clusters According to

Table 7, the average change of stabilization energy for 3D clusters are less on the corrugated Ag(110) surface than on Ag(100) in general. Especially clusters with handles, which fit the surface morphology better on the corrugated Ag(110) surface, become more stabilized compared to Ag(111).

3.4. DFT results

For each $(\text{ZnO})_n$ cluster size from $n = 1$ to 16, low energy clusters from the IP-based global optimizations were further investigated using DFT calculations. Specifically, the low-energy cluster structures optimized with IPs, both on the Ag(111) support and in free space, were used as starting points for DFT geometry optimizations.

For the simple Zn-O monomer stick, upon DFT optimization both atoms remained above their hollow site positions. The O atom moves towards the support by 0.39 Å with the height of the O atom over the surface plane decreasing to 1.61 Å. The Zn atom moves slightly in the same direction, and the height of the Zn atom is lowered to 2.00 Å from the value of 2.08 Å obtained with IPs. For sizes $n = 2$ and 3, the IP calculations gave the ring structure as global minimum both for free space and on the surface. In free space, the DFT calculations confirm that the linear stick structures are less stable than the rings with energy differences of 0.35 and 0.92 eV/ZnO respectively for $n = 2$ and 3. However on the support the linear sticks become more stable than the rings with energy differences of 0.35 eV/ZnO for $n = 2$ and 0.11 eV/ZnO for $n = 3$. These results are also

in line with the previous work of Bristowe *et al*²⁰⁹ where they studied ZnO adsorption on Ag(111) surface for up to three ZnO units using DFT. Compared to the IP results, the (ZnO)₂ four-membered ring becomes more parallel to the surface in the DFT calculations, where the centre of the ring moves to the on-top position and the O atoms lay close to neighboring Ag surface atoms. The Ag atoms nearest the O atoms of the (ZnO)₂ ring move 0.26 Å outwards and the Ag surface atom below the ring middle moves 0.36 Å inwards while the other surface atoms exhibit maximum displacements of 0.05 Å. The heights of the ring atoms from the surface plane decrease to 1.92 and 1.95 Å for Zn atoms and 1.97 and 2.04 Å for O atoms. Similar surface distortions are also observed in the six-membered (ZnO)₃ ring case, where the surface Ag atom below the ring centre moves 0.22 Å inwards while two of the Ag surface atoms close to two of the O atoms (see Figure 75) move 0.09 Å outwards. The remaining Ag surface atoms exhibit maximum displacements of 0.03 Å from the surface plane. For the stick structures, as in the IP calculations the (ZnO)₂ and (ZnO)₃ clusters retain linear their O-Zn-O configurations and bend about O atoms. At the same time, the O atoms close to on-top sites of the Ag surface move slightly away from the surface.

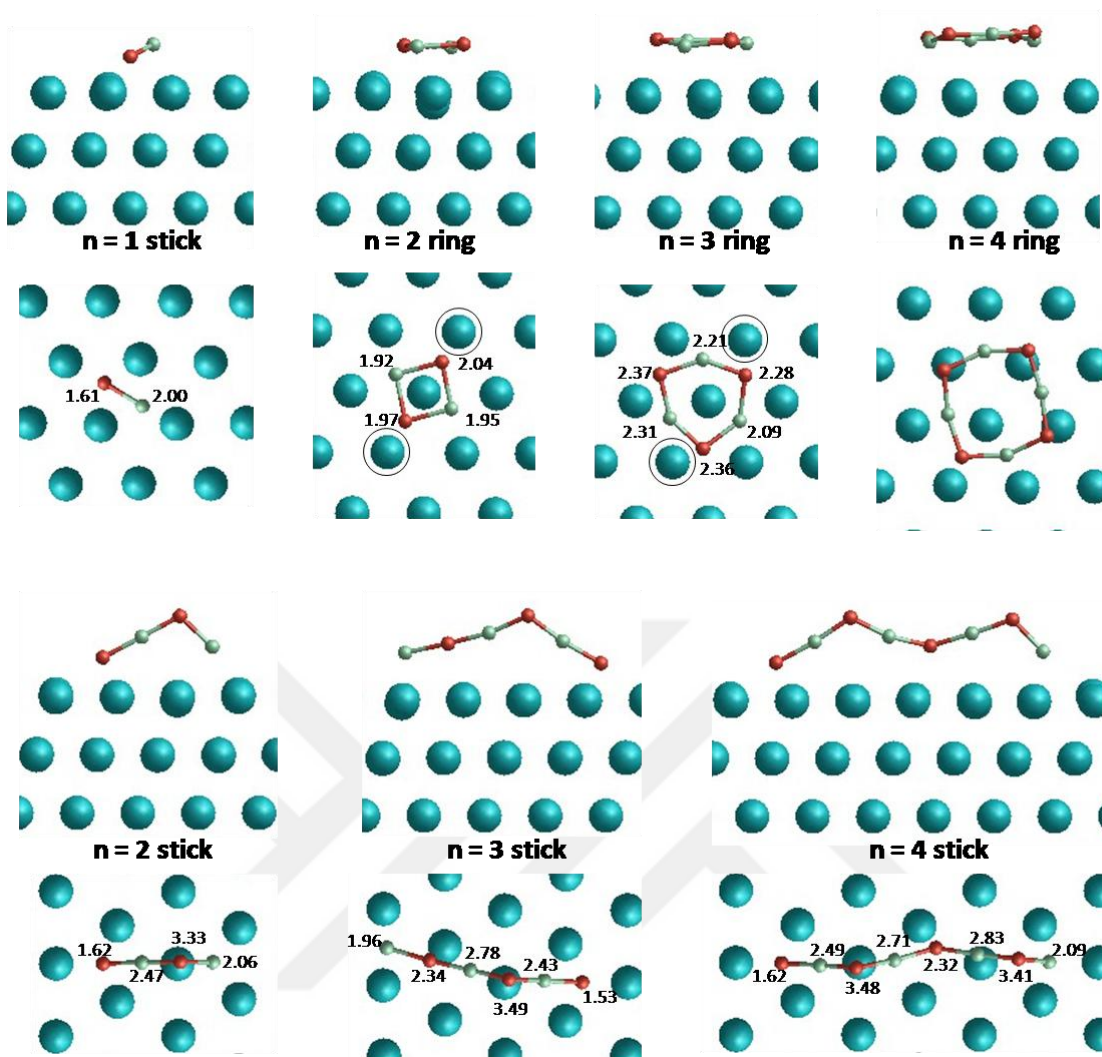


Figure 75. Side and top views of ring and stick structures of sizes $n = 1$ to 4 on Ag(111) surface. Numbers represent the heights from the surface plane for each of the individual Zn and O atoms. Black circles indicate the silver surface atoms, which displaced outwards from the surface plane.

For $n = 4$ and $n = 5$, as for the IP results, the DFT calculations predict ring structures to be the global minima on the surface. We have also constructed one stick configuration for size $n = 4$ to compare, which ended up being 0.01 eV/ZnO higher in energy than the eight-membered ring structure, 4A. Although being close in energy, considering the trend from $n = 2$, that the ring structures become more stable while the sticks become less stable as the size increases, no stick structure is expected to be global minimum from this size on. It should be noted that the higher energy candidate clusters of sizes $n = 4$ to $n = 9$ were found to undergo a strong reconstruction on the surface, which is mainly attributed to their relative instabilities in free space with respect to the global minima of the corresponding size. For $n = 6$, the ring structure is found to be the DFT

global minimum in free space, surpassing the drum structure, which was the global minimum both in free space and on support using the IPs. However for the Ag(111)-supported cluster case, another 2D structure, consisting of fused rings, becomes energetically more favorable than the ring structure. Moreover, two other $(\text{ZnO})_6$ structures also surpass these structures, which are reconstructed structures of higher energy starting clusters selected from the IP results. One of these structures is a distorted planar structure consisting of three joint rings, two six- and one four-membered ring, with a “dangling” Zn atom, which fits the hollow position on the surface. The global minimum structure can be thought of as half of the stable sodalite cage of size $n = 12$. Similarly, for size $n = 7$, the global minimum structure on support was found to be one of the reconstructed 2D structures, which can be also considered as the ground state for $n = 6$ size with one of its four-membered rings opened up to make a third six-membered ring. However in free space, the $(\text{ZnO})_7$ ring structure was found again to be the global minimum, as for cluster sizes: $1 < n < 7$.

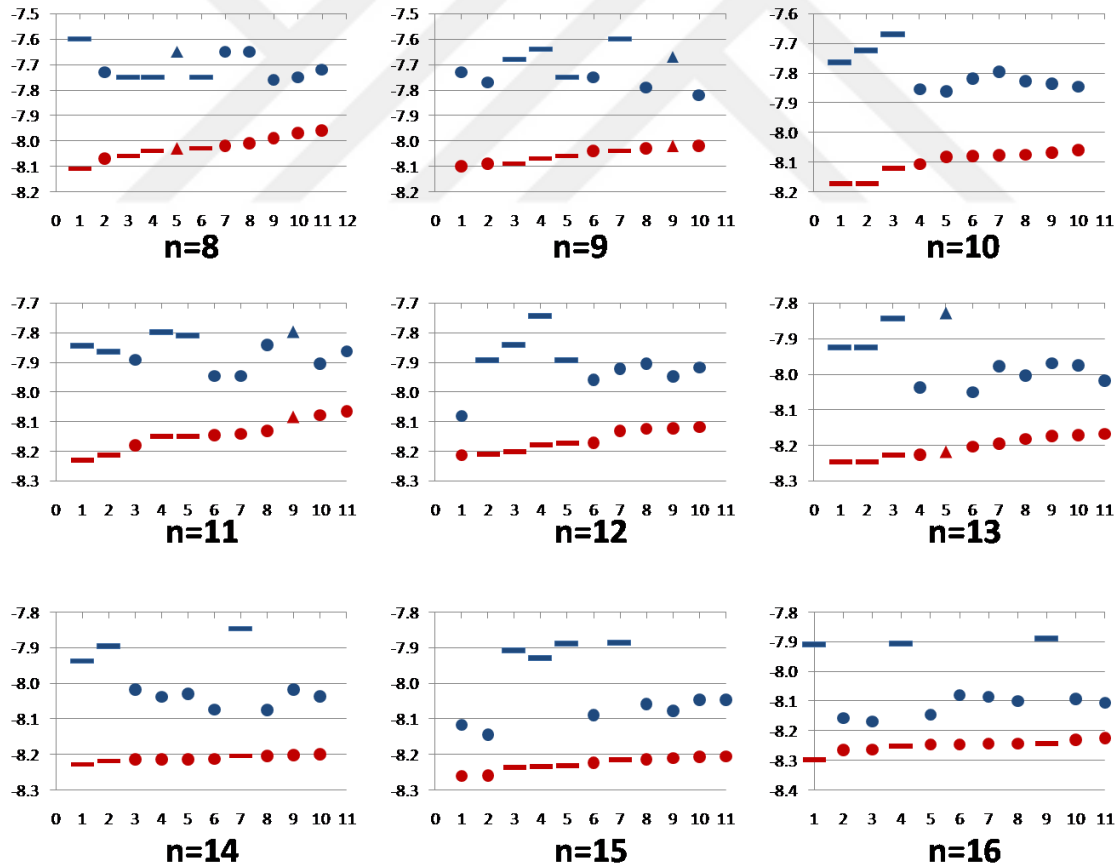


Figure 76. Binding energies of low-energy clusters calculated with DFT for sizes $n=8-16$ both in free space and on the Ag(111) surface.

For the size $n = 8$, the global minimum in free space was found to be the same as with the IPs, and is the first bubble cluster that becomes the global minimum in free space with DFT. Considering cluster size increase, from this size onwards bubble structures become global minima in free space up to the largest considered size $n = 16$ considered. For this size interval of $n = 8$ to 16, clusters 9A, 10A, 11A, 12A, 15A and 16A were the global minima structures using both IPs and DFT. For sizes $n = 8$ and 14, the second lowest energy structures at the IP level, 8B and 14B, become DFT global minima, while for size $n = 13$, the DFT global minimum is the third lowest energy structure from IPs.



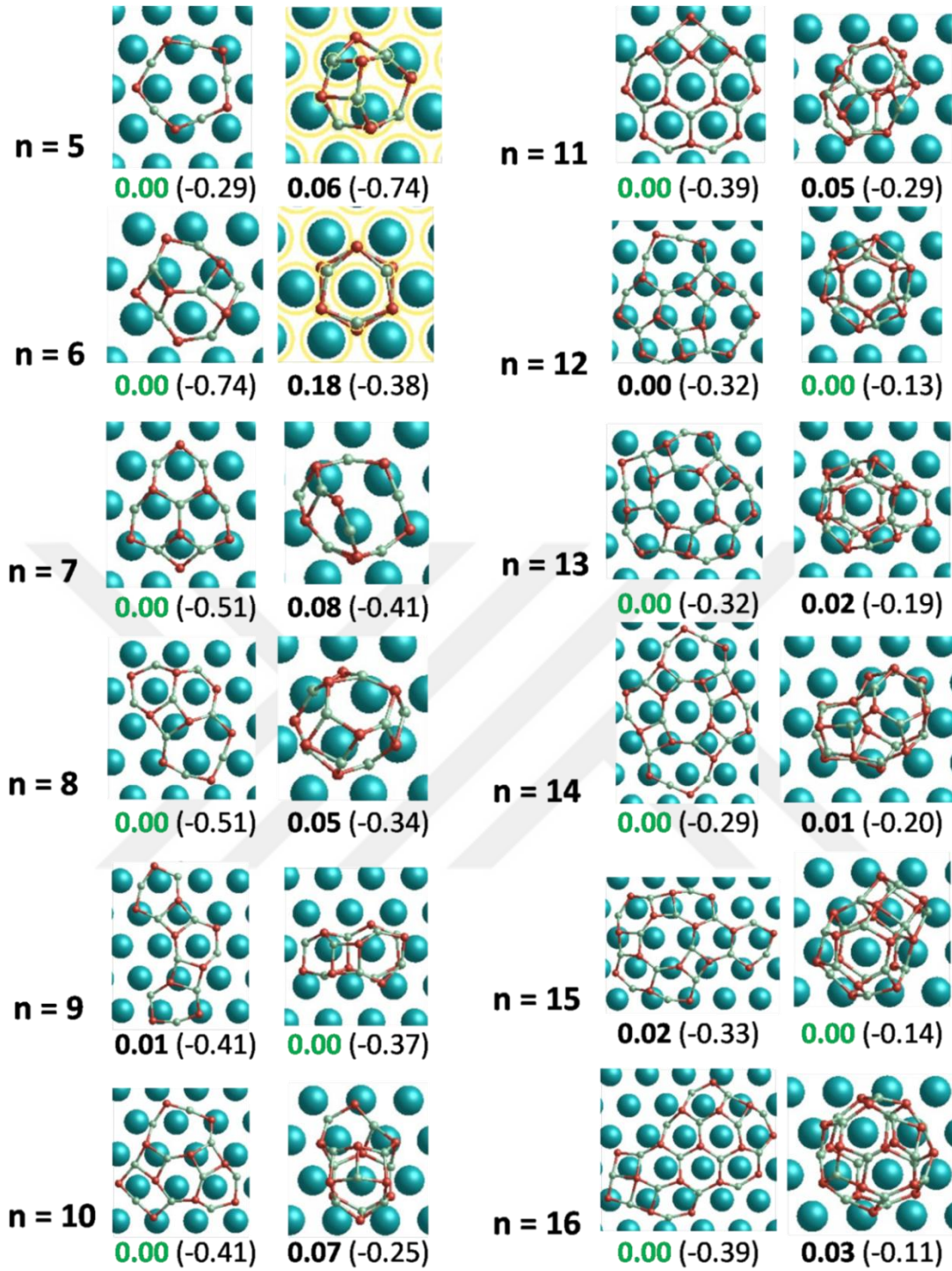


Figure 77. Structures and energetics of the lowest energy 2D and 3D $(\text{ZnO})_n$ nanoclusters on the Ag(111) support. Relative energies are given under the structures and the stabilization energies due to the support are given in parentheses.

Following our conclusions from the work using IPs, that the 2D structures stabilize and come into the range of stable clusters with the presence of support, we have also calculated for each cluster size the most stable three 2D structures with DFT. In

agreement with the IP results, higher stabilization energies were observed for 2D structures on the surface than for the supported 3D structures. However, a clear separation of the stabilization energies between 2D and 3D clusters could only be observed after size $n = 10$. The DFT results, also concur with the IP results with respect to the stability trends of the 2D structures in free space where in each case the global minima are ring structures up to size $n = 7$ and the energy difference of the best 2D and 3D clusters lies within 0.1 eV/ZnO up to size $n = 12$.

Considering the DFT results for the supported nanoclusters, the competition between 2D and 3D clusters is found to be in favour of 2D clusters for most sizes, unlike the IP results. For sizes $n = 9, 12$ and 15 , the 3D clusters are found to be global minima, from which the only size that has the same global minimum structure for both free space and on support is the $n = 12$ cluster with the sodalite cage structure. Recall also that with the IPs these three sizes had the largest energy difference between the lowest energy 3D and 2D clusters. In Figure 78 it can be seen that for the free space case, the sodalite cage is exceptionally stable, where it has a lower energy per formula unit than the global minima of the clusters that are one and two ZnO units larger. The lowest energy 2D cluster at this size is 0.19 eV/ZnO higher in energy than the sodalite cage in free space, however this energy difference drops to below 0.01 eV/ZnO in the supported case. The second lowest energy 3D $(\text{ZnO})_{12}$ cluster in free space is 0.13 eV/ZnO less stable than the sodalite cage, however the stabilization when on the support is similar to the sodalite cage and the energy difference between the two 3D clusters remains close to that in free space (0.09 eV/ZnO). In Figure 80 it can be seen from second order energy difference graph that clusters with sizes $n = 9$ and $n = 12$ have a higher stability in free space with respect to other sizes, however the situation changes in the Ag-supported case, where the other sizes have 2D global minima. For sizes $n = 9$ and 15 , the Ag-supported global minima structures are different from those in free space and the binding energy differences in free space between these clusters and the corresponding free space global minimum clusters are 0.09 and 0.03 eV/ZnO, respectively. The stabilization for size $n = 9$ is stronger as the binding energy difference with free space global minimum becomes 0.08 eV/ZnO on support whereas for size $n = 15$, they are similarly stabilized, and the binding energy difference with the free space global minimum is as small as 0.01 eV/ZnO on support. The 2D structures for sizes $n = 9$ and 15 are again very high in

energy with respect to the free space global minima, 0.14 and 0.24 eV/ZnO above 3D structures respectively, whereas they stabilize considerably more on the Ag(111) support and the binding energy differences with the global minimum on support decrease to 0.01 and 0.02 eV/ZnO, respectively. For other sizes, where 2D structures are global minima on the silver support, the same conclusion holds that the 2D structures stabilize considerably more, see Figure 70. In general, the 2D structures have distorted planar structures, where the internal parts, which include three-coordinated atoms, stay higher above the surface than the external two-coordinated atoms.

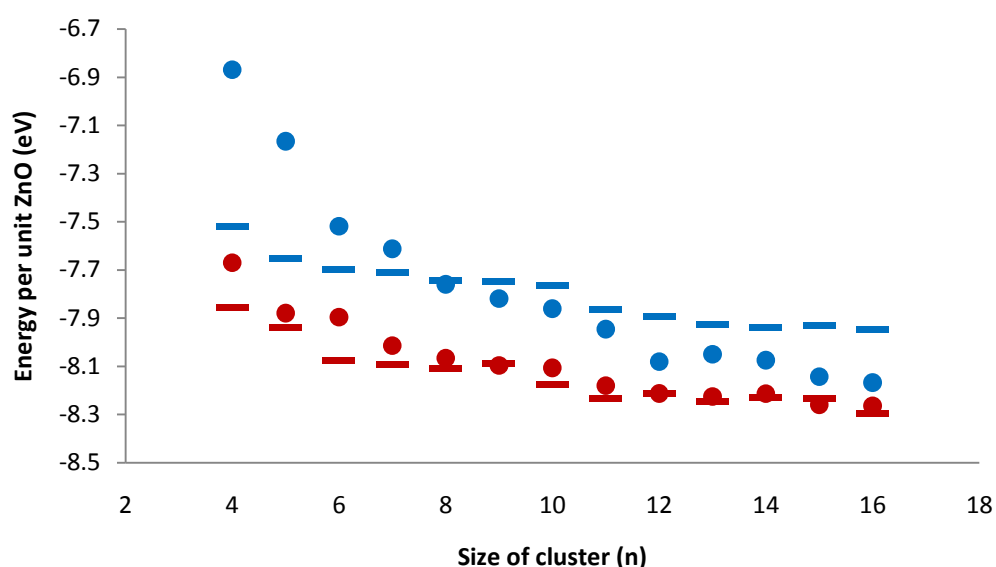


Figure 78. Energetic ordering of free space (blue) and supported (red) nanoclusters with respect to cluster size with DFT. Sticks represent 2D clusters and circles represent 3D clusters.

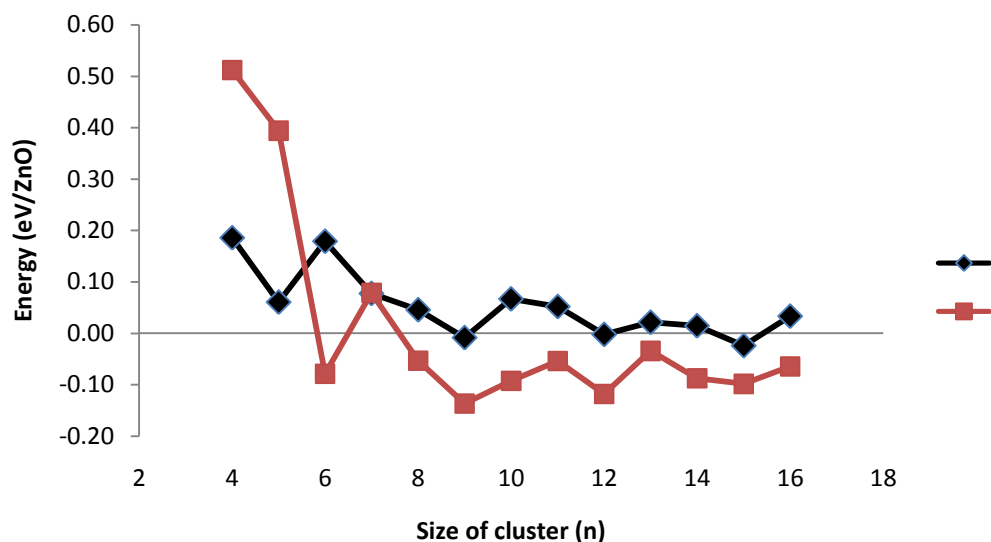


Figure 79. Energy difference between the lowest energy Ag(111)-supported 2D and 3D clusters with respect to the cluster size. Positive values are where the 2D clusters are more stable than the 3D clusters.

The energy differences between the lowest energy 3D and 2D clusters on the Ag(111) support are shown in Figure 79 for IPs and DFT. The curves look very similar after size $n = 7$. While 3D structures quickly become more favored in the IP calculations with increasing cluster size, the DFT calculations generally tend to predict 2D structures to be more stable.

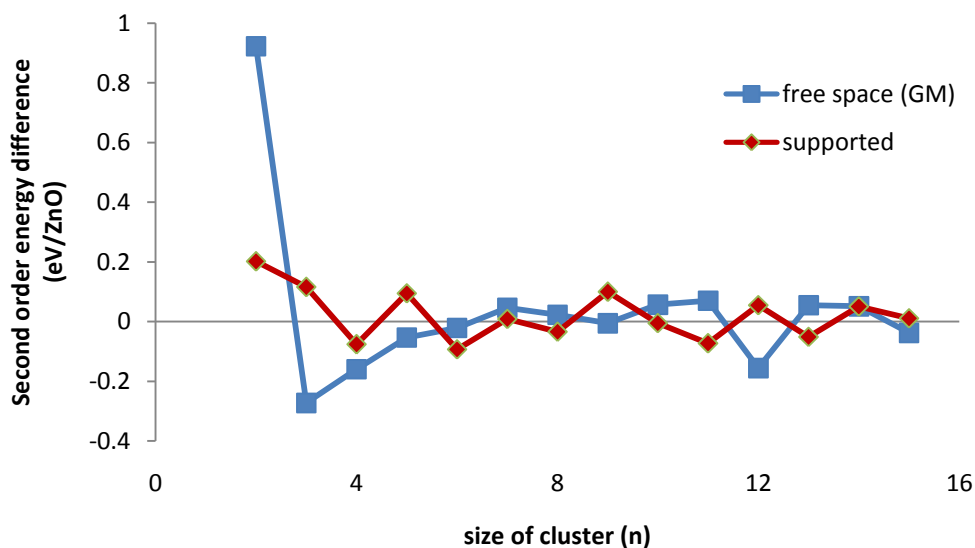


Figure 80 Second order energy difference for lowest energy free space and Ag(111)-supported clusters with respect to increasing cluster size.

The effect of the Ag support was also compared for different surfaces of silver at DFT level calculations. The DFT results show more stabilization for 2D structures than for 3D structures as well as even changes in the global minimum on the support. Heavy reconstructions also occurred for some of the cluster structures of the considered sizes of $n = 6, 7$ and 8 . The global minima structures on the Ag(111), Ag(100) and Ag(110) surfaces for some selected cluster sizes are given in Figure 81. For $n = 6$, results for Ag(111) and Ag(100) are the same, where a 2D structure is a distorted half sodalite cage is preferred. On the corrugated Ag(110) surface, however, the global minimum is another 2D structure, which emerged from a dramatic reconstruction of the 6U structure. This structure, with two four-membered rings attached to an eight-membered ring, was not found in the IP global optimizations, probably due to the relatively high energy cost of having the four- and eight-membered rings compared to six-membered rings. For sizes $n = 7$ and 8 , the global minima structures were all different on the Ag(111), Ag(100) and Ag(110) surfaces. It should also be noted that like the global minimum of size $n = 6$ in the Ag(110) case, the global minima of $n = 7$ and 8 also emerged from clusters reconstructing on the surfaces. Clearly, different surface symmetries may lead to distinctive cluster structure reconstructions.

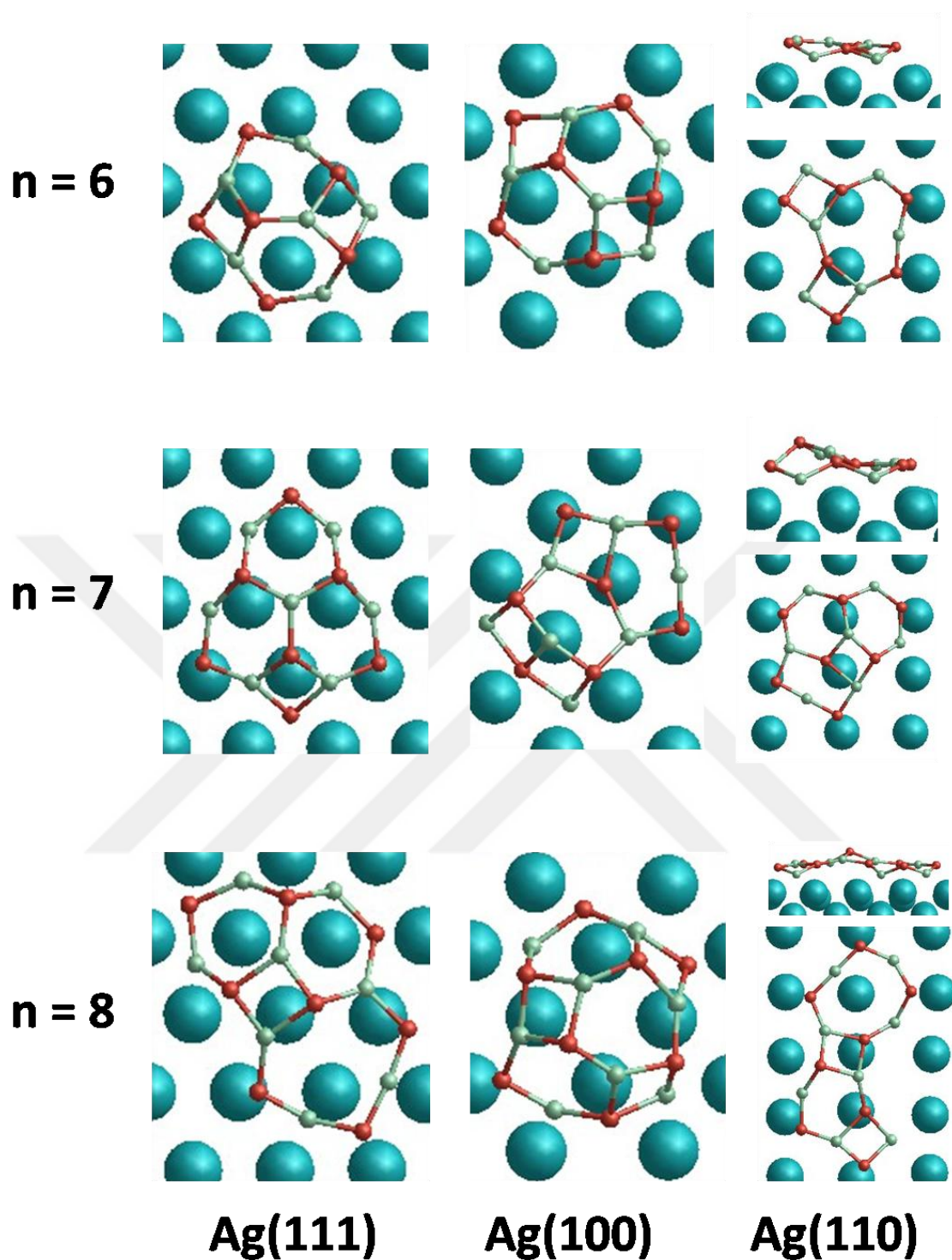


Figure 81. Lowest energy $(\text{ZnO})_n$ cluster structures on the $\text{Ag}(111)$, $\text{Ag}(100)$ and $\text{Ag}(110)$ surfaces.

5 Conclusions

In this study, we have reported many low energy structures of $(\text{ZnO})_n$ nanoclusters on Ag supports for sizes $n = 1-16, 20$ and 24 , and compared them with the corresponding free space nanoclusters. We observed that the presence of the support affects the ranking of the nanoclusters on the surface, but more drastically, it also stabilizes selectively 2D type structures, which are not stable in free space, with respect to the 3D clusters after a certain size. According to our results with IPs, 2D clusters in free space become considerably higher in energy than the 3D configurations with the increasing size. Thus, the presence of the support during the global optimization stage becomes crucial to find these low energy surface-stabilized clusters. Although the energy difference between 2D and 3D clusters are found to be lower in free space with DFT results, a similar separation of binding energies of these two structural families emerges clearly at higher sizes, starting from $n = 12$. With the extra surface stabilization, 2D clusters come in the range of the first few lowest-energy structures on the support by competing with 3D clusters, both for IPs and DFT level of theory. The extra stabilization is attributed mainly to the contact area, which is evidently greater for 2D clusters where all the atoms can interact with the surface. Moreover, the contact area determines the energetic rankings of 3D clusters on the support, which results in ellipsoid bubbles or inflated double layers being of lower energy on the support, whereas totally symmetric 3D clusters are more stable in free space. Another determining factor for ZnO cluster stability on the Ag supports was found to be the degree of matching of the cluster structure with the surface morphology. For 2D clusters, the flat Ag(100) surface is also found to be a better match than the corrugated Ag(110) surface with IPs, while the 3D clusters can fit the latter corrugated surface better. Generally, however, the flat Ag(111) surface provides the highest degree of stabilization for all clusters. The six-membered ring, which is one of the main motifs for both 3D and 2D clusters, matches best the Ag(111) surface because it follows the same six-fold (C_6) symmetry (or its subgroup trigonal C_3 , with a three-fold axis, taking into account the distinction between Zn and O atoms). The preferential stabilities of the 2D ZnO cluster structures containing six-membered rings can also be seen as the initial stages of thin film growth and in line with the experimentally observed six-membered-ring-based hexagonal layered-ZnO sheets on the Ag(111) surface.

CHAPTER IV: One monolayer ZnO on Ag(111) and hydrogen transport

1. Introduction

The possibility of a two-dimensional (2D) layered phase of zinc oxide (layer-ZnO) was first predicted theoretically by Freeman et al¹²³ where it was shown that free-standing thin films of wurtzite ZnO (wz-ZnO—the most stable ambient bulk phase of ZnO) are less stable than a phase based on 2D-ZnO sheets with a layer ordering analogous to that in hexagonal boron nitride. From these original density functional theory (DFT) calculations thin isolated slabs of layer-ZnO of up to nine or more hexagonal sheets were reported to be energetically more stable than the corresponding c-oriented wz-ZnO slab. More recent DFT calculations by Morgan¹²⁴ have shown that the excess stability range of the layer-ZnO phase in isolated thin films is limited to a thickness of four hexagonal sheets, whereupon a body centred tetragonal (BCT-ZnO) phase is energetically preferred. For very thin films of one to four sheets, where both the above theoretical results agree upon the energetic preference for layer-ZnO, experiments have indeed prepared layer-ZnO supported on both Ag(111)¹²⁵ and Pd(111).¹²⁶ For monolayer coverage, the layer-ZnO can be viewed structurally as a graphene analogue. Detailed calculations confirm that a single unsupported 2D-ZnO sheet has a planar structure.²²⁷ Using DFT and interatomic potentials we investigate the strength of the interaction of a single planar 2D-ZnO sheet with the Ag(111) surface and how this affects the structural properties of the sheet. Building upon previous predictions of multi-centre bond (MCB) assisted hydrogen transport through Zn₃O₃ hexagonal rings in the sodalite ZnO (SOD-ZnO) system²²⁸, we also investigate how H atoms interact with a 2D-ZnO sheet when passing through a Zn₃O₃ aperture.

2. Methodology

We employ three different methodological approaches in our study. Both periodic and cluster DFT calculations were used to calculate structures, energies and electronic states. In addition, we used classical interatomic potentials (IPs) to further study some structural and energetic properties and trends. For the periodic DFT calculations we

used the VASP code²²² employing the generalized gradient approximation (GGA) PW91 functional,²²¹ where the effect of core electrons on the valence states was described via the projector augmented wave (PAW) approach.^{176,192} One-electron valence states were expanded in a plane wave basis up to an energy kinetic cutoff of 500 eV. For the cluster DFT calculations we used the GAMESS-UK²²⁹ code with a combination of the B3LYP hybrid exchange–correlation functional²³⁰ with the all-electron Ahlrichs pVDZ basis set.²³¹ The periodic classical calculations used the GULP code²¹⁸ and employed the ZnO IP by Whitmore et al.,²¹⁹ an embedded-atom model IP for Ag due to Cleri and Rosato²³² and custom-parametrized IPs for the Ag–Zn and Ag–O interactions. In the latter case we fitted the geometries and energies of a series of periodic DFT calculations of a Zn₆O₆ cluster interacting with a four-layer thick Ag(111) slab to Buckingham IPs for Ag–O and Ag–Zn. Although these metal–oxide IPs only have a two-body form and neglect an explicit account of polarization effects known to be important in metal–oxide interface interactions (e.g. image forces²³³), it is probable that such interactions (present in the DFT-modelled system) are, to some degree, subsumed in the IP parametrization. Furthermore, and importantly for the current study, due to the manner of their parametrization, they avoid any dependence on incommensurate mismatching between the Ag(111) surface and the 2D-ZnO layer.

In the DFT and IP periodic calculations both minimal 1:1 cell (i.e. with one unit cell of 2D-ZnO supported on one unit cell of Ag(111)) and a 7:8 supercell (i.e. 7 unit cells of 2D-ZnO and 8 unit cells of Ag) were used to describe the ZnO on-Ag(111) system. In the DFT calculations the unit cell case used a 5×5×1 Monkhorst–Pack²³⁴ (MP) grid of *k*-points for the reciprocal space integration, whereas Γ -point integration was considered to be sufficient in the larger 7:8 system. In the case of the IP calculations additional 2D-ZnO:Ag(111) supercells of sizes 5:6, 6:7, 8:9 and 13:15 were also considered. In all Ag-containing calculations the Ag support was represented by a slab of four layers with the bottommost layer fixed to the atomic positions of bulk Ag (taken from a bulk Ag energy minimization at the corresponding level of theory). For the isolated 2D-ZnO sheet calculations the *a* and *b* lattice parameters were fully optimized with no constraints. The binding energies (BEs), calculated using the total energy difference between the combined and separated systems (i.e. $E[2D\text{-}ZnO\text{-on-Ag}(111)] - E[Ag(111)\text{-slab}] - E[2D\text{-}ZnO]$), are quoted using two ways of calculating $E[2D\text{-}ZnO]$:

(i) via unconstrained optimizations of fully relaxed 2D-ZnO sheets and (ii) from optimizations where the 2D-ZnO sheet is constrained to have the same a and b lattice parameters as the corresponding Ag slab. Dispersion corrections to the binding energies in the DFT calculation were estimated using the DFT-D2 method due to Grimme.²³⁵ Here the dispersive energy correction was applied to the total optimized ZnO-on-Ag(111) system using a single-point evaluation of parametrized two-body dispersive interaction terms. All periodic calculations used a vacuum separation in the c direction (i.e. perpendicular to the Ag(111) surface) of 12 Å, which was found to be sufficient to avoid the effects of spurious interactions between repeated images.

For studying the interaction of atomic hydrogen with a Zn₃O₃ ring, a 4×4×1 supercell of a single unsupported planar 2D-ZnO sheet consisting of 32 atoms was used in the periodic DFT calculations. In order to obtain the projected density of states (PDOS) and projected charge densities of localized states calculations were done using a 11×11 × 1 MP mesh of k -points. In the cluster DFT calculations a finite system consisting of a Zn₃O₃ ring with its six nearest-neighbour Zn₃O₃ rings (24 atoms in total) was employed. All H transport barriers were computed via constrained energy minimizations (i.e. where the positions of the H atom and one or more 2D-ZnO atoms not in the Zn₃O₃ ring were fixed) at points along a line through the centre of a Zn₃O₃ ring and perpendicular to the plane of the 2D-ZnO sheet/cluster, until forces were lower than 0.01 eV Å⁻¹.

3. Results and discussion

3.1. Interaction of a 2D-ZnO single sheet with Ag(111)

A summary of relevant distances and energies for the 2D-ZnO-on-Ag(111) system is given in Table 8. For the smallest 1:1 2D-ZnO-on-Ag(111) system the mismatch between the isolated optimized unit cell of the 2D-ZnO sheet and the Ag(111) slab in the a - b direction is found to be between +12 (DFT) and +14 (IP) per cent. This means that, in order for the 2D-ZnO sheet to be accommodated in the fixed unit cell of the Ag(111) slab, it must be significantly compressed. For this reason the Ag-supported 2D-ZnO sheet in the 1:1 system is significantly buckled away from its energetically favoured

planar free-space structure to have all Zn atoms bending inwards towards the Ag surface and the O atoms outwards, together with having relatively reduced Zn–O distances. Comparing this ZnO–Ag combined system with a similarly a – b constrained system but with the buckled 2D-ZnO sheet far from the Ag(111) surface gives a binding energy of the distorted ZnO sheet with the Ag(111) surface of between 0.39 and 0.94 eV/ZnO, depending on the level of theory employed (see Table 8). Using the energy of the fully optimized 2D-ZnO unit cell (i.e. without the artificial a – b constraint of the Ag(111) unit cell slab) and of the isolated Ag(111) unit cell slab as reference energies, however, shows that the 1:1 system is unstable to spontaneous ZnO–Ag separation.

Table 8. Energies and relevant distances for the 2D-ZnO-on-Ag(111) system. Column headings correspond to (i) level of theory: IP, DFT or DFT-D2, (ii) model: ratio of ZnO to Ag unit cells used, ((iii)–(iv)) a_x : lattice parameter of isolated optimized subsystem (Å), (v) ratio of a parameters of the individually optimized ZnO sheet and the Ag(111) slab, ((vi)–(vii)) maximum and minimum distances in the 2D-ZnO-on-Ag(111) system (distances between ZnO and Ag(111) are in a direction normal to the surface and the ZnO sheet (Å)) and (viii) $BE_{\text{ZnO-Ag}}$: binding energy between ZnO sheet and Ag(111) surface (eV/ZnO). The first values correspond to BEs calculated using the energy of a relaxed isolated 2D-ZnO sheet, whereas the second values use the energy of a 2D-ZnO sheet constrained to have the corresponding Ag(111) supercell lattice parameters.

Level of theory	Model ZnO:Ag	a_{ZnO}	a_{Ag}	$a_{\text{ZnO}}/a_{\text{Ag}}$	Zn–O range	Zn–Ag(111) range	O–Ag(111) range	$BE_{\text{ZnO-Ag}}$
IP	1:1	3.237	2.888	1.121	1.74	2.03	2.52	–0.62/0.94
IP	8:9	5.898	25.996	0.996	1.87–1.92	2.09–2.48	1.73–2.81	0.85/0.85
IP	7:8	2.661	23.107	0.981	1.89–1.93	2.10–2.46	1.94–2.53	0.80/0.83
IP	13:15	2.085	43.326	0.971	1.90–1.94	2.05–2.48	2.05–2.48	0.75/0.83
IP	6:7	9.424	20.219	0.961	1.92–1.96	2.09–2.47	2.05–2.47	0.62/0.83
IP	5:6	6.186	17.330	0.934	1.88–2.52	2.10–2.49	2.08–2.47	0.44/0.85
DFT	1:1	3.360	2.938	1.144	1.69	2.48	3.18	–0.94/0.39
DFT-D2	1:1	3.360	2.938	1.144	1.69	2.48	3.18	–0.56/0.77
DFT	7:8	3.536	23.504	1.001	1.94–1.96	2.68–2.79	2.81–2.87	0.17/0.17
DFT-D2	7:8	3.536	23.504	1.001	1.94–1.96	2.68–2.79	2.81–2.87	0.59/0.59

From the unconstrained IP-based optimization of the 2D-ZnO unit cell we find a flat sheet to be most energetically favoured in line with the fully optimized isolated 2D-ZnO sheet from unconstrained DFT optimizations. Multiples of this IP-optimized flat sheet were also used to calculate the a_{ZnO} values in IP explorations of a series of X:Y systems starting from $a_{\text{ZnO}}/a_{\text{Ag}}$ mismatches less than 1 and gradually increasing to unity. We

find that, although, as expected, the smaller the mismatch the larger the unconstrained 2D-ZnO on-Ag(111) binding energy, only when the mismatch is less than 1% does the constrained ZnO-on-Ag(111) binding energy become very similar to the unconstrained case (i.e. showing that the corresponding X:Y model is not unduly constraining the relaxations of the separate ZnO and Ag subsystems). For the IP calculations the best model in this respect was found to be the 8:9 system where the 2D-ZnO sheet is stretched by 0.3%. For the DFT calculations the 7:8 system was found to require a compression of the 2D-ZnO sheet of only 0.1%. It is noteworthy that a 7:8 commensurate ZnO-on-Ag(111) ordering is also that which is observed in experiment,¹²⁵ tending to support the accuracy of the DFT calculations. The 7:8 2D-ZnO-on-Ag(111) system from the DFT optimizations is shown in Figure 82.

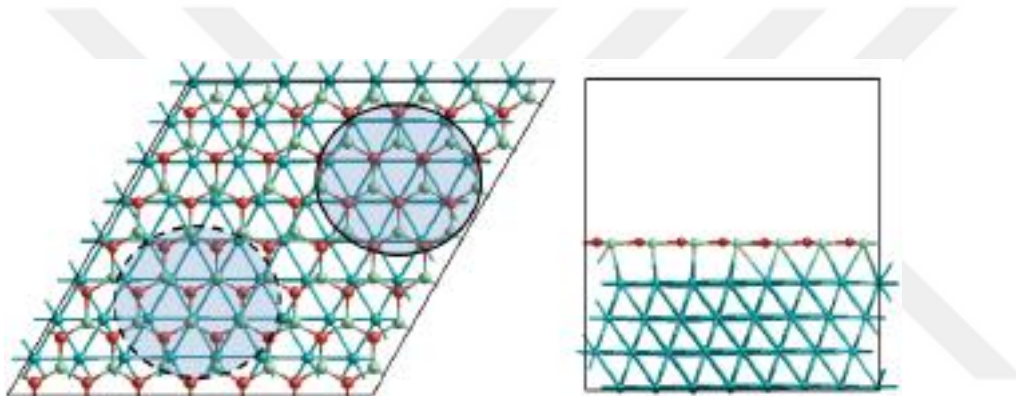


Figure 82. Top (left) and side (right) views of the 2D-ZnO-on-Ag(111) 7:8 system after optimization using DFT. The solid bounded region highlights where the oxygen atoms (red/dark grey balls) are near to being directly above the Ag atoms (blue/grey balls) in the underlying surface slab. The dashed bounded region highlights where the zinc atoms (light green/light grey balls) are near to being directly above the Ag atoms.

The 2D-ZnO-on-Ag(111) binding energy for these optimal systems ranges from 0.17 eV/ZnO for the bare 7:8 calculation to 0.85 eV/ZnO for the 8:9 IP calculation. The higher binding energy for the latter calculation is unlikely to be due to any improvement in the description over a pure GGA DFT treatment, especially considering that the Zn–Ag and O–Ag IPs are two-body fits to pure GGA DFT calculations. Nevertheless, it is likely that the 7:8 pure DFT-calculated 2D-ZnO-on-Ag(111) binding energy is a lower bound to the true binding energy due to the inherent omission of dispersive interactions in pure GGA DFT calculations. Applying a dispersion correction to the energy of the DFT optimized 7:8 system using the empirically parametrized two body DFT-D2 method gives a 2D-ZnO-on-Ag(111) binding energy of 0.59 eV/ZnO at the equilibrium

DFT ZnO–Ag(111) separation. A recent investigation of organic molecules on Ag(111) has shown that this two-body corrective scheme tends to significantly overestimate the adsorption energies with respect to experiment.²³⁶ Another experimental study of 2D-BN sheets on Ag(111)²³⁷ has confirmed that the 2D-BN-on-Ag(111) binding energy is negligible, as predicted by pure DFT,²³⁸ and thus that dispersive interactions do not play a significant role in this 2D-sheet-on-Ag(111) interaction. We also note that our calculations show no evidence of charge transfer or covalent bonding between the Ag(111) surface and the supported 2D-ZnO sheet, with both having indistinguishable atomically partitioned charges in isolation and in the combined system. Considering the above we suggest that the actual 2D-ZnO-on-Ag(111) binding energy is likely to be in the energy range 0.15–0.5 eV/ZnO, and likely mainly due to non-bonding-induced polarization effects.

In both IP and DFT calculations (taking the 8:9 and 7:8 systems as examples, respectively) the Ag-supported ZnO sheet is found to slightly deviate from perfect planarity; the energetically preferred structure in isolation. In the DFT optimized system all the Zn atoms in the supported 2D-ZnO sheet are closer to the Ag(111) surface than their nearby O atoms (i.e. Zn atoms have generally smaller z coordinates—by $\sim 0.1\text{\AA}$ —than nearby O atoms, where z is measured from the base of the Ag slab). Taking this sheet and re-optimizing in the absence of an Ag(111) substrate recovers the planar 2D-ZnO sheet. In the IP 8:9 2D-ZnO-on-Ag(111) system we find that the oxygen atoms oscillate both above and below nearby Zn atoms by approximately $0.3\text{\AA}$. We find that in this case these small local distortions are due to a real instability of the IP-treated isolated 2D-ZnO flat sheet which only emerges when one allows for more degrees of freedom than allowed for in the minimal unit cell case. This instability emerges for the 7:8 and 8:9 systems where the 2D-ZnO sheet is stretched by less than 2% and results in an increase in the range of O–Ag(111) distances observed (see Table 8).

In addition to these local structural oscillations, in both the DFT and IP calculations the deviations in the z coordinates of the Zn and O atoms follow a gradual rumpling or flexing, with amplitude $\sim 0.1\text{\AA}$ (DFT) and $\sim 0.15\text{\AA}$ (IP), which is mirrored by a similar out-of-phase rumpling of the atoms in the uppermost layers of the Ag slab, with amplitude $\sim 0.2\text{\AA}$ (DFT) and $\sim 0.35\text{\AA}$ (IP). The rumpling of both the Ag(111) surface and the 2D-ZnO sheet appears to be due to variations in the interaction between the two

subsystems. We find that when O atoms are closest to being directly above an Ag atom (i.e. at an on-top position) the interaction seems to be strongest, and vice versa. The z coordinates of the Zn atoms also follow the tendency of the O atoms where the Ag(111)-sheet separation is greatest, but are smallest for intermediate separations. In Figure 83 we show contour plots of the locally averaged z coordinates of the Zn and O atoms in the supported ZnO sheet and in the corresponding uppermost atoms in the supporting Ag(111) slab for the DFT-optimized 7:8 system. The upper right-hand part of each plot is where the O atoms are lowest and the Ag atoms highest (i.e. indicating a stronger interaction). In Figure 82 we circle the corresponding region where O atoms are close to being perfectly at on-top positions. Conversely, the lower left-hand part of each plot is where the 2D-ZnO sheet and the Ag(111) surface are furthest apart and where the O atoms are furthest from on-top positions (shown by a dashed bounded region in Figure 82).

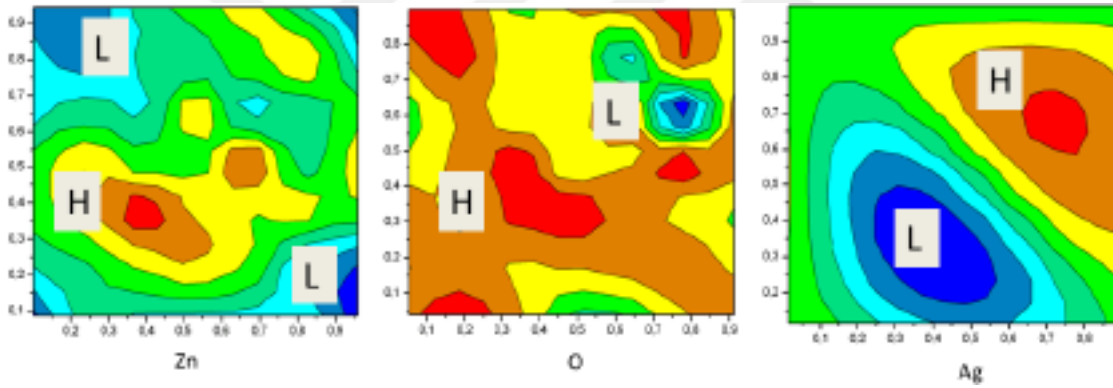


Figure 83. Contour plots of the locally averaged z coordinates of Zn, O and Ag atoms in the 7:8 system shown in Figure 82. The fractional x-y coordinates in the square plots correspond to those in the oblique angled 7:8 supercell. The ‘L’ and ‘H’ labels correspond to relatively lower and higher regions (where the height is taken as the magnitude of the z coordinate measured from the bottom of the Ag slab).

3.2. Transport of hydrogen through a 2D-ZnO single sheet

The interaction of atomic hydrogen with the unsupported 2D-ZnO system was studied using both periodic and cluster DFT calculations. In particular, we focused on the interaction of H with a Zn_3O_3 ring when passing through the sheet. When H is far from the sheet the electronic states of each are distinct and non-interacting. Taking first the

periodic GGA DFT calculations, we see this non-interacting situation in the PDOS in Figure 84 (a) where the narrow unperturbed H 1s state (solid line) is superimposed on top of the unperturbed 2D-ZnO states.

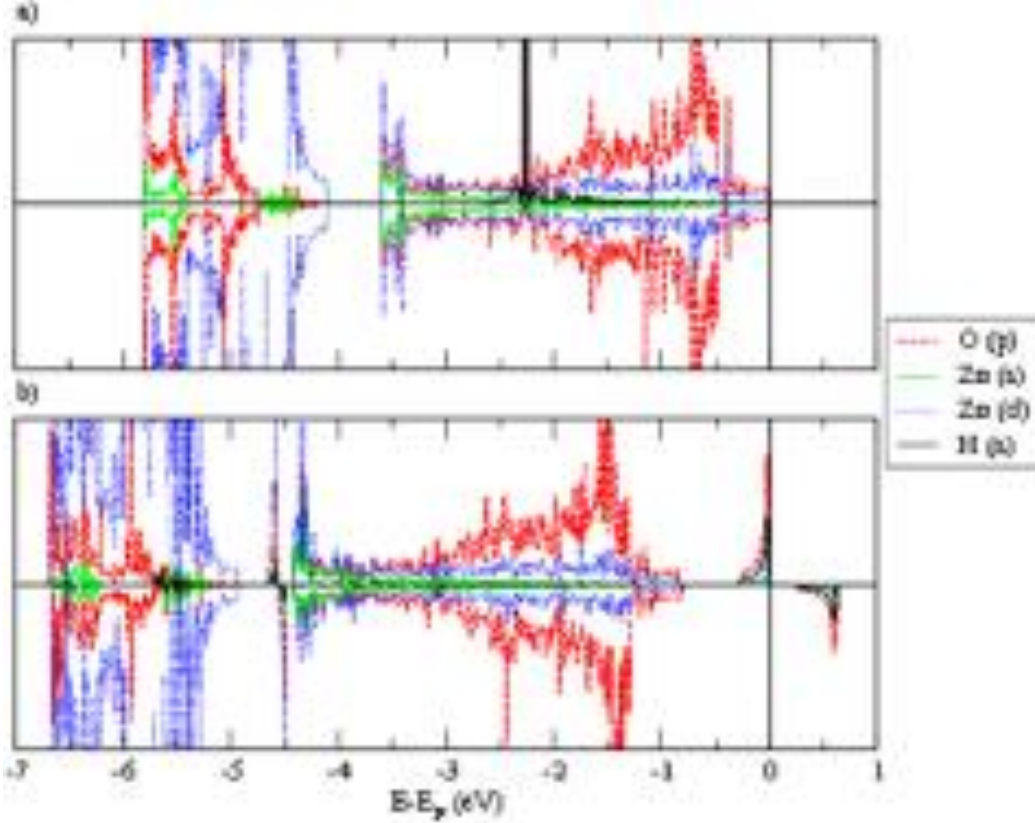


Figure 84. PDOS for the hydrogen and 2D-ZnO sheet where (a) the hydrogen atom is far from the sheet and (b) H is in the centre of a Zn_3O_3 ring of the sheet ($\text{H}@\text{Zn}_3\text{O}_3$).

H atoms are found to bind relatively weakly in an on-top manner to the Zn (0.32 eV) and O (0.04 eV) sites thus raising the possibility of transport through the 2D-ZnO sheet at suitably high temperatures. Upon approaching the centre of a Zn_3O_3 hexagonal ring along a line perpendicular to the plane of the sheet, the H atom becomes firstly weakly adsorbed until a minimum energy position is reached at a distance of 1 Å from the 2D-ZnO sheet (−0.04 eV relative to the separate sheet and H atom). Subsequently entering the ring from this position incurs an increase in the relative system energy from this weak minimum to a maximum of +0.11 eV at the centre of the Zn_3O_3 ring. The full calculated barrier is shown in Figure 85. The energy cost solely due to the H-induced structural distortion of the 2D-ZnO sheet is calculated to be 1.27 eV. Thus the interaction between H and the 2D-ZnO sheet, when H is in the centre of a Zn_3O_3 ring

(H@Zn₃O₃), compensates for this effect by 1.16 eV. From our previous studies on H interacting with Zn₃O₃ environments^{228,239} and other results concerning interactions of atomic H with undercoordinated centres in ZnO²⁴⁰ we were led to look for evidence of possible MCB formation in the H@Zn₃O₃ system.

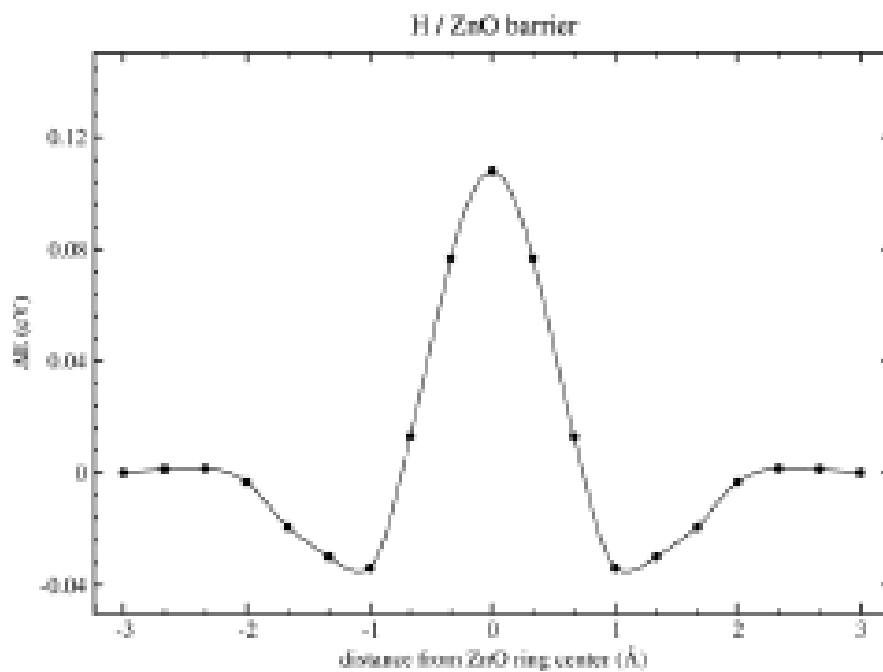


Figure 85. Transport barrier for a single H atom to pass through a Zn₃O₃ ring of a 2D-ZnO sheet (GGA DFT calculation using a 4×4 supercell).

The PDOS of the H@Zn₃O₃ system (see Figure 84(b)) shows a number of distinct differences with respect to the non-interacting case (Figure 84(a)). The first notable change is that the Fermi level is now located at an isolated α -spin state, which is separated from the top of the O p-dominated 2D-ZnO conduction band by about 0.5 eV. This singly occupied state is easiest to visualize by the spin density of the system, which shows spin density on both the H atom and the three nearest O atoms in the surrounding Zn₃O₃ ring (see Figure 86). In the cluster hybrid DFT calculations this state corresponds to an α -spin highest occupied molecular orbital (HOMO). The spin density of this state (see Figure 86) is found to be very similar to that from the periodic GGA calculations, tending to confirm the general reliability of both methods. From analysing the charge distribution associated with this state, the spin on the O centres comes from charge deficiency (i.e. partially occupied O p-like states) and that on the H centre from a localized electron. From an orbital component analysis of the cluster DFT calculation,

the electron on the H centre appears to be mainly localized in an H 2s-like state. The corresponding unoccupied state (hole) can be found as a β -spin unoccupied peak at approximately +0.5 eV above the Fermi level in Figure 84 (b).

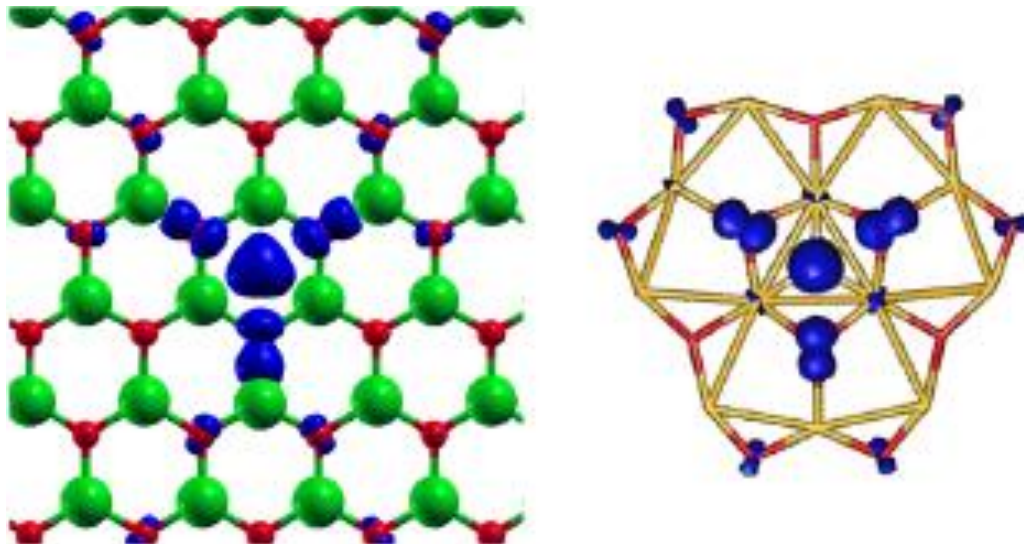


Figure 86. Spin density of the H@Zn₃O₃ system for the 3×3 supercell GGA DFT calculation (left) and the B3LYP cluster calculation (right).

The α -HOMO state is relatively high in energy, which thus further points towards the existence of a compensating low energy H@Zn₃O₃ state to explain the low calculated transport barrier. In the periodic DFT calculations we find considerable disruption of the H@Zn₃O₃ PDOS with respect to the non-interacting system, especially for energies >3.5 eV below the α -HOMO. From inspection of the PDOS it was difficult to see any specific indication of MCB formation involving the H centre. In the hybrid cluster DFT calculations we were able to search the atomic orbital components of each discrete molecular orbital to find those which involved the H s-states and states of neighbouring atoms. From such a search the most probable candidate for an MCB bonded state is an α -spin/ β -spin pair of states found at -3.9 eV. This state involves both the Zn 4s states of the nearest three Zn atoms to the H centre, and the H 1s state (see Figure 87). This state is very similar in appearance and in its orbital constituents to that found for H atoms passing through the SOD-ZnO polymorph [6]. As in the H@SOD-ZnO case the present state requires charge donation to make a doubly occupied bonded state. The spin density plots in Figure 86 suggest that charge is depleted from the O p-states. Plotting the charge density difference of the periodic system (Figure 87) we confirm that charge is transferred from the O p-states to the region mainly between the H centre and its three

nearest Zn neighbours. We suggest that a consistent interpretation of these data is that (i) when the H atom is in the centre of a Zn_3O_3 ring the considerable spatial confinement causes the H 1s electron to occupy a higher energy, more diffuse 2s-like state (the α -HOMO state), (ii) to charge-compensate, the surrounding three O atoms donate charge to the charge-depleted region in the ring, and (iii) the donated charge (two electrons) lowers the energy of the system by filling a hybrid state formed by the combination of the empty H 1s orbital and the three surrounding empty Zn 4s orbitals (the MCB state).

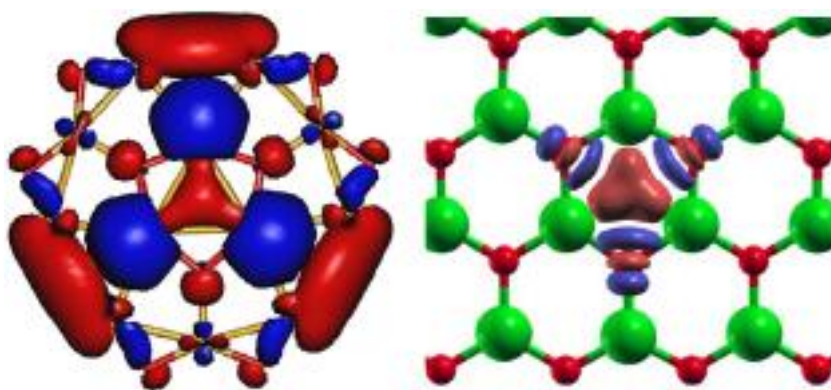


Figure 87. The proposed Zn 4s–H 1s MCB orbital from the B3LYP cluster calculation (left) with the large density difference of the periodic DFT calculations (right). Relative charge increase is found in the centre of the ring and to a lesser extent on the oxygen sites (lighter grey) whereas charge is depleted (dark grey) from the p-like lobes of the oxygen sites.

4. Conclusions

We have employed a range of modelling methods to understand (i) the structure and interactions in the experimentally prepared 2D-ZnO-on-Ag(111) system and (ii) how H atoms interact with the 2D-ZnO sheet as they pass through a Zn_3O_3 ring. The former calculations reveal subtle variations in the structure of both the supported 2D-ZnO sheet and the Ag(111) support itself which are not observed in the non-interacting system. The importance of the degree of 2D-ZnO/Ag(111) commensurability is also highlighted for calculating accurate sheet-on-substrate binding energies. The calculations of the unsupported 2D-ZnO sheet interacting with hydrogen provide strong evidence for H forming a low energy Zn 4s–H 1s MCB state when passing through a Zn_3O_3 ring of the 2D-ZnO sheet, thus allowing for relatively facile H transport through the sheet. We note that 2D-ZnO has been prepared on Pd(111)¹²⁶ which is often employed in hydrogen

membrane applications.²⁴¹ Palladium is fragile and expensive, however, which could potentially be addressed by using hybrid 2D-ZnO–Pd membranes or similar systems.



CHAPTER V: Effect of Finite Size on Epitaxial growth of ZnO on Ag(111)

1. Introduction

In general, there are three types of epitaxial growth of an adsorbate on a substrate: (i) Volmer-Weber (VW), (ii) Frank-van der Merwe (FM) and (iii) Stranski-Krastanov (SK).²⁴² In VW growth, internal adsorbate interactions are so dominant over the adsorbate-substrate interactions that 3D islands form on the substrate. Layer by layer growth is enhanced in FM growth, where the higher adsorbate-substrate interactions lead to adsorbates preferring surface sites and in which growth proceeds by fully formed layers. The SK growth mode lies between these two growth types, in which both 2D layers and 3D islands occurs. In SK growth, a transition from the layer-by-layer growth to island based growth occurs at a critical layer thickness, which is dependent on several chemical and physical properties of the adsorbate and substrate (e.g. surface energies, lattice parameters). Figure 88 shows a schematic representation of these three main types of growth.

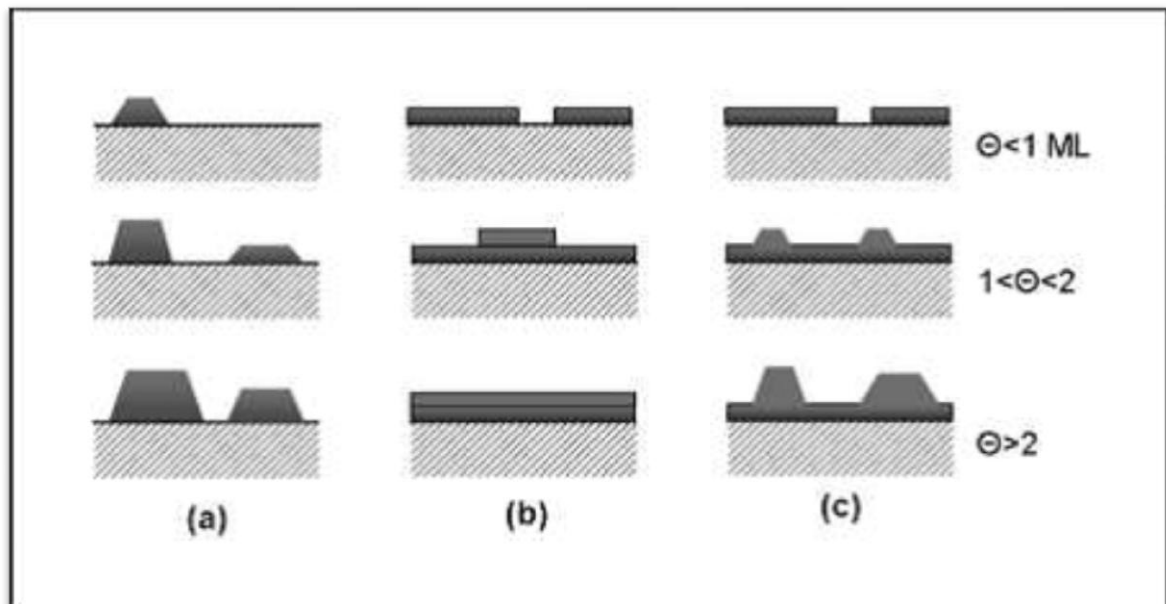


Figure 88. Main growth types in thin film formation; (a) Volmer-Weber, (b) Frank-van der Merwe, (c) Stranski-Krastanov. Here Θ stands for the coverage.

As mentioned in the previous two chapters, ZnO nanofilms have been grown on Ag(111) metal substrates with 0-4.5 monolayer (ML) coverages.²⁴⁷ With increasing coverage in this range a depolarized ZnO structure was observed for the first two full MLs followed by a phase transition to a new structural type starting from third layer. Figure 89 shows two STM images of 2.2 ML ZnO coverage from this work, from which the the triangular and truncated triangular forms of the islands can be observed for the incomplete third adlayers of ZnO, which was the basis of our model constructions To study the finite size effects of such islands on the the structure ZnO we modelled stoichiometric ZnO films with coverages between 2 ML and 2.7 ML. Where computationally feasible we also explicitly included the Ag(111) substrate. We note that the smallest coverage for which accurate experimental data was reported is for 2.7 ML ZnO films on Ag(111). We further note that the experiment data for the 2.7 ML film show that although the first 2 MLs are complete, the 3rd ML has 60% coverage with 10% of the 4th ML being already present. This feature of the observed films is also taken into account in our models.

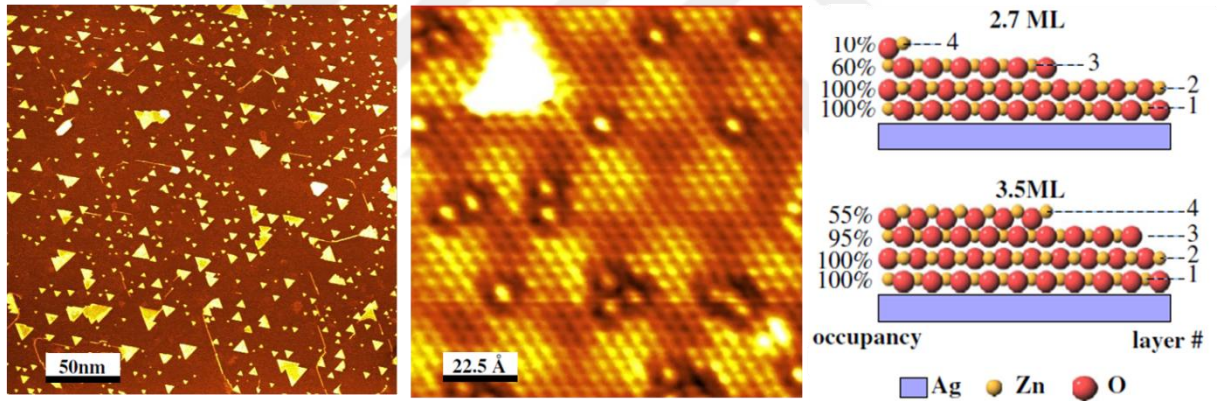


Figure 89. STM images of 2.2 ML ZnO on Ag(111) and schematic structure models of 2.7 and 3.5 ML ZnO on Ag(111)¹²⁵

2. Methodology

In this study we have used *ab-initio* density functional theory (DFT) as implemented in the VASP code¹⁷⁶ using the generalized gradient approximation PW91 exchange-correlation functional. The projector augmented wave (PAW) approach¹⁹² was used to describe the effect of core electrons on the valence states. One-electron valence states were expanded in a plane wave basis up to an energy kinetic cutoff of 400 eV. A 4 layer Ag slab with 8x8 surface periodicity was generated to simulate the Ag substrate which

is experimentally known to be commensurate with a 7x7 supercell ZnO thin film grown on top. The lattice vector in the adsorption direction (z) was kept at 30 Å, which ensures 12 Å vacuum separations between periodic images for the highest coverage considered. Due to the spatial extent of the system, calculations were done only at Γ point in reciprocal space. All of the atomic positions were optimized until the forces on the atoms became less than 0.2 eV/nm. The binding energies (BE) were calculated by using the total energy differences between the combined and separated systems according to the formula:

$$BE = \frac{E[\text{ZnO on Ag(111)}] - E[\text{ZnO}] - E[\text{Ag(111)}]}{n}$$

where n is the number of ZnO unit in the system. All of the considered ZnO coverage models were prepared by initially placing Zn and O atoms according to their positions in a layered phase, while the Ag atoms are placed according their bulk positions.

3. Results and Discussion

3.1. ZnO coverages of 1 and 2 ML on Ag (111)

The 1 ML single sheet of ZnO on Ag(111) surface is discussed in detail in chapter 4.3. Briefly, the Ag-supported ZnO sheet slightly deviates from perfect planarity, which is the preferred structure for an isolated single ZnO sheet. This deviations are characterized in two groups: (i) local structural oscillations, where the Zn atoms are slightly closer (~ 0.1 Å) to the surface than the O atoms, and (ii) a gradual rumpling of the ZnO sheet with a 0.1 Å amplitude which is mirrored by an out-of-phase rumpling of the outermost atoms of the Ag surface. The Ag and ZnO sheets come closer according to this rumpling where the O atoms coincide with on-top positions on the surface. However, for 2 ML ZnO on Ag(111), in-phase rumpling is affected by the additional ZnO layer, with inter layer ZnO interactions in the z -direction being stronger than Ag-ZnO interactions. The binding energy of the 2 ML ZnO film on Ag(111) decreases to 0.09 eV/ZnO from the value of 0.17 eV/ZnO for 1ML ZnO coverage. As for local structural oscillations in the 2ML film, unlike for the 1 ML case, no Zn atoms were found to be closer to the Ag(111) surface, while small variations in local interlayer separations occurred throughout the unit cell for a 13 % of the bilayer connections.

These minor interlayer structural distortions (see Figure 90c) do not follow the pattern of either a WZ or a BCT bond ordering but are appear to simply be substrate-induced perturbations to a perfect flat bilayer 2ML film. It should be be also noted that for free standing 2ML ZnO nanofilms, both WZ and BCT structures directly relaxes to the a perfectly flat bilayer of the layered phase. For 3 layers in free space, the same spontaneous transformation to the layered phase happens for the WZ structure, whereas the BCT phase can conserve its structure while being slightly compressed. Furthermore, the energetic stability of 3 layers of BCT-ZnO is found to be the almost exactly the same as that of a 3ML film of the layered phase. For 4 ML films while the BCT phase become the most stable polymorph in free space, there exists also a wide range of other energetically competing phases, which are lower in energy than the layered phase. The possible polymorphic structures of free-standing 4 ML ZnO films are discussed in detail in chapter 5.

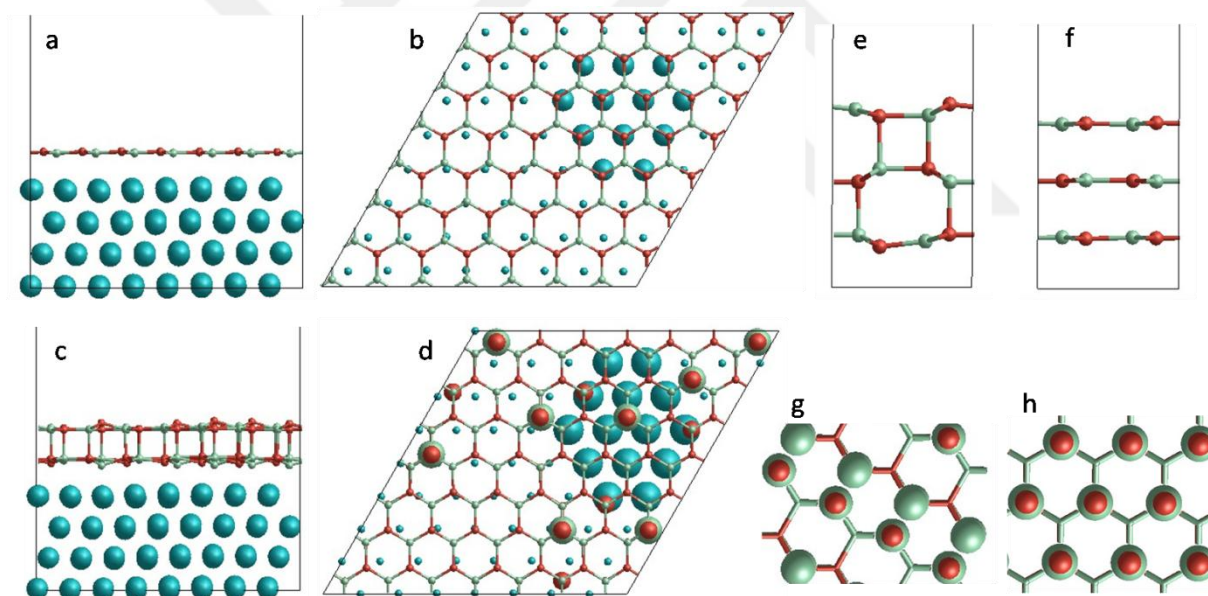


Figure 90. Optimized structures of 1 ML ZnO on Ag(111) surface (a-side view, b-top view), 2 ML ZnO on Ag(111) surface (c-side view, d-top view). e and f shows side views of the optimized geometries of 3 layer thick BCT-ZnO and layered-ZnO. g and h illustrate the interlayer spacings in the BCT and WZ ZnO structures. The larger balls for Zn and O atoms are used to indicate where the interlayer separations occur, while the bigger balls for Ag atoms in b and d are used for indicating the surface rumpling, i.e. where the surface atoms move outwards.

3.2. ZnO coverages of 2.2, 2.3 and 2.75 ML on Ag (111)

To study the effect of finite size, i.e. incomplete layers of ZnO on top of completed ones, found during growth, stoichiometric 2.2, 2.3 and 2.76 ML ZnO coverages on the Ag(111) surface were modelled. The 2.2 ML model contains 3 layers of ZnO, of which the incomplete top adlayer is a simple stoichiometric extension obtained from a hexagonal adlayer ZnO island.

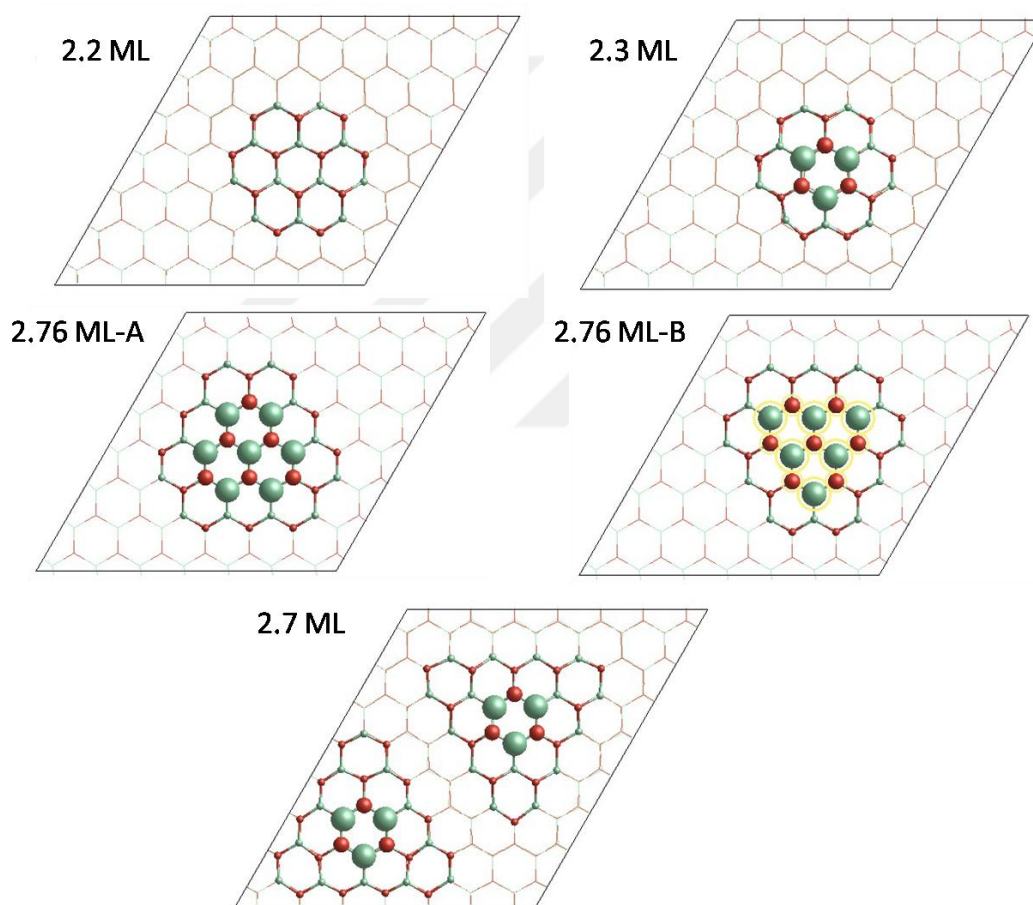


Figure 91. Initial structures of ZnO coverage models. Red and Green stands for O and Zn atoms, respectively. The first two complete MLs are shown with thin sticks while the third layer is shown with a larger ball and stick model and the top layer is differentiated by the largest balls.

The 2.3 ML model was obtained by adding a single hexagonal unit on top of the 2.2 ML hexagonal island, which helps us to compare the effect of a second adlayer, separately. The 2.2 ML hexagonal island model can be also extended in three directions to make a

triangle, but which would result in a non-stoichiometric model in conflict with experiment. Although the small islands in the STM images appear triangular, atomic resolution has not been obtained and such images may result from hexagonal islands which can be also be regarded as truncated triangles. One possible strategy to construct stoichiometric films having triangular adlayers is to compensate the excess atoms of one kind in a triangular island with other islands having reduction of the same atom type. This can be done, for example, by constructing a small triangular island on top of a relatively larger truncated triangle such as in the case of our 2.76 ML models. In this type of construction, two possibilities emerge according to the choice of which type of atom will be excess on which adlayer. In our study we constructed adlayer islands with both an excess of O atoms on the first adlayer (2.76 ML-A) and vice versa (2.76 ML-B) in order to compare their relative stabilities and structures. We note that adding a smaller island on top of the larger island is also in line with the experimentally observed pattern of growth for such films (see above).

It is more difficult to construct simple models with triangular islands in the first adlayer since stoichiometric compensation is not possible for a single triangular island. However, by constructing two types of triangular island on the first adlayer, they are able to stoichiometrically compensate each other. Due to the 7:8 ZnO-Ag commensuration, such a two island system was out of our computational limit while also taking into account Ag surface. Thus, we have considered only a free standing 2.70 ML ZnO system together. For comparison, we have calculated all other systems as free standing structures corresponding to same structures also modelled with the Ag(111) surface taken into account.

Figure 92 shows the optimized structure of the 2.2 ML coverage model. The binding energy with the Ag substrate was found to be 0.08 eV/ZnO, which is almost the same value as that for the 2 ML coverage case. A priori it would typically be expected that the binding energy per ZnO unit of the 2.2 ML with the surface would be decreased since the third adlayer of ZnO is further from the Ag surface. However, that the adsorption energy is higher than for the 2 ML case seems to be due to the structural reconstructions in the adlayer islands. After the optimization the edge Zn atoms of the 3rd layer move 0.42 Å towards the centre of the island while the rest of the Zn and O atoms does not

displace more than $0.05 \text{ \AA}$ in x-y plane. As for distortions in z-direction, the local variations in interlayer separations observed in the 2ML case almost disappear, while ordered separations are found in the island. In Figure 92 it can be seen that the central hexagonal core of the island and the corresponding part of the first two ML under the this core converges to display the WZ structure which is, in turn, becomes encircled with smaller regions which display BCT-like structural motifs. The remaining bilayer part of the system not under the island preserves the layered ZnO structure. In the Ag(111) surface some minor rumpling of the Ag atoms in also observed, whereby the Ag atoms coinciding O positions of the film move slightly upwards towards the ZnO film.

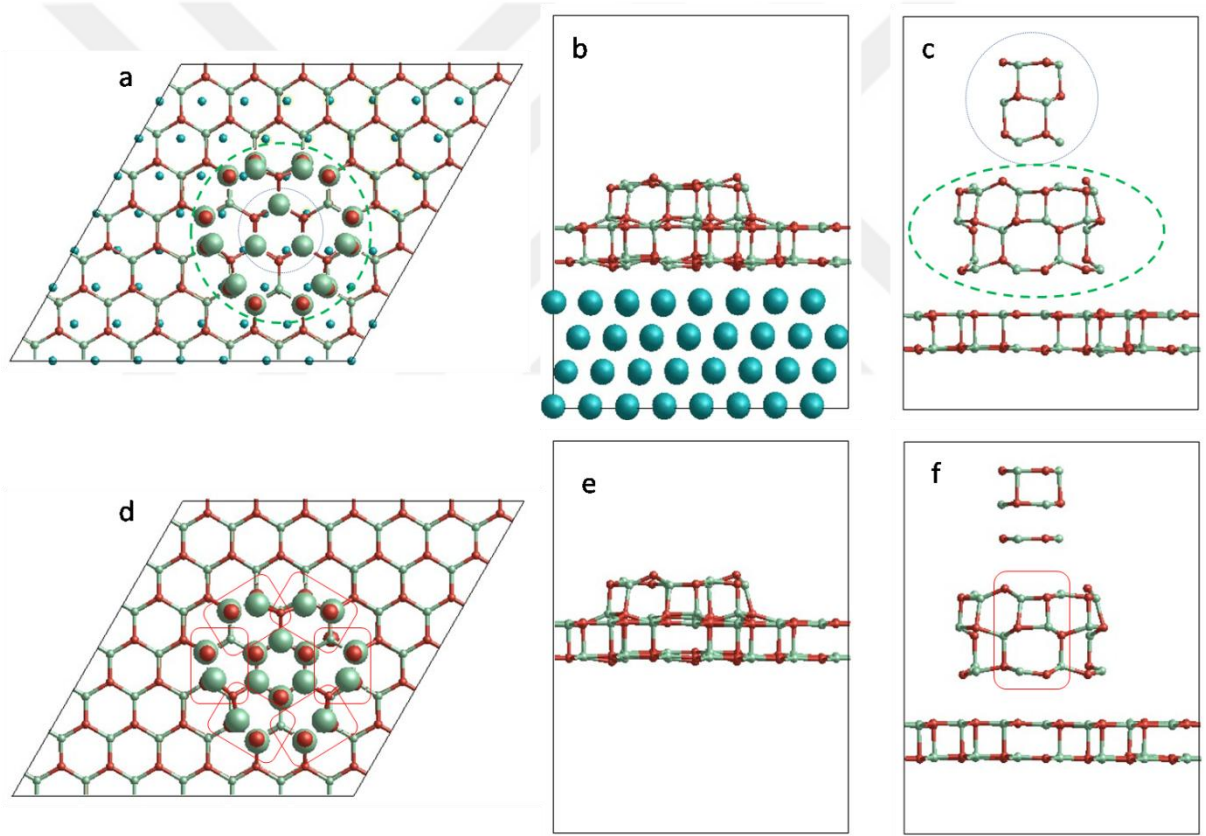


Figure 92. Optimized structures of both supported (a,b,c) and unsupported (d,e,f) 2.2 ML ZnO. Bigger balls are used to differentiate where the interlayer separations occur in top view figures (a and d). In c and f, cylindrical parts shown in a are separated from each other in side views. Red rectangular indicate the encircling BCT reconstructions which are not commensurate with each other.

If we compare the Ag(111)-supported 2.2 ML model with its free standing counterpart, the WZ phase does not form in the island, and the core of the island system remains in

the layered phase. However, the BCT motifs are still found at the corners of the adlayer island, which is more compressed than in the Ag-supported case. Wen et al²⁴³ studied theoretically free space nanostructures formed from 2 to 6 ML stackings of the hexagonal ZnO unit with the same size and stoichiometry as that which we employ as an adlayer island in our 2.2 ML model,. According to their results, the layered phase is more stable for 2 and 3 layered nanoclusters while the WZ phase becomes more stable for 4 and more layers. This result is also in line with our free standing 2.2 ML model, where the WZ-structured central hexagonal core found in the Ag(111)-supported case relaxes to the layered phase if unsupported. The emergence of the WZ phase is also affected by the addition of a hexagonal Zn_3O_3 unit added as a 4th layer in our 2.3 ML model on Ag(111). In this case, while first two layers under the core of the island have the WZ structure, the other two layers belonging to the incomplete adlayers converge to the layered phase. The BCT motifs form on the three edges of the hexagonal island and in the corresponding part of the first two layers immediately below the island. While the layered and WZ phases have trigonal symmetry the BCT structure does not and thus these three separate BCT-structured regions cannot extend and join each other to make an extended BCT phase commensurate with the WZ phase, the layered phase or even the Ag(111) surface. The overall mix of BCT and WZ structures in the the 2.2 ML and 2.3 ML models is also very similar to the structure of a hypothetical predicted ZnO polymorph which we named T1 in ref ²⁴⁴ (see also Figure 93). The only difference with respect to the pure T1 polymorph in the Ag-supported 2.2 ML case is that the core hexagon part displays a WZ structure, whereas T1 has a layered structure. With the addition of a 4th sublayer, as in the Ag-supported 2.3 ML model, the inner core becomes more of a mixture of WZ and layered structures and thus closer to the T1 structure. We note that the free standing 2.2 ML film displays the T1 structure exactly, as seen in Figure 93.

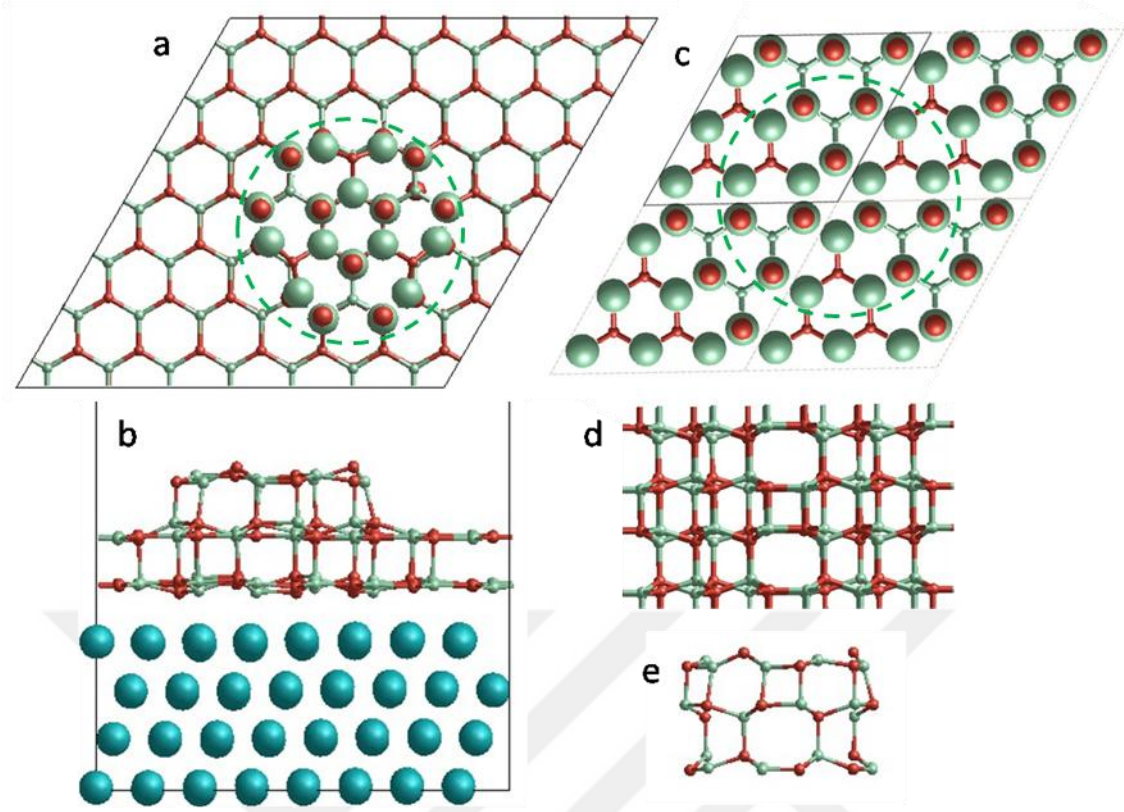


Figure 93. Comparison of 2.2 ML island with the T1-ZnO cut: a) Top view of unsupported 2.2 ML ZnO, b) side view of supported 2.2 ML ZnO, c) top view of T1-ZnO, d) side view of T1-ZnO, and e) cylindrical cut of the islands perimeter.

When we consider the 2.76 ML-A and 2.76 ML-B models, we observe similar structural reconstructions within and below the adlayer island as found in the 2.2 and 2.3 ML models. The inner core of the triangular island forms a WZ structure which is surrounded by edges having the BCT structure and corners with the T1 structure, as shown in Figure 94. The remaining part of the film around the island preserves the layered phase for the 2.76 ML-A model, while some local small interlayer distortions are observed in the 2.76 ML-B model. If we compare both models with their unsupported counterparts, the difference is found again only in the inner core of the island, where the WZ phase is more distorted and is mixed with the layered phase. The outer edge BCT reconstructions and corner reconstructions to the T1 structure are also observed in the islands the in free standing films. The same reconstructions are also observed for one size smaller island (2.65 ML) calculated without presence of the support, implying that the reconstructions are general of this type of island and hold for both adlayer islands having a Zn excess or a O excess.

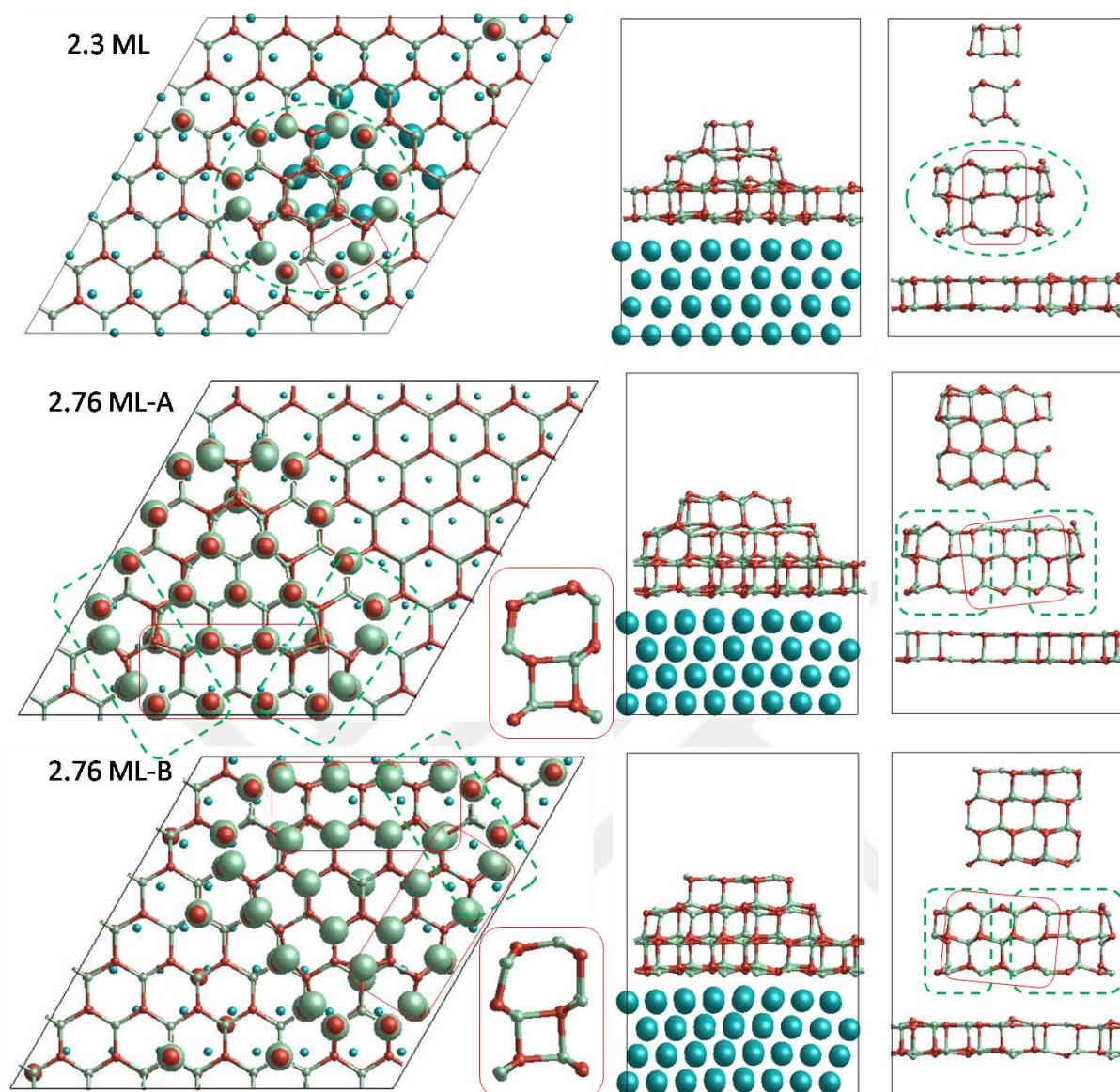


Figure 94. Top and side view structures of 2.3 ML, 2.76 ML-A and 2.76 ML-B models. Red circles indicate BCT reconstructions while green circles indicate T1 reconstructions.

Energetically, in the unsupported films, models having adlayer islands with a O excess case were found slightly more stable than the Zn excess case by 0.003 eV/ZnO. The 2.76 ML-A model film is also found to be energetically more preferred than the 2.76 ML-B model by 0.005 eV/ZnO. This result tends to support the fact that the islands with excess O in the first adlayer are more stable than those with excess Zn. Considering that the observed BCT and T1 reconstructions are not affected with the presence of the Ag surface, we constructed a 2.70 ML unsupported ZnO film model with fully triangular adlayer islands, instead of truncated triangular islands (Figure 95). In this case, two compensating triangles should be present in the model as it is not possible to

compensate excess atoms in the islands with a second smaller adlayer. We note that we have also added a small stoichiometric Zn_3O_3 hexagonal unit on top of the triangular islands in this model in order to obtain the experimental 2.7 ML coverage and be more structurally compatible with the observed films, where a small amount of the 4th ML is observed to start before the 3rd ML is complete (see above).

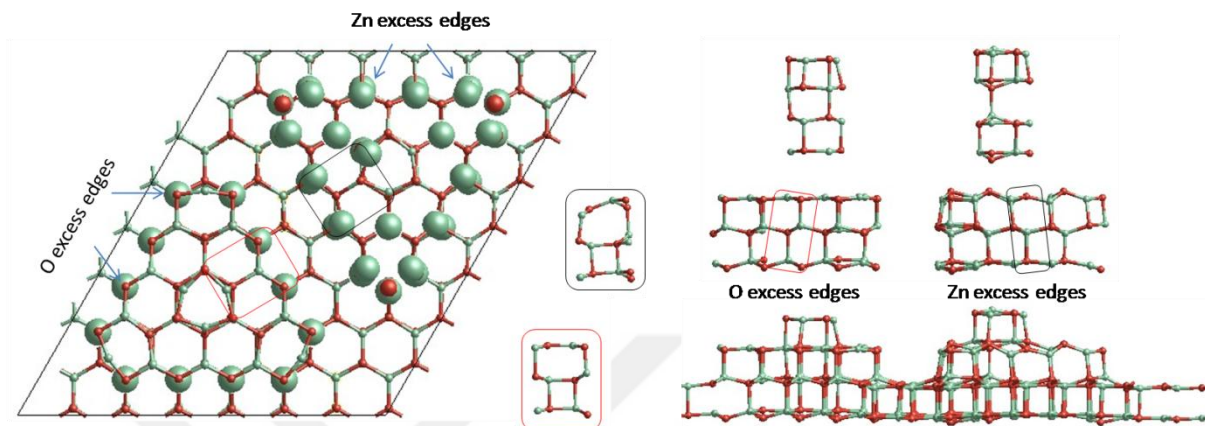


Figure 95. Top and side view structures of 2.70 ML free standing model. Black circle indicates the BCT reconstructed edge on Zn-excess island while Red circles indicates the BCT reconstructed edge on O-excess island.

In 2.70 ML case, the above-mentioned T1 reconstructions are not observed at the corners of the triangular islands and the edge BCT reconstructions are relatively more distorted and constrained to a smaller area, as shown in Figure 95. The considered 2.70 ML model was found to be approximately 0.04 eV/ZnO lower in energy than the other considered models formed mainly by truncated triangles. Table 9 summarizes the edge and corner proportions of these free standing ZnO films and their relative energies. These data imply that models with full triangles seem less favourable than the truncated ones, probably due to the higher percentage of corner atoms in the former.

Table 9 Relative energies (eV/ZnO) of considered free standing ZnO models and their corresponding corner and edge atom percentages.

coverage	Relative energy (eV/ZnO)	% corner atom	% edge atom	# of ZnO unit
2 ML	0.00	0.0	0.0	98
2.2 ML	0.03	0.0	5.5	110
2.3 ML	0.06	2.7	8.0	113
2.76 ML (A)	0.06	3.3	6.7	135
2.76 ML (B)	0.06	3.3	6.7	135
2.65 ML (A)	0.08	4.6	7.7	97
2.65 ML (B)	0.08	4.6	7.7	97
2.70 ML	0.12	9.9	4.0	151

As the smallest coverage considered in detail in experiment was a 2.7 ML ZnO film supported on Ag(111) we compare our calculated results with this case. We find that our Ag(111)-supported 2.3 ML, and in particular, our 2.76 ML-A model, agree reasonably well in terms of all observed structural parameters (see Table 10). Assumption of a WZ structure yields a poor match with nearly all experimental structural data. Although a pure layered phase model matches the observed interlayer spacing between layer 1 and 2 (d_{Zn-Zn}) reasonably well, it fails to match the measured intralayer Zn-O z-coordinate separation values (u) and interlayer Zn-O distances (d'_{Zn-O}) even for the first two layers in the 2.7 ML experimental film. Our Ag(111)-supported 2.3 ML and 2.76 ML-A island-containing models, however, improve the match with experiment with respect to intralayer z-coordinate Zn-O separation values, while maintaining (or even slightly improving) the reasonable agreement of the layered phase for the observed 1-2 interlayer spacing. The z-coordinate separation values (u) our relatively small models tend to be generally lower those found in experiment. We note that several sizes of islands occur in experimental growth, and with island size increase the contribution of the WZ phase in the centre of island will increase which, in turn, is expected to result in an increase in the intralayer Zn-O separation values (u). This tendency, seen for example in going from our 2.3 ML model to the 2.76 ML-A model, would tend to improve the agreement with experiment for larger models.

Table 10. Comparison of structural data for calculated model systems with experimental results¹²⁵ in terms of interlayer Zn-Zn distances (d_{Zn-Zn}), interlayer Zn-O (d'_{Zn-O}) distances and intralayer z-coordinate Zn-O spacings (u).

	d_{Zn-Zn} (Å)			u (Å)				d'_{Zn-O} (Å)	
Layer:	1-2	2-3	3-4	1	2	3	4	1-2	2-3
2.7ML (exp)	2.36	2.50	2.50	0.20	0.26	0.28	0.57	2.10	2.22
2.2ML	2.44	2.36	x	0.10	0.08	0.16	x	2.08	2.28
2.3ML	2.44	2.44	2.60	0.12	0.09	0.14	0.08	2.08	2.19
2.76M-A	2.50	2.52	2.62	0.08	0.09	0.18	0.44	2.06	2.21
2.76ML-B	2.51	2.52	2.75	0.09	0.09	0.03	0.19	2.12	2.19
BCT-4L	2.62	2.71	2.62	0.10	0.01	0.01	0.10	2.08	2.11
WZ(bulk)	2.65	2.65	2.65	0.64	0.64	0.64	0.64	2.01	2.01
T1-4L	2.48	2.48	2.48	0.07	0.01	0.01	0.07	2.14	2.23
layered	2.30	2.38	2.30	0.05	0.02	0.02	0.05	2.33	2.37

Table 11 summarizes the calculated ZnO film-to-Ag substrate binding energies of the considered models and the relative energies of the corresponding free standing ZnO systems. According to Table 11, the binding energy with the Ag surface for 2ML ZnO is relatively less than the island models. This result is in line with the relatively high stability of the complete free standing bilayer structure. On the contrary the relatively unstable single ZnO sheet having the highest energy as free standing layer, binds most strongly with the Ag substrate. The addition of a 3rd layer in the case of the 2.2 ML model increases the binding energy very slightly, while being relatively destabilized as a free space system, which implies that Ag surface can interact with the partially covered films with reconstructed islands slightly more strongly than for a complete bilayer. However the addition of a 4th adlayer on top of 2.2 ML as in the case in 2.3 ML case leads to a slight decrease in the binding energy relative to the 2 and 2.2 ML models. This decrease is probably due to the 4th layer being relatively far from the Ag surface, and the fact that the addition of a small amount of the 4th layer does not cause such extensive reconstructions as in the case of 2.2 ML coverage. As the 3rd adlayer island size increases as, for example in the cases of the 2.76 ML models, although the internal ZnO structure is not energetically stabilized with respect to the lower coverage films, the binding energy slightly increases. We note that 2.76 ML-A model was found to be slightly (0.003 eV/ZnO) more stable than 2.76 ML-B model, where the main difference is that in the 2.76 ML-A model the edge atoms of the 3rd adlayer island are O instead of Zn.

Table 11. Energetic comparison of ZnO-Ag models.

coverage	ZnO-Ag binding energy (eV/ZnO)	Relative energies of free standing ZnO films (eV/ZnO)
1ML	0.17	0.21
2ML	0.08	0.00
2.2ML	0.08	0.03
2.3ML	0.07	0.06
2.76ML-A	0.09	0.06
2.76ML-B	0.09	0.06

In Figure 89, it can be seen that several sizes of triangular and/or truncated triangular islands are likely to form in a ZnO deposition ranging from 1 to 10 nm in size. Our

models of 2.3 ML and 2.76 ML coverage on the Ag(111) surface give island sizes of 1.0 and 1.7 nm, respectively. Considering that our 2.65 ML and 2.76 ML models have different sized truncated triangular islands and exhibit the same edge and corner reconstructions, we believe that such reconstructions will be common for triangular types of island of larger sizes. The inner part of the island is likely to be formed by a mix of trigonally symmetric WZ and layered phases. We also suggest that truncated corners of islands will generally follow an atomic ordering based on the T1 structure and the edges to follow the BCT structure. We also note that BCT reconstructions have also been observed experimentally by He et al.¹²⁷ in ZnO (10 $\bar{1}$ 0) surfaces. The T1 reconstruction gives the corner atoms, which are initially connected only to two atoms in the same layer, the possibility to also connect to the bottom layer. For the edges, similarly, the reconstructions of all two connected atoms with the layer below the island result in the BCT structured regions. Based on the above we suggest a general island structure as illustrated in Figure 96.

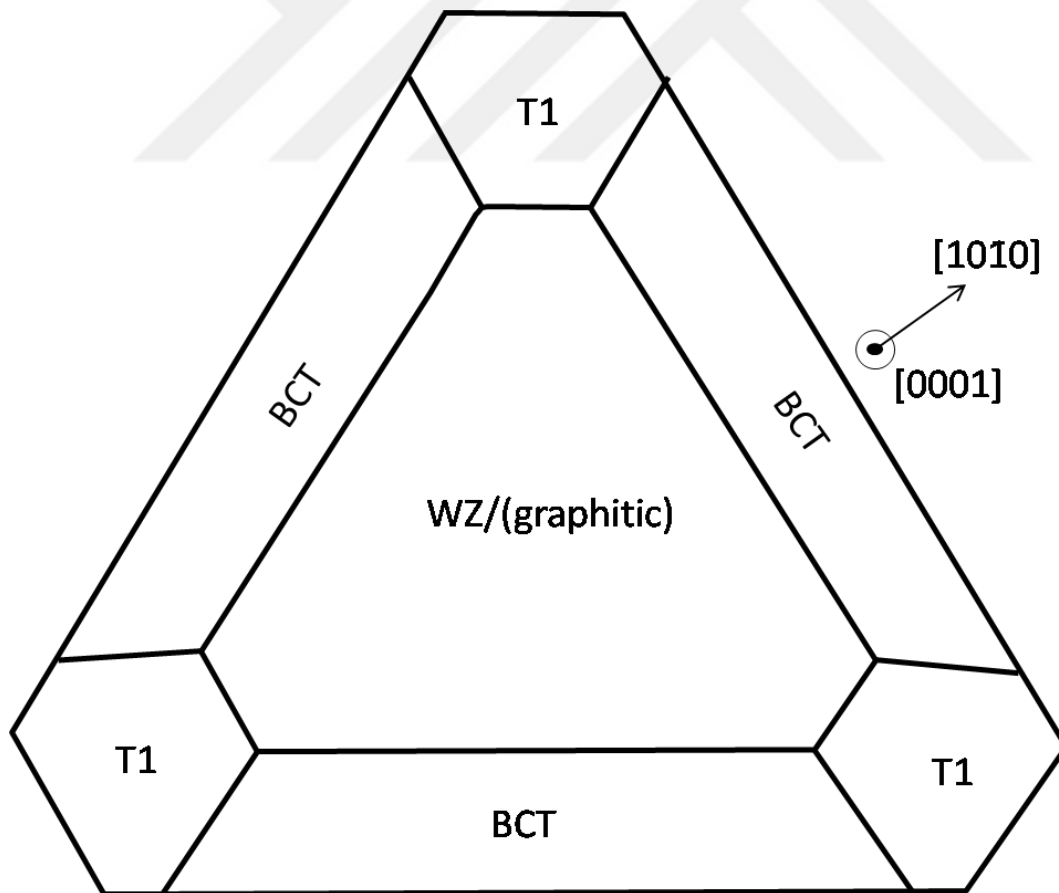


Figure 96. Illustrative model for a truncated triangular ZnO island.

According to our models and the experimental results¹²⁵ the ZnO growth lies somewhere between FM and the SK growth modes. Although first two layers are said to exhibit only the layered ZnO phase, the influence of adlayers seem to induce structural changes in the layers underneath, namely first two complete MLs.

4. Conclusions

Following the experimental reports, and in particular measurements of a 2.7 ML Ag-supported ZnO film, we have theoretically creating models with 2 to 2.7 ML coverage by creating islands on a 3rd (and 4th) adlayer on top of a complete 2ML bilayer. The triangular adlayer islands are found to cause a structural transition to the WZ structure in the island core and in local region in the two layers immediately below the island core. The islands are also found to have BCT structured reconstructions on their edges and T1 structured reconstructions on their corners. These models are found to better match the experimental structural data for the 2.7 ML film with respect to models assuming a purely layered or a purely WZ structure.



CHAPTER VI: Comparison of 3D-2D polymorphism of ZnO**1. Introduction**

Size reduction of inorganic materials to the nanoscale often induces alternative atomic ordering, or polymorphism, relative to the most stable bulk crystal.²⁴⁵ Nanoscale thin films are attractive well-defined systems to study this effect for theory and experiment. The (nano)technologically²⁴⁶ important wide band gap wurtzite (wz) semiconductor ZnO, for example, exhibits polymorphism in [0001]-oriented nanofilms on Ag(111)²⁴⁷ and Pd(111).²⁴⁸ For 3 monolayer (ML) thickness, these supported nanofilms have [0001]-stacked graphite like flat hexagonal layers with the stacking order of hexagonal BN. This layered form of ZnO (layered-ZnO) was first predicted to be more stable than wz-ZnO in density functional (DF) calculations for free-standing nanofilms ≤ 9 MLs.²⁴⁹ The structure of layered-ZnO appears to be driven by the elimination of the energetic cost of the electric dipole due to ionic ordering in the stacking direction in nonreconstructed [0001]-oriented wz-ZnO films. Recent theoretical work has highlighted epitaxial strain as a possible means to stabilize supported layered-ZnO nanofilms for >9 MLs.²⁵⁰ Other DF studies of unsupported nanofilms have showed that the BCT-ZnO²⁵¹ structure is more stable than layered-ZnO and nonreconstructed wz-ZnO for [0001]-stacked nanofilms for 4–18 MLs.¹²⁴ The lack of (0001) basal plane trigonal symmetry in BCT-ZnO, however, is incompatible with epitaxial growth on (111) surfaces of fcc metals²⁵⁰ and other substrates would be required.²⁵² Although BCT-ZnO is not a likely competing phase in experiments where layered-ZnO has thus far been observed, its relevance as a structural modification is highlighted by its observation at reconstructed ZnO (10 $\bar{1}$ 0) surfaces¹²⁷ and, as a predicted phase in strained wz-ZnO nanorods.¹⁶² Considerably expanding the handful of previously considered nanofilm polymorphs, we report over 20 ZnO polymorphs in both nanofilm and bulk form providing us with an unprecedented overview of the (nano)structural and energetic possibilities of this important material. We show that (i) the stability range of nanofilms and their energetic ordering are radically different than that of bulk polymorphs, (ii) there exist at least three nanofilm structures with trigonal basal plane symmetry compatible epitaxial growth on fcc metal (111) surfaces that are more stable than layered-ZnO, (iii) BCT-ZnO is one of many structurally related and near

energetically degenerate polytypic phases, (iv) with increasing thickness atomically reconstructed wz-ZnO becomes more stable than BCT-ZnO for ~ 14 MLs, and is always more stable than nonreconstructed wz-ZnO, and (v) BCT-ZnO and layered-ZnO nanofilms are unstable to novel polymorphs under in-plane strain.

2. Methodology

For all nanofilm and bulk structures, all unit cell parameters were optimized with all atoms optimized (forces < 0.01 eV/Å⁻¹) with periodic DF calculations employing the PW91 functional,²²¹ using the VASP code.²²² The projector augmented wave approach^{176,192} was used to describe the effect of core electrons on valence states, with the latter represented by a plane wave basis with a 500 eV cutoff. Nanofilms were separated by over 10 Å in the c-stacking direction to avoid spurious periodic interactions. Reciprocal space k -point sampling was achieved through appropriate Monkhorst-Pack grids.²³⁴ All nanofilms have between 32 and 128 atoms per cell, with supercell tests (up to 3×3) showing that all energies were converged to < 0.0005 eV/ZnO. We generate 24 polymorphic structures using a bottom-up methodology based on nets first used to enumerate and classify bulk silicates having structures based on perpendicular linkages between two-dimensional hexagonal sheets.⁸⁵ Following the connectivity of the ten such nets in Ref. 85 with Zn-O bonding, we could generate nine distinct relaxed bulk ZnO polymorphs (including layered-ZnO, wz-ZnO, and BCT-ZnO). Such polymorphs have been predicted to be relatively stable bulk phases for wurzite materials²⁵³ and silicon.¹⁶⁶ For our remaining 15 polymorphs, we created new nets based on mixing together the “primary” nets which generated the nine stabilized polymorphs. New mixed nets were biased to those containing primary nets which previously generated more stable polymorphs. Using this method to search for stable nanofilm polymorphs has specific considerations: (i) a net which generates one bulk polymorph can often generate two [0001]-oriented nanofilms depending on the bulk cut, (ii) energetically detrimental polar surfaces can be avoided by consideration of the connectivity of the generating net.

3. Results and Discussion

We first focus on 4 ML ZnO nanofilms, where experiments have not yet discerned a definite preferred atomic structure. Although nonreconstructed wz-ZnO is structurally unstable at this thickness (spontaneously converting into layered-ZnO) all other polymorphs either preserved their structure or converged to structures other than layered-ZnO. Unlike unreconstructed wz-ZnO, all other considered polymorphs have no dipole in the [0001] stacking direction. In a fully ionic picture the dipole in wz-ZnO can be quenched by atomically reconstructing the polar surfaces such that 25% of the charge on both terminating surfaces is compensated.¹¹⁰ Structural relaxation and/or internal charge transfer may also assist dipole reduction¹²⁰ as in DF calculations of nonreconstructed wz-ZnO nanofilms.^{249, 254} Attempting to stabilize the wz-ZnO structure in 4 ML nanofilms, we transferred 25% of the Zn (O) ions from the (0001)-Zn(O) surface to the (0001)-O(Zn) surface, both as separated ions, and following experimental reconstruction patterns for bulk surfaces.^{119,121} In all cases atomically reconstructed wz-ZnO 4 ML nanofilms were found to be > 0.08 eV/ZnO less stable than other 4 ML nanofilms considered.

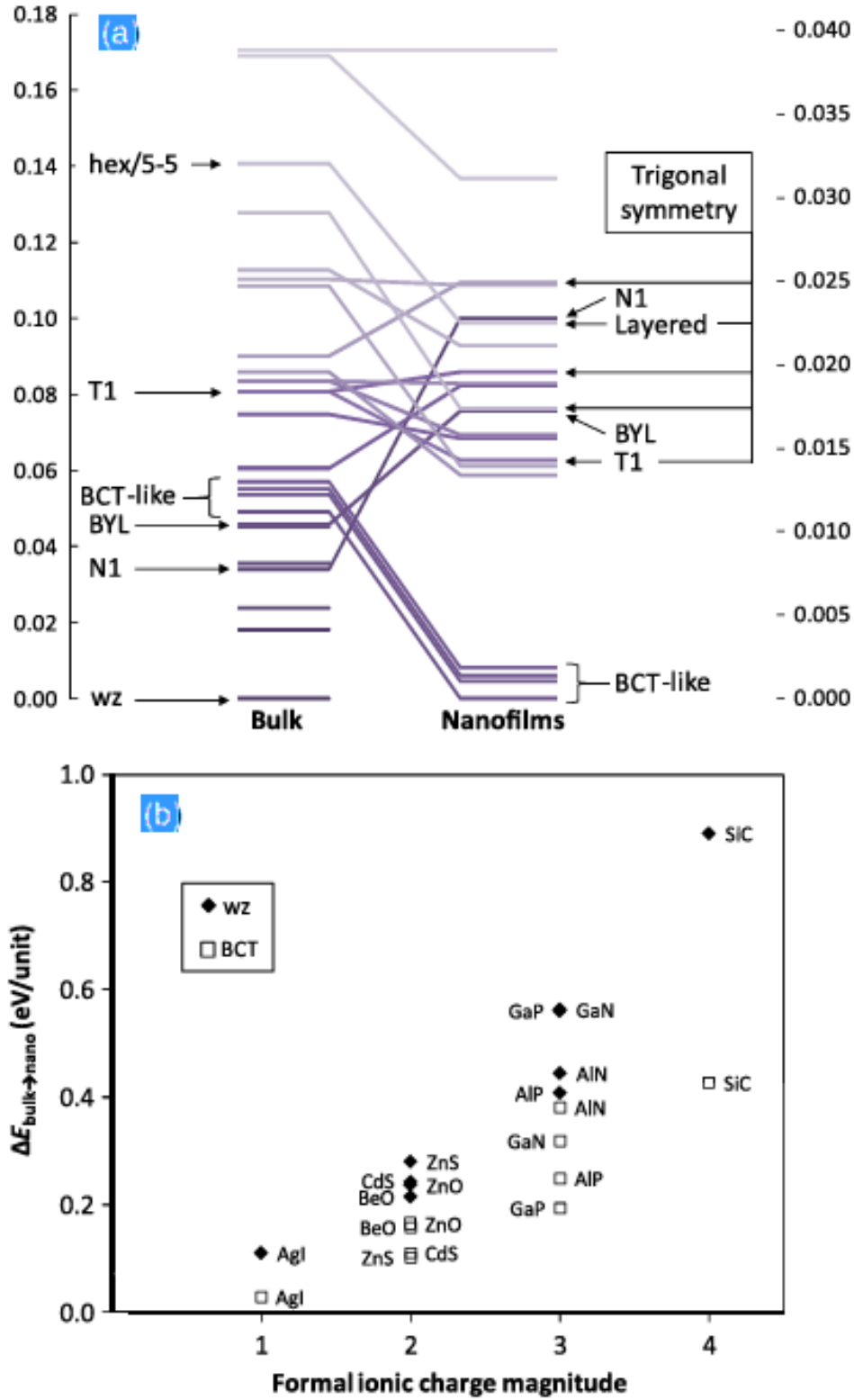


Figure 97. (a) Comparison of relative energies (eV/ZnO) of ZnO polymorphs as bulk and 4 ML nanofilms. Right and left energy y axes relate to bulk and nanofilm energies, respectively. (b) $\Delta E_{\text{bulk} \rightarrow \text{nano}}$ (eV/unit) for wz and BCT for ten wurtzite materials.

In Figure 97 (a) we compare the energetic stabilities of 4 ML nanofilms and the corresponding bulk phase for a wide range of polymorphic structures, relative to the most stable nanofilm or bulk phase, respectively. For any single polymorph the nanofilm stability is typically lower than in the bulk by ~ 0.1 eV/ZnO. We highlight two important general features: (i) the energy scale spanned by 4 ML nanofilms (0.04 eV/ZnO) is over four times smaller than that of the corresponding bulk structures (0.17 eV/ZnO), (ii) a significant stability reordering of corresponding structures occurs between 4 ML nanofilms and the bulk. The former suggests that interchanges between different polymorphs should be easier in nanofilms than in the bulk. On the ZnO(0001) surface, competition between nearly energetically degenerate reconstructed structures is found to be strongly dependent on temperature and the oxygen environment.²⁵⁵ Our stoichiometric 0K structures provide a good starting point to explore such effects in nanofilms. The latter feature implied by Fig. 1(a) is that thin nanofilms are more likely to exhibit non-wz-ZnO phases. The most dramatic bulk-to-nanofilm energetic reordering occurs in the wz-to-BCT stability crossover. Using these two polymorphs as indicators of bulk and nanofilm stability, respectively, we can predict whether the energetic reordering in ZnO is general to other materials. The wz-to-BCT stability crossover can be quantified via the bulk-to-4ML-nanofilm destabilisation energy difference ($\Delta E_{\text{bulk} \rightarrow \text{nano}}$, i.e., $E_{\text{nanofilm}} - E_{\text{bulk}}$, in eV/ZnO), being considerably lower for BCT-ZnO than for wz-ZnO. In Fig. 1(b) we plot the $\Delta E_{\text{bulk} \rightarrow \text{nano}}$ for BCT and wz for ten materials showing that BCT is always less destabilized than wz such that a bulk-to-nanofilm stability crossover always occurs. The extent of the crossover is material specific, with $\Delta E_{\text{bulk} \rightarrow \text{nano}}$ linearly increasing relative to a material's formal ionic charge [with $\Delta E_{\text{bulk} \rightarrow \text{nano}}(\text{wz}) > \Delta E_{\text{bulk} \rightarrow \text{nano}}(\text{BCT})$ for all materials]. This strongly indicates that our findings for ZnO are applicable to many other materials. In the remainder we explore various physical implications suggested by the unique overview provided by Fig. 1(a).

Consistent with previous studies the most energetically stable 4 ML nanofilm has the BCT-ZnO structure. Within a very small energy range above BCT-ZnO for both bulk phases (0.01 eV/ZnO) and nanofilms (0.0025 eV/ZnO), we find three other structures. We call these structures BCT-like as they can be regarded as polytypes (i.e., different stacking sequences of structurally similar infinite two-dimensional layers²⁵⁶) with the

constituent layers being parallel to the c axis. Polytypism also occurs in the stacking of the $a - b$ aligned hexagonal layers with wurtzite (aligned stacking) and zinc blende (antialigned stacking) being the end members. For BCT-like structures, BCT is one end member with aligned layer stacking, with an antialigned layer stacked structure (which we name BCT- ω , see Fig. 2) forming the other end member. Stacking variations allow potentially infinite possibilities, each giving rise to a distinct BCT-like polytype. Although close in energy, no structural changes in BCT- ω occurred in classical NPT molecular dynamics calculations (1 atm and 300–500 K for 100 ps), using dedicated potentials²¹⁹ and the GULP code.²⁵⁷ The dynamical stability of BCT like polytypes (and c -stacked polytypes) may be due to the energetically expensive requirement of wholesale changes in bonding between all aligned layers for interconversions.

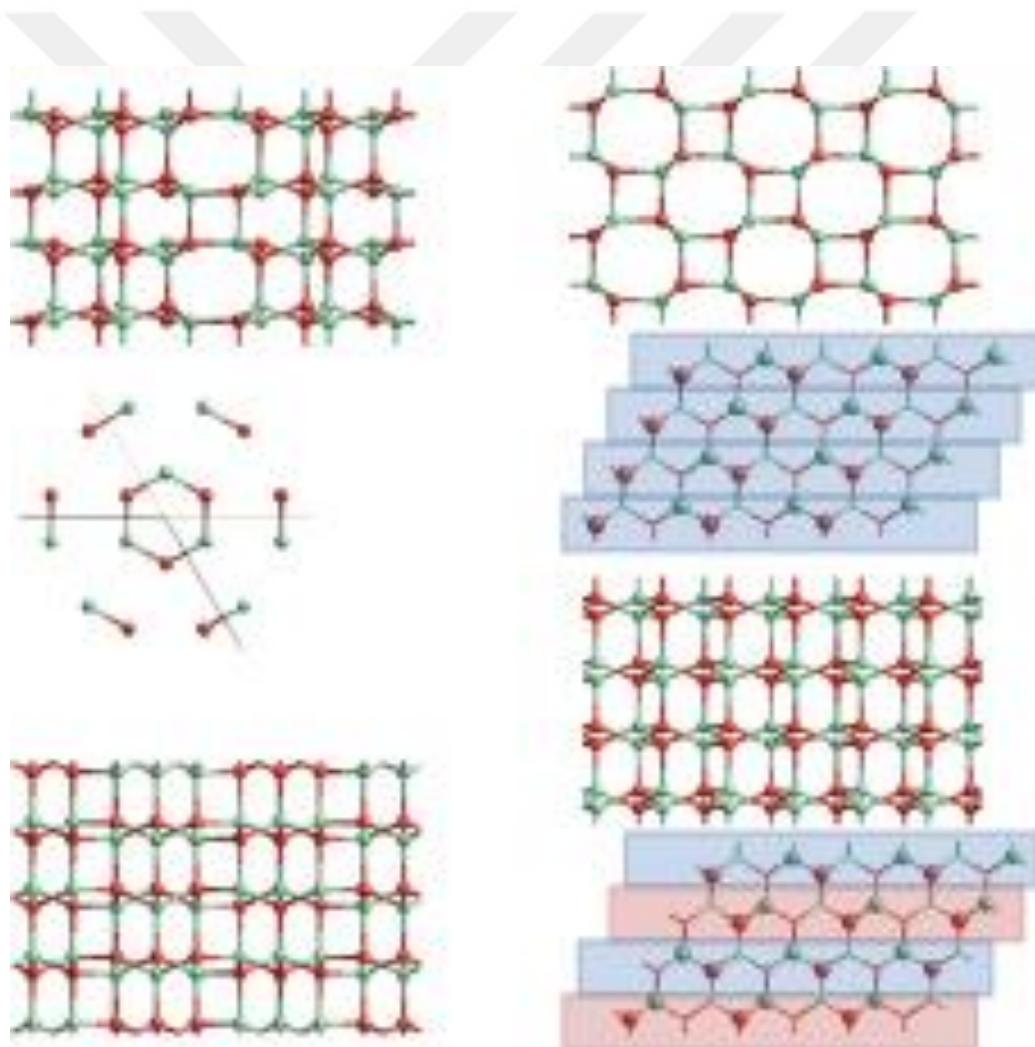


Figure 98. Selected polymorphs. Top left: T1 with its trigonal basal plane, bottom left: BYL, right: BCT (upper) and BCT- ω (lower) with respective c -aligned stacking sequences.

Although having high stabilities, due to their lack of trigonal (0001) basal plane symmetry, the BCT-like ZnO nanofilms are unlikely to explain the experimental observation that the fcc metal-supported layered-ZnO phase disappears for 3 ML.^{247,248} Unlike the observed of Zn deficiency on bulk-terminated polar (0001)-Zn surfaces,¹¹⁹ in Ref. 247, the 1:1 ZnO stoichiometry was kept fixed within all layers indicating that any dipole reduction is via another mechanism. The good structural agreement between experiment and theoretical calculations for free standing layered-ZnO nanofilms²⁴⁹ for the very thin 1–3 ML regime, indicates that metal support has a minor effect on nanofilm structure. Calculations on 1 ML layered-ZnO supported on Ag(111) (see Chapter IV) also show no indication of metal-ZnO charge transfer, confirming the rather passive role of the Ag support. The experimentally prepared 3.5 ML ZnO Ag(111)-supported nanofilm has a 55% 4 ML coverage (the third ML coverage being 5% undercomplete), and thus is formed by 50% of stoichiometric 4 ML ZnO.

Considering our set of stoichiometric nonpolar 4 ML nanofilms, we find three which have trigonal (0001) basal plane symmetry and are more energetically stable than layered-ZnO. The most stable of these (T1) is labeled in Figure 97 (see also Figure 98). In Table 12 we compare the calculated structures of T1-ZnO and layered-ZnO 4 ML nanofilms and bulk wz-ZnO with the experimental interlayer structural data for the 3.5 and 4.5 ML samples from Ref. 246. For interatomic distances between layers 1 and 2 in both 3.5 and 4.5 ML experimental samples, the best match with the calculated data is mainly for 4 ML layered-ZnO.

Table 12. Comparison of differences in calculated structural data [interlayer Zn-Zn ($d_{\text{Zn-Zn}}$) and Zn-O ($d_{\text{Zn-O}}$) distances] for layered-ZnO and T1-ZnO 4 ML nanofilms and bulk wz-ZnO with experimental data for 3.5 and 4.5 ML.²⁴⁷ Best matches are underlined.

	3.5 ML			4.5 ML		
$d_{\text{Zn-Zn}}(\text{\AA})$	Layer 1-2	Layer 2-3	Layer 3-4	Layer 1-2	Layer 2-3	Layer 3-4
Exp.	2.30	2.53	2.66	2.25	2.54	2.62
Layered	<u>0.00</u>	-0.15	-0.36	<u>0.05</u>	-0.16	-0.32
T1	0.18	<u>-0.05</u>	-0.18	0.23	<u>-0.06</u>	-0.14
wz (bulk)	0.35	0.12	<u>-0.01</u>	0.40	0.11	<u>-0.03</u>
$d'_{\text{Zn-O}}(\text{\AA})$						
Exp.	2.27	2.40		2.10	2.26	
Layered	<u>0.06</u>	<u>-0.03</u>		0.23	0.11	
T1	-0.13	-0.18		<u>0.04</u>	<u>-0.03</u>	
wz (bulk)	-0.26	-0.39		-0.09	-0.25	

Following Ref. 247 this strongly indicates that this polymorph dominates the first two MLs. For layers 3 and 4 the interatomic Zn-O and Zn-Zn distances strongly point to an alternative structure in both samples, with the calculated bulk wz-ZnO interlayer distances matching well with experiment. Although free-standing 4 ML wz-ZnO nanofilms are inherently structurally unstable, it is perhaps possible in experiment that epitaxial effects and/or charge transfer from the support may help to stabilize more bulklike 4 ML nanofilm structures. Alternatively, the experimental data may point to another polymorphic structure for the 3.5 and/or 4.5 ML nanofilms. In Table 12, the calculated interlayer data for the T1-ZnO 4 ML nanofilm shows good agreement with the experimental data for the interatomic distances between layers 2 and 3, particularly for the 4.5 ML sample. Allowing for the estimated experimental error ($\pm 0.1 \text{ \AA}$) an interpretation of the experimental data for layers 2 and 3 by layered-ZnO or wz-ZnO may also be possible. However, that there is at least one other candidate nanofilm structure that is fully compatible with the experimental interlayer data opens the possibility that such polymorphs could play a role in the observed structural instability of metal-supported ZnO for $>2 \text{ ML}$.^{247,248}

Relative nanofilm structural stability can also be influenced by thickness. A previous study showed that BCT-ZnO is more energetically stable than layered-ZnO and unreconstructed wz-ZnO from 4–18 ML.¹²⁴ From Figure 97 we can choose a structure having an energetic stability between BCT-ZnO and layered-ZnO for 4 ML, and between wz-ZnO and BCT-ZnO in the bulk phase (e.g., N1 or BYL²⁵⁸ in Figure 97). We can then predict that at some nanofilm thickness >4 ML this phase will be more energetically favored than ZnO BCT. In Figure 99(a) we plot the energetic stability of BYL-ZnO (see also Figure 98) and that of BCT-ZnO relative to nanofilm thickness. Extrapolating from the calculated data points for 8, 12, 16, and 20 ML, we predict a crossover at a thickness of approximately 26 ML at which BYL-ZnO [blue line, Figure 99(a)] will be more stable than BCT-ZnO [gray line, Figure 99(a)]. Following previous work,^{249,250,124} we also include unreconstructed wz-ZnO films (structurally stable for >9 ML only) for comparison [green line, Figure 99(a)]. We find that the BCT-to-BYL crossover occurs slightly before the thickness at which it is estimated that unreconstructed wz-ZnO becomes more stable than BCT-ZnO (~ 28 ML¹²⁴). We also consider reconstructed wz-ZnO nanofilms. Although for 4 ML we could not stabilize the wz-ZnO structure, for ≥ 8 ML nanofilms atomic reconstruction can stabilize the wz-ZnO structure. Here we employ a simple individual ion transfer approach to quench the dipole in the 8–20 ML wz-ZnO nanofilms. As expected from our attempts with 4 ML nanofilms, 8 ML free-standing atomically reconstructed wz-ZnO nanofilms are considerably less stable than most other nanofilms (e.g., BCT-ZnO or BYL-ZnO). For increasing thickness, however, the stability of such nanofilms rapidly increases such that atomically reconstructed wz-ZnO becomes the most energetically stable ZnO phase for >16 ML [red line, Figure 99(a)], well before either BYL-ZnO or unreconstructed wz-ZnO nanofilms start to energetically compete with BCT-ZnO. For all thicknesses considered, and by extrapolation, for all thicknesses ≥ 9 ML, our results imply that atomically reconstructed wz-ZnO should be always more stable than unreconstructed wz-ZnO. We note that the individual ion transfer method has been estimated to be 0.3 eV less efficient per transferred ion than more sophisticated atomic reconstructions.¹¹⁹ In Figure 99(a) a dashed line shows the estimated downward shift due to such an improved model that has the main effect of causing the crossover with BCT-ZnO to occur at >14 ML rather than >16 ML.

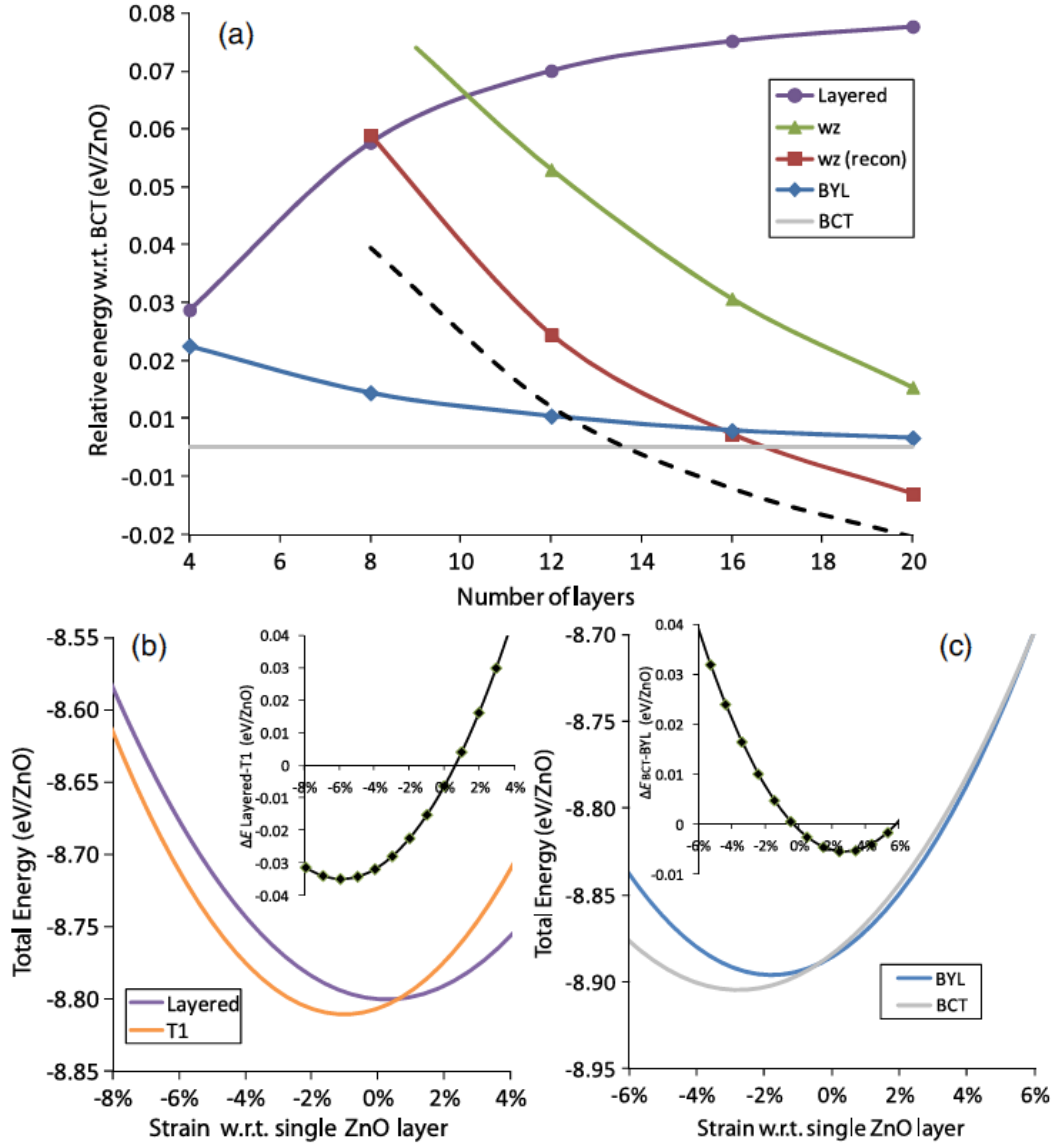


Figure 99. (a) Selected nanofilm energetic stability variation with thickness, (b) energy variation with in-plane strain for 4 ML layered-ZnO versus T1-ZnO, (c) energy variation with in-plane strain for 8 ML BCT-ZnO versus BYL-ZnO. Strains are relative to 1 ML layered-ZnO. Insets show polymorph energy differences.

Finally, we consider the effect of uniform in-plane $a - b$ strain on relative nanofilm polymorphic stability. We examine two systems: (i) T1-ZnO versus layered-ZnO in 4 ML nanofilms, and (ii) BYL-ZnO versus BCT-ZnO in 8 ML nanofilms. In the first case, as the two polymorphs are compatible with growth on metal (111) substrates, our calculations indirectly investigate the possible effect of epitaxy on nanofilm polymorphism. In a similar study in Ref. 249 only unreconstructed 4 ML wz-ZnO was used as a comparison with 4 ML layered-ZnO and thus the latter was proposed to be the

most stable nanofilm structure for all strains. In Figure 99(b) it can be seen that, although layered-ZnO is favored for larger positive strains, for small positive strains through to moderately compressive strains T1-ZnO is favored energetically. Our results imply that substrates with in-plane lattice mismatches that induce small compressive epitaxial strains could help to stabilize T1-ZnO. In the second case we investigate the role of strain in potentially altering the energetic ordering of low energy free-standing BYL-ZnO 8 ML nanofilms relative to BCT-ZnO. For 8 ML nanofilms reconstructed wz-ZnO is not energetically competitive with BCT-ZnO or BYL-ZnO but the latter two phases are close in energy. Under small positive strains we find that there is a small window of excess stability for the BYL-ZnO phase where energetic stability of the two nanofilms is inverted [see Figure 99(c)]. These results further confirm other theoretical studies which suggest that mechanical forces applied to ZnO nanosystems may be a fertile route to access new polymorphs.^{250,162}

4. Conclusions

In summary, we have developed a method to generate a wide range of new low energy nanofilm and bulk polymorphs using nets as a basis. Consideration of the energetic of these structures permits an unprecedented overview of nanoscale polymorphism in ZnO and its evolution with size and strain. Our results provide convincing evidence that low energy polymorphism in nanofilms of wurtzite materials should be very rich, and significantly beyond the handful of polymorphs previously considered in the literature. Our results strongly suggest that many new nanofilm polymorphs should be experimentally accessible, and in some cases (e.g., T1-ZnO), may have even already been observed.



CHAPTER VII: 3D polymorphism and effect of pore system (dimensionality): “Bandgap Engineering through Nanoporosity in ZnO”

1.Introduction

The tremendous success of solid-state device technologies is underpinned by our understanding of semiconductor physics and driven by our ever increasing ability to adapt and optimize the properties of such materials. This interplay between fundamental and applied approaches to materials research is well illustrated by the ongoing rapid development of the wide band gap (E_{gap}) semiconductor zinc oxide (ZnO) for a variety of applications such as ultraviolet (UV) optoelectronics, solar cells and (bio)chemical sensors.^{8,135,259,260} For the first of these, efforts have focused on E_{gap} engineering through forming pseudo binary alloys of wurtzite ZnO (wz-ZnO, $E_{\text{gap}} = 3.44 \text{ eV}$ ²⁶¹) with rocksalt MgO (rs-MgO, $E_{\text{gap}} = 7.8 \text{ eV}$) to push the wz-ZnO E_{gap} further into the UV spectral range.⁴¹ Due to metastable solid solubility constraints wz-Mg_xZn_{1-x}O alloys can give maximum ΔE_{gap} increases of $\sim 0.55 \text{ eV}$ (for $x=0.33$) before rs-MgO segregation. For sensor and solar cell applications increasing the surface area to volume ratio is paramount for enhancing device efficiency. One way to achieve this goal is to create nanoporous ZnO, as achieved by several experimental groups.^{262,263,264} In recent years *ab initio* calculations based on Density Functional theory (DFT) have greatly assisted in our fundamental understanding of ZnO. In particular, such calculations have been used to investigate both E_{gap} engineering²⁶⁵ and molecular sensing.^{266,267}

Herein, we use DFT calculations to compute the energetic stability (E_{rel}) and ΔE_{gap} shifts relative to wz-ZnO of 105 distinct ZnO polymorphs with varying degrees and types of nanoporosity. We find that nanoporosity (i.e. void volume proportion, V_{pore}) is inextricably linked with both E_{rel} and ΔE_{gap} . Generally, increasing V_{pore} tends to increase both E_{rel} and ΔE_{gap} . Within this broad pattern, however, we find significant variations in ΔE_{gap} ($\sim 0.5 \text{ eV}$) for ZnO structures which can have almost exactly the same V_{pore} or E_{rel} values but different pore system dimensionality (D_{pore}). Taking an upper limit to the range of E_{rel} as that of the experimentally prepared dense rs-ZnO polymorph¹⁷, we estimate that altering V_{pore} and/or D_{pore} of a structure could lead to tailored ΔE_{gap} shifts

up to ~ 1.5 eV. Our study strongly suggests that V_{pore} and/or D_{pore} could be employed in an effective morphological approach to E_{gap} engineering thus opening the door to optoelectronically tunable sensors, solar cells and other devices which could take advantage of this versatile combination.

2. Methodology

Following previous studies,^{159, 268} we mined databases containing 4-connected nets (4CNs)^{85, 269, 270, 271, 272} to obtain the underlying bonding topologies to produce a large range of ZnO structures. In addition to the 26 previously reported low density ZnO polymorphs,²⁷³ we include 60 new 4CN-based structures, and 19 more structures based on manually creating nanoporous [001]-directed one dimensional ($D_{\text{pore}} = 1$) linear nanopores with different shapes, diameters and patterns of inter-pore spacing in bulk wz-ZnO (wz-ZnO-NP structures). These wz-ZnO-NP structures were deliberately designed to avoid metastable internal (0001) polar surfaces. We note that none of the 4CN-based polymorphs appear to have internal polar surfaces. Other computational approaches to studying novel nanoporous ZnO materials based on using cage-like nanoclusters as building blocks have also been reported.²⁷⁴ This approach tends to give rise to structures with relatively high porosities and high metastabilities with respect to most of the structures reported herein and only a few such structures are included in our study. All structures were optimised and checked to be energy minima by phonon calculations using the GULP²⁵⁷ code with an empirical potential.²¹⁹ Subsequent DFT structure optimisations combined the gradient corrected PBE¹⁹¹ functional and a projector augmented wave¹⁹² description of atomic cores as implemented in the VASP 5.2 code.^{176, 222, 275} To minimize spurious dependency of basis-set quality on unit-cell size, all reported energies and structures correspond to two sequential optimizations of both atomic positions and cell parameters (until forces were < 0.01 eV/Å⁻¹) and a final single point calculation. Calculations used a 500 eV plane-wave cut-off, with Γ -centred Monkhorst-Pack k -point grids²³⁴ chosen so that the energy differences between polymorphs were converged to < 0.01 eV. The optimised cell parameters, fractional coordinates, energetic stabilities and PBE E_{gap} values of all 105 nanoporous ZnO polymorphs is provided in the Supporting Information. *Ab initio* molecular dynamics (using the above set-up) was used on a small representative set of structures to further

verify thermal stability. V_{pore} and D_{pore} values were obtained using the Zeo++ code.²⁷⁶ A probe size of 0.55 Å radius was chosen as the smallest size for which wz-ZnO was still reported as being nonporous (i.e. $V_{\text{pore}}=0$). Ionic radii of 0.74 Å and 1.40 Å were used for Zn and O ions respectively. The reliability of the PBE functional for predicting ΔE_{gap} shifts was tested using many body GW calculations to calculate E_{gap} for 13 selected ZnO structures with a varied range of V_{pore} and E_{rel} . The optimal GW setup was derived using a wz-ZnO unit cell for which we concluded that a manifold of virtual bands close to ten times the number of electrons in the cell was necessary to ensure convergence. This procedure was used for all other structures. The initial optimized structures and eigenvalue and eigenvector guesses were generated with a PBE pre-run. We then used the partially self-consistent GW scheme, as implemented in VASP 5.2, to update the eigenvalues up to convergence with a threshold of 0.01 eV. A plot of $E_{\text{gap}}(\text{GW})$ versus $E_{\text{gap}}(\text{PBE})$ could be fitted well with straight line ($R^2=0.93$) confirming a good linear correspondence between both data sets, see Figure 100. A similar linear systematic underestimation of $E_{\text{gap}}(\text{GW})$ data by $E_{\text{gap}}(\text{PBE})$ data has been reported for a wide range of materials.²⁷⁷ GW recalculates the eigenvalues taking into account the electron-electron screened potential, but the orbitals are still PBE orbitals. It is therefore reasonable to assume that some sort of linear trend is preserved, i.e. larger PBE gap implies larger GW gap. As the wz-ZnO $E_{\text{gap}}(\text{GW})$ value slightly underestimates the experimental E_{gap} of 3.44 eV²⁶¹ by 0.36 eV, we report $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ values (i.e. $\Delta E_{\text{gap}}(\text{PBE})$ values corrected by the linear scaling of the $E_{\text{gap}}(\text{PBE})$ data with respect to the $E_{\text{gap}}(\text{GW})$ data in Figure 100) the as estimated predictions of ΔE_{gap} values throughout.

3. Results and Discussion

We first estimate the synthetic viability of our 105 ZnO polymorphs through their calculated E_{rel} (i.e. energy relative to wz-ZnO) values by taking an upper bound of +0.3 eV/ZnO, corresponding to the E_{rel} of the experimentally synthesized rs-ZnO polymorph.^{17,159} In Figure 101a we plot E_{rel} versus V_{pore} for all ZnO polymorphs, showing that the majority (88%) of structures are within the delimited E_{rel} viability range together with a tendency for E_{rel} to increase with increasing V_{pore} . This type of relation has been reported previously for smaller calculated data sets of purely 4CN-

based materials^{159,273} and experimentally found for a variety of porous materials.²⁷⁸ Unlike the 4CN-based polymorphs, the wz-ZnO-NP structures exhibit three-coordinated atoms on their nanopore walls, but their E_{rel} values (open data points in Figure 101a) follow the same general stability pattern relative to V_{pore} . In fact, a number of wz-ZnO-NP structures in our set are found to be the most stable polymorphs relative to their V_{pore} values. Within the studied range of structures, as V_{pore} increases, the range of E_{rel} values corresponding to a given V_{pore} also tends to increase indicating that, there are more relatively stable (i.e. with respect to E_{rel} of rs-ZnO) ways to make structures with higher V_{pore} values than with smaller V_{pore} values. Of course, this increase in the range of E_{rel} with increasing V_{pore} , if it continues, implies that polymorphs with relatively large V_{pore} values (i.e. approximately $V_{\text{pore}} > 0.5$) will be metastable relative to rs-ZnO and thus few, relatively stable polymorphs will be found.²⁷⁴

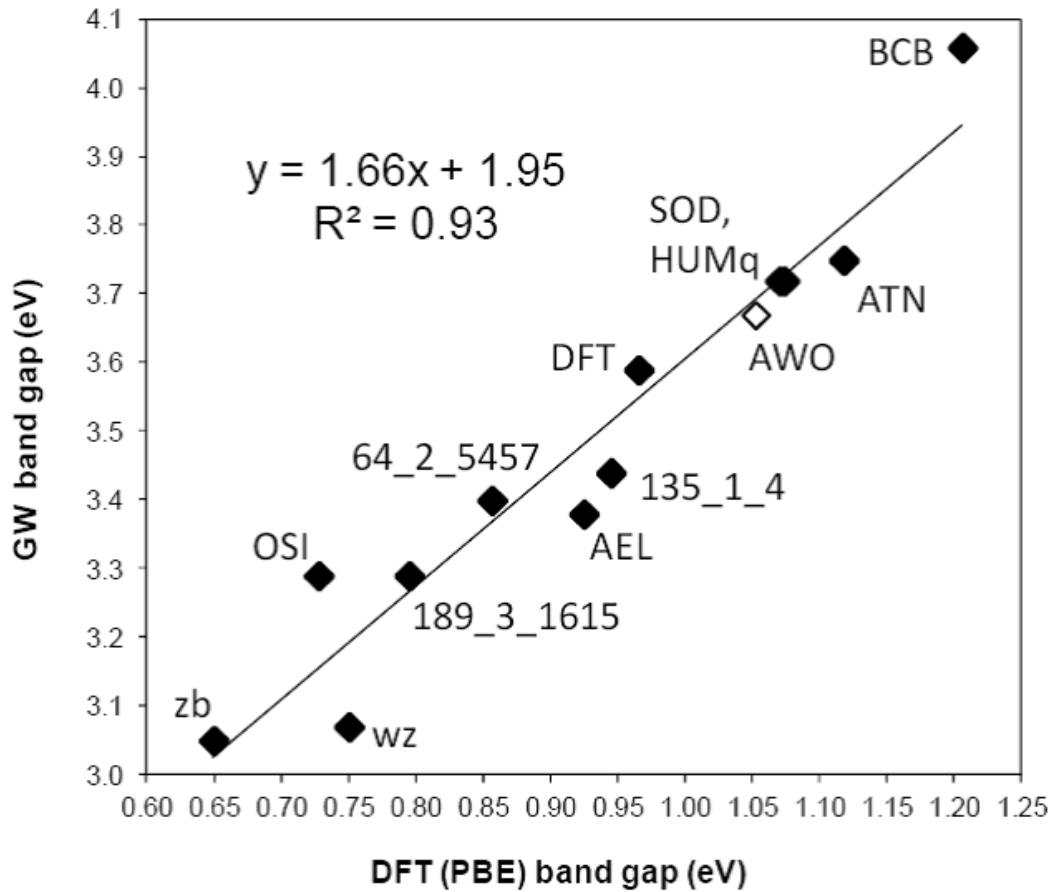


Figure 100. $E_{\text{gap}}(\text{GW})$ versus $E_{\text{gap}}(\text{PBE})$ for 13 structures showing the linear fit. The open point relates to a structure with an indirect E_{gap} . Structures and properties of the labelled polymorphs can be found in the full list also in the SI.

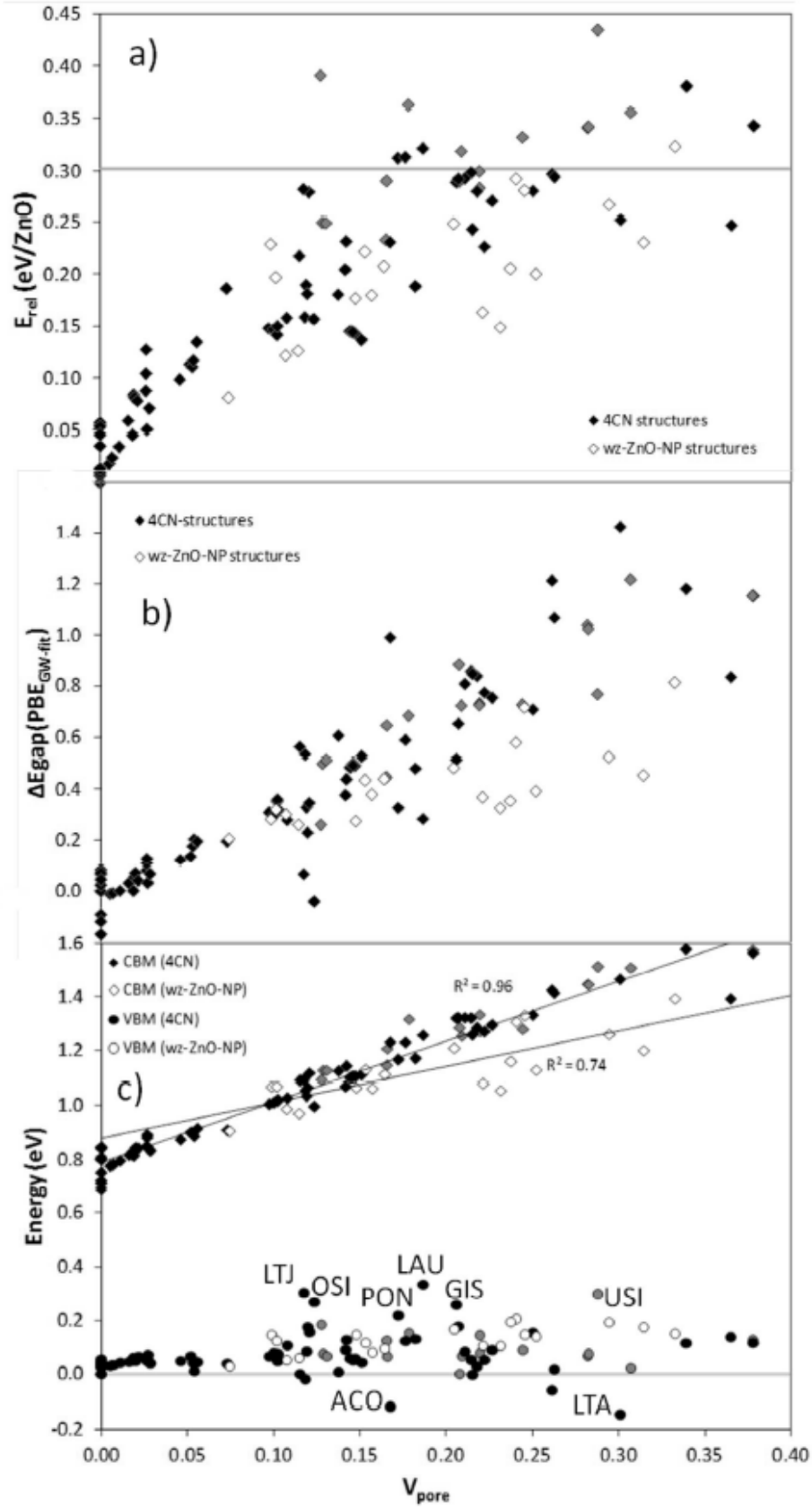


Figure 101. Variation relative to V_{pore} of: a) E_{rel} (grey line indicates E_{rel} of rs-ZnO), b) $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$, c) VBM and CBM values of all structures where some structures with outlying VBM values are labelled.

For electronic structure we find that the $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shifts also generally increase with increasing V_{pore} (see Figure 101b). Only considering polymorphs in the defined viable energy range (i.e. below the grey line in Figure 101a), nanoporosity can induce $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shifts up to ~ 1.5 eV. Although our polymorphs have relatively low densities, this is primarily due to increased void spaces in the structures and not increased average bond lengths, which would reduce E_{gap} values (see effect of strain on ΔE_{gap} in wz-ZnO in Figure 102).

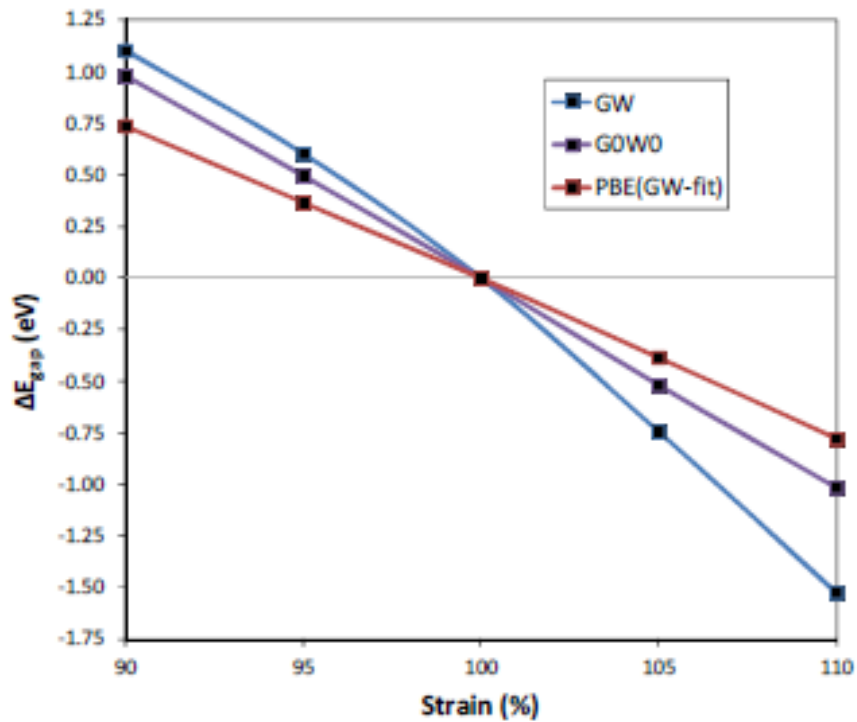


Figure 102. ΔE_{gap} versus strain for wz-ZnO calculated at various levels of theory. The linear fit to the GW data for porous non-strained structures has been applied to the DFT PBE data.

As with E_{rel} , the range of possible $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shifts for a given V_{pore} value also tends to increase with increasing V_{pore} . Although E_{rel} and ΔE_{gap} are not generally strongly correlated, we note that the minority (14%) of structures with indirect bandgaps (grey points in Figure 101 and Figure 105) have relatively higher E_{rel} values. In Figure 103 we show three selected pairs of structures where each pair has similar V_{pore} values,

but significant differences in $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$. For the pair of structures with the highest V_{pore} values, both are also found to have very similar E_{rel} values. In the case of the 19 wz-ZnO-NP structures, unlike the wide scatter observed in the E_{rel} values, their $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ values tend to lie in a narrower range (0.61 eV) and often have the smallest $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ values relative to their V_{pore} value. Although the nanoporous channels in the wz-ZnO-NP polymorphs are not large enough to exhibit extended bulk terminated surfaces, by virtue of their [001] orientation they tend to display infinite one dimensional “nano-facets” of both the stable (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces of wz-ZnO33. These surfaces, and thus the interior channel walls of the wz-ZnO-NP structures, possess 3-coordinated atoms, with associated relatively higher local structural distortions. Due to these features, the (11 $\bar{2}$ 0) surface, in particular, is predicted to induce a ΔE_{gap} shift of -0.24 eV³⁴, tending to modulate positive ΔE_{gap} shifts due to nanoporosity.

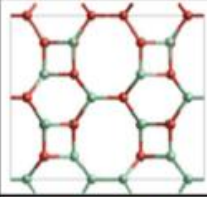
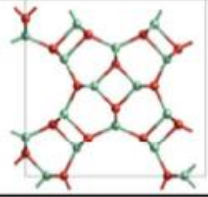
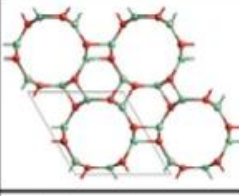
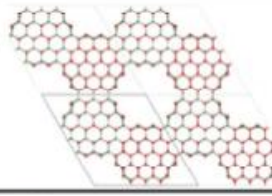
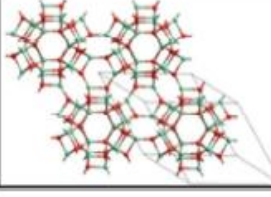
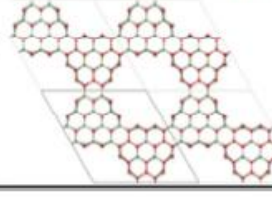
	UEI $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.51 eV E_{rel} : 0.25 eV/ZnO Pore_{max} : 0.30 nm V_{pore} : 13% D_{pore} : 3		OSI $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.04 eV E_{rel} : 0.16 eV/ZnO Pore_{max} : 0.39 nm V_{pore} : 12% D_{pore} : 1
	OFF $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.88 eV E_{rel} : 0.29 eV/ZnO Pore_{max} : 0.37 nm V_{pore} : 21% D_{pore} : 3		wz-NP-12 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.33 eV E_{rel} : 0.15 eV/ZnO Pore_{max} : 1.1 nm V_{pore} : 23% D_{pore} : 1
	LTA $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.43 eV E_{rel} : 0.25 eV/ZnO Pore_{max} : 0.64 nm V_{pore} : 30% D_{pore} : 3		wz-NP-18 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.46 eV E_{rel} : 0.23 eV/ZnO Pore_{max} : 1.1 nm V_{pore} : 31% D_{pore} : 1

Figure 103. Comparison of a range of properties for three pairs of polymorphs having similar V_{pore} values. Key: green-zinc, red-oxygen, grey line-unit cell.

For our set of polymorphs, each having the same composition with very small variance in local atomic charge (± 0.05 e according to Bader partitioned charges²⁷⁹), and the majority having 4-coordinated ions having similar local structural environments (e.g. Zn-O bonds between 1.95-2.05 Å, and average deviation of the Zn-O-Zn and O-Zn-O

bond angles relative to the tetrahedral value of 109.47° of $\leq 15^\circ$), we expect the highly localized deeply shielded core level energies to be very similar in all structures. Taking the average energy of the Zn 1s core states as a common reference value for comparing band energies, in Figure 101c we plot the valence band maximum (VBM) and the conduction band minimum (CBM) for all structures (relative to wz-ZnO) versus V_{pore} . The plot reveals a number of insights into the physical basis underlying the results in Figure 101b. First, the VBM levels for most structures lie within ± 0.2 eV that of wz-ZnO with a no strong general increasing or decreasing tendency relative to V_{pore} . Second, VBM energies which differ most relative to that of wz-ZnO tend to correspond to structures having larger local structural distortions. In Figure 101c we label a few of the points corresponding to structures with outlying VBM values. For example, structures OSI and PON have some particularly long bonds (~ 2.2 Å), structures ACO and LTA have some very short bonds (~ 1.9 Å) and all apart from OSI have highly distorted bond angles ($>17.5^\circ$ average tetrahedral deviation). These specific structural features seem to be mainly responsible for the scatter of ΔE_{gap} shifts (i.e. through VBM variability) for similar V_{pore} values. Third, the CBM shows a linear increase with increasing V_{pore} , providing further insight into the overall increase in ΔE_{gap} with increasing V_{pore} in Figure 101b. The 4CN-based polymorphs have CBM values lying in a narrow (~ 0.2 eV) increasing band of energy with respect to V_{pore} . The wz-ZnO-NP structures seem to follow a similar but slightly shallower trend, in line with their relatively smaller ΔE_{gap} shifts with increasing V_{pore} . Further, evidence supporting the generality of this phenomenon is also provided by our calculated data for other important semiconductor materials. In Figure 104 we show the VBM and CBM values for a selection of nine polymorphs of CdS and CdSe with a range of V_{pore} values. As with the case of the full set of 105 structures realised as ZnO we see the same average stability of the VBM and a clearly linearly increasing CBM with increasing V_{pore} .

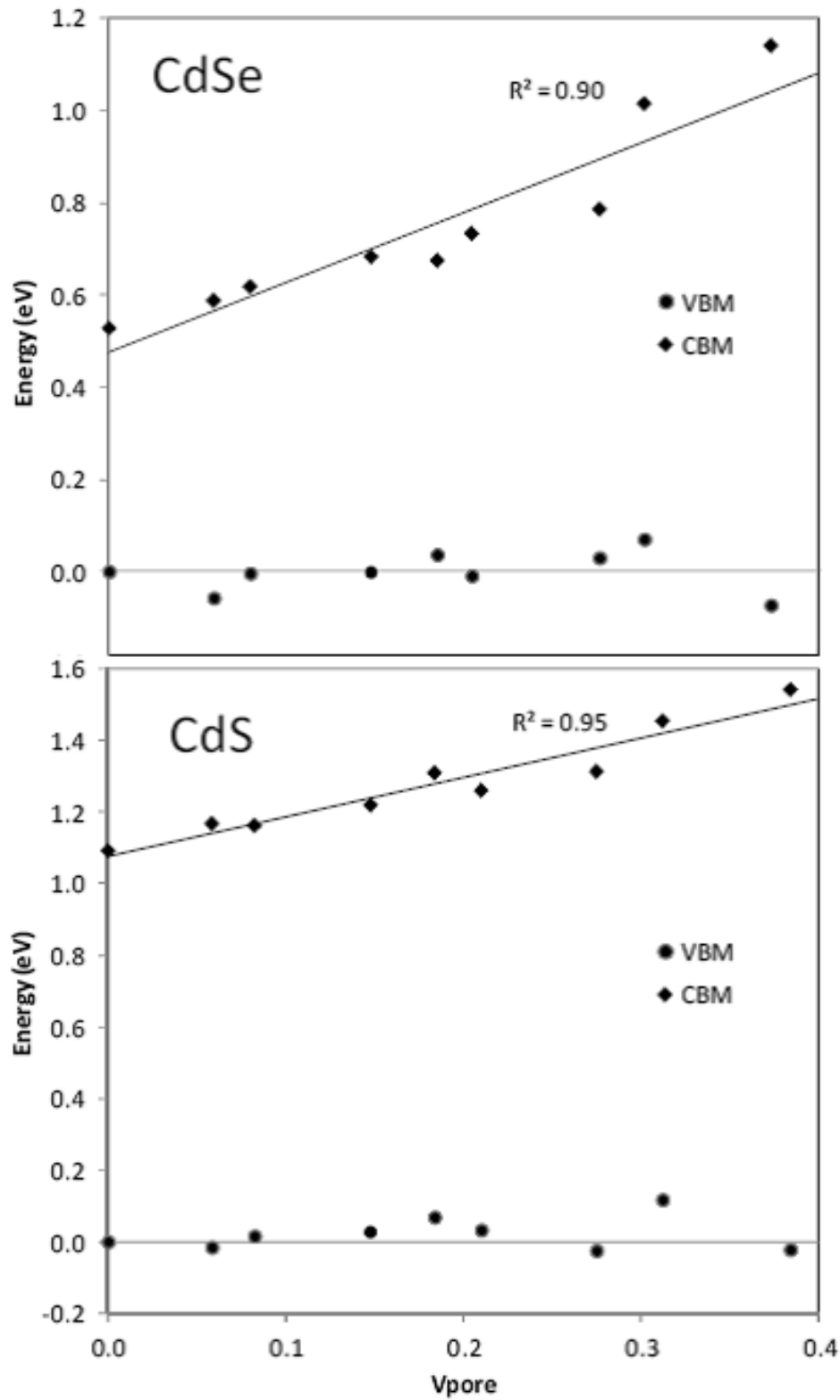


Figure 104. VBM and CBM dependence on V_{pore} for a selection of 4CN-based structures realised as CdSe (upper) and CdS (lower) polymorphs.

From an electronic band structure perspective we can see how increasing nanoporosity could produce a general trend for increasingly positive ΔE_{gap} shifts as we find in the CBM data. Starting with an infinite dense material, bands are produced through the accumulation of periodic orbital overlaps from atomic bonding in the crystal. Band dispersion results from overlap variation in such sums with respect to different crystal directions. Introducing regularly repeated void spaces in a dense crystal periodically removes atoms and thus their band-forming capacity, tending to resulting in proportionally smaller band widths. Assuming that such void formation does not introduce new mid-gap states through defects and that the remaining atomic/electronic structure of the material is relatively unperturbed, the band positions will remain fairly constant and their bandwidths will be reduced. Specifically considering this effect with respect to the VB and CB we would expect a tendency of increasing ΔE_{gap} with increasing V_{pore} . This effect will tend to be more pronounced for: (i) higher V_{pore} values, and (ii) more dispersive bands. Although the descriptive periodic-atom removal model described above does not strictly apply to the full set of nanoporous structures we consider (e.g. the atomic structures of the zeolitic polymorphs are quite distinct from wz-ZnO) we propose that the general tendency for ΔE_{gap} increase with increasing V_{pore} follows from the essential physics underlying our interpretation. To examine this link more explicitly, in Figure 105 we plot the bandwidth of the CB and VB of every nanoporous polymorph with respect to $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ (Figure 105a) and V_{pore} (Figure 105b). Clearly, the plots show a general tendency for an decrease in the bandwidth of both the CB and VB with both increasing $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ and V_{pore} strongly supporting our interpretation. In particular, we note that the CB is generally significantly more dispersive than the VB, which as suggested above, would account for the larger effect of porosity-induced dispersion reduction in the position of the CBM relative to the VBM, as we observe.

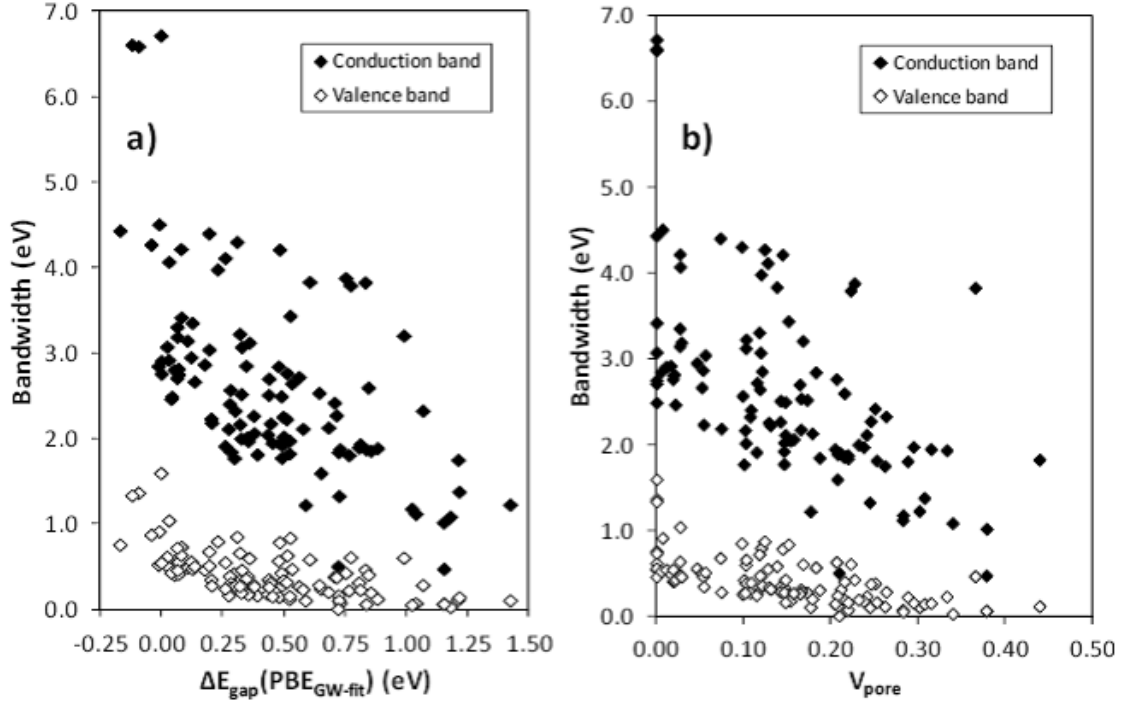


Figure 105. Plots of conduction band and valence band bandwidths versus: a) $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ and b) V_{pore} .

Considering the Γ point, where the VBM and CBM are located for 86% of all our structures, band energies are determined by in-phase orbital overlap in all directions equally. For a given V_{pore} , we would expect the most effective way to increase ΔE_{gap} would be to have internal void space which restricts overlap in most directions throughout the crystal. In this way we can imagine that ΔE_{gap} should tend to also increase with increasing D_{pore} . Conversely, low dimensional pore systems which leave directions where little or no void space is encountered, would result in less dispersion reduction. As a further test of our proposal, in Figure 106a we investigate the correlation of ΔE_{gap} with D_{pore} by binning our $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ data with respect to the D_{pore} value of each respective structure. Consistent with our suggested physical mechanism, with increasing D_{pore} from 0-3, we see a striking monotonic increase in the average and highest $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shift. For each D_{pore} value we observe a range of $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shifts which reflect specific differences in structure and V_{pore} . Following our results Figure 101b and Figure 101c, the variance in $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ for each D_{pore} value is also reasonably well correlated to V_{pore} and E_{rel} , as is shown by the incremental shading of data bars in Figure 106a. As our D_{pore} values depend somewhat

on the probe radius and ionic radii chosen in the Zeo++ code²⁷⁶ we take average data as most physically meaningful for each D_{pore} . The dependence of both the average $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shift and the average E_{rel} magnitude on D_{pore} in our wide-ranging set of structures suggests that there may be a fundamental restriction on the obtainable ΔE_{gap} and E_{rel} ranges for any particular D_{pore} , in line with the interpretation given above.

An additional factor, of importance for any practical application of nanoporosity for E_{gap} -engineering of materials, is the effect of pore size distribution on the size of the obtainable ΔE_{gap} shift for any given V_{pore} . Based on the above arguments, we may expect that many smaller pores may be a more effective way to introduce voids that are encountered in more directions throughout a crystal, and thus produce higher ΔE_{gap} shifts, than fewer large pores. In Figure 106b we plot $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ against the ratio of the largest pore diameter (Pore_{max} , as measured by a spherical probe) to V_{pore} for all structures with $V_{\text{pore}} > 0$, where we subtract the effect of only $1/V_{\text{pore}}$. The $(\text{Pore}_{\text{max}} - 1)/V_{\text{pore}}$ ratio is highest for structures with large V_{pore} values accomplished with relatively small pores and vice versa. Overall, the data confirm a sharp increase in the maximum range of obtainable $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ values for decreasing $(\text{Pore}_{\text{max}} - 1)/V_{\text{pore}}$ values. Specific to wz-ZnO-NP structures, in the inset in Figure 106b we show the $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ values of six structures with similar V_{pore} values but different pore size distributions. Four of these structures are closely grouped with $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shifts between 0.33-0.39 eV and have respective Pore_{max} values between 0.94-1.1 nm. The structure with the largest Pore_{max} value only has one pore size, but the others in this subset also have additional smaller diameter (< 0.6 nm) pores. The two remaining structures have only smaller pore sizes (Pore_{max} : 0.57 nm and 0.55 nm) and show the highest corresponding $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ shifts (0.58 eV and 0.72 eV). This confirms the importance of smaller Pore_{max} values for obtaining higher ΔE_{gap} shifts.

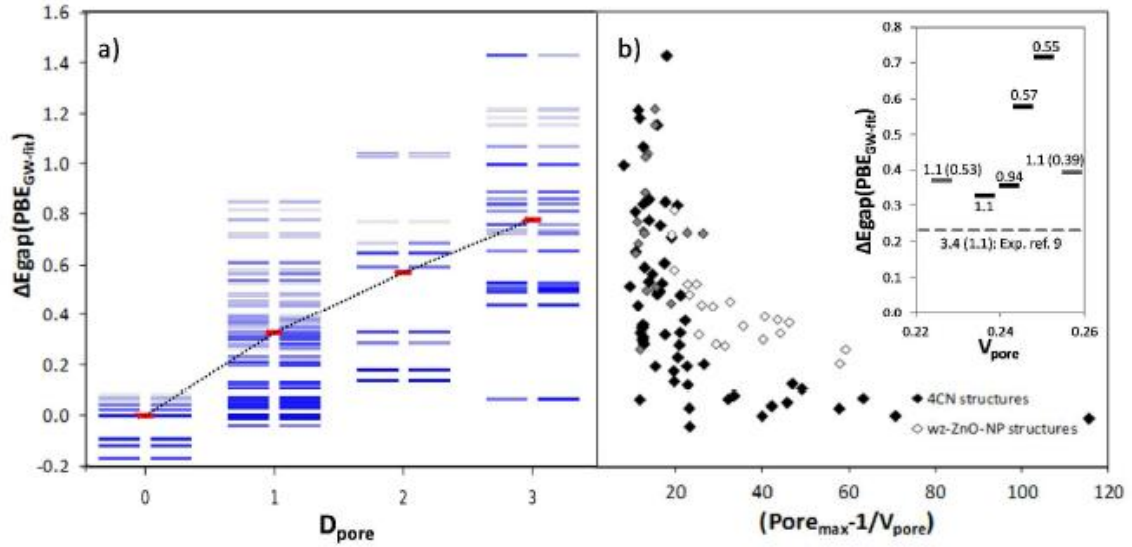


Figure 106. Dependence of $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ on: a) D_{pore} , where shaded bars show $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ values ordered by increasing magnitude (dark to light) relative to V_{pore} (right) and E_{rel} (left) for each D_{pore} (dashed line indicates average trend), b) $(\text{Pore}_{\text{max}}-1)/V_{\text{pore}}$ (inset shows ΔE_{gap} values of wz-ZnO-NP structures with similar V_{pore} values but different labelled Pore_{max} values – smaller pore sizes are in parentheses).

We have found one experimental report of a measured ΔE_{gap} shift of +0.23 eV in nanoporous ZnO.²⁶⁴ The reported sample has nanopore diameters ranging from 1 nm to 3.1-3.4 nm and intervening highly crystalline pore walls of similar or larger thicknesses. Although we do not know the V_{pore} of this sample, taking into account only Pore_{max} (i.e. 3.4 nm) we can compare it with our calculated wz-ZnO-NP data (dashed line in Figure 106b inset). Considering the many potential differences between our structures and this specific experimentally prepared sample (e.g. V_{pore} , D_{pore} , surface states, defects, impurities, etc) the order of magnitude of the ΔE_{gap} shift is very consistent with our predictions. We note that the experimentally observed ΔE_{gap} shift in ref 264 was ascribed to quantum confinement by the authors. This would entail a more symmetric opening of the E_{gap} through band position shifts w.r.t wz-ZnO, which we do not observe in for our structures. We see no fundamental reason why further experimental efforts should not be able to reduce the Pore_{max} in such wz-ZnO-NP samples to achieve greater E_{gap} control.

4. Conclusions

Nanoporosity-induced bandwidth reduction is predicted to be a general means to controllably increase the band gap in semi-conducting materials. We also note that experimental progress has also been made in the fabrication of (cosubstituted) 4CN-based nanoporous ZnO polymorphs. The ATN zeolitic ZnO framework has, for example, been synthesised with 25% Zn atoms substituted by Li and K¹⁶⁸. A theoretical study of such materials¹⁶⁹ has shown that they have significantly larger band gaps than wz-ZnO which appears to be due to their nanoporous ZnO framework and the “alloying” effect of the Li and K cations (viewing such materials as alloys of Li₂O, K₂O and ZnO). Due to the generality of the physical arguments put forward, we expect that the V_{pore} and, moreover, D_{pore} and Pore_{max} , could similarly affect E_{gap} values in a wide range of materials. The ability to use V_{pore} , D_{pore} and Pore_{max} to tailor ΔE_{gap} values potentially provides a new route to producing E_{gap} -engineered materials and devices with the added functionality of nanoporosity. We hope that our work provides inspiration for increased experimental work in this area.

Summary

Throughout this thesis, we have studied ZnO and its properties in a bottom-up manner through a dimensionality range starting from 0D nanoparticles to 3D bulk phases. For the 0D clusters and the 2D nanofilms studied we also considered the effect of a support in models designed to study ZnO thin film growth on the Ag(111) surface.

In chapter 3, we have studied ZnO nanoclusters on a Ag support and compared their properties with free space ZnO nanoclusters. In this chapter we highlighted the importance of the presence of the support during the global optimization of the clusters (i.e. as opposed to global optimization of the clusters in free space and then introducing a support). Our results show that the presence of the support strongly affects the energetic stability ranking of the nanocluster isomers. More drastically, after a certain cluster size, the support also stabilizes selectively 2D type structures, which are not stable in free space, with respect to the 3D clusters. The extra stabilization of supported 2D clusters is attributed mainly to the contact area, which is evidently greater for 2D clusters where all the atoms can interact with the surface. The importance of the contact area is also observed for 3D clusters, as ellipsoid bubbles or inflated double layer clusters being of lower energy than more spherical clusters on the support whereas the latter, more symmetric 3D clusters are more stable in free space. Matching of the cluster structure with the surface morphology was found to be another factor determining cluster stability. The Zn_3O_3 six-membered ring, which is one of the main motifs for both 3D and 2D clusters, matches best with the Ag(111) surface because it follows the same six-fold (C_6) symmetry (or its trigonal C_3 subgroup with a three-fold axis, taking into account the distinction between Zn and O atoms). However because of the lattice size differences, such matching dies away for larger ZnO clusters. The preferential stabilities of the 2D structures of ZnO clusters can be seen as the initial stages of thin film growth and is found to be in line with the experimentally observed layered ZnO sheets on the Ag(111) surface.

In Chapter 4, we have considered a full 2D-ZnO sheet on Ag(111) surface and also investigated also how H atoms interact with it. Following our results for ZnO nanoclusters on the Ag surface, we highlighted the importance of the degree of 2D-

ZnO:Ag(111) unit cell commensurability for calculating accurate sheet-on-substrate binding energies. We have found a 8:9 commensurate monolayer to be more favored with interatomic potentials and a 7:8 commensurate monolayer with DFT calculations, where the latter is found in experiment. Our calculations showed no evidence of charge transfer or covalent bonding between the Ag(111) surface and the 2D-ZnO sheet, but did show that the ZnO sheet and the Ag(111) surface exhibit small structural distortions in order to maximize their mutual interaction. Calculations of the unsupported 2D-ZnO sheet interacting with hydrogen provided strong evidence for H forming a low energy Zn 4s–H 1s multi center bonding state when passing through a Zn_3O_3 ring of the 2D-ZnO sheet, thus allowing for relatively facile H transport through the sheet.

In chapter 5, we have extended our study of supported 2D ZnO nanofilms with higher coverage models, including triangular islands on top of two full monolayers, prepared to model the experimental system. Our results showed that the triangular adlayer islands induce a transition to the WZ structure in the island core and in local region in the two layers immediately below the island core. The islands are also found to have BCT-structured reconstructions on their edges and T1-structured reconstructions on their corners. These models are found to better match the experimental structural data for the experimental 2.7 ML Ag-supported ZnO film with respect to models assuming a purely layered or a purely WZ structure.

In chapter 6, we focused on 4ML nanofilms and compared bulk and the 4 ML nanofilm polymorphism of ZnO. Our results revealed that the stability range of nanofilms and their energetic ordering are radically different than that of bulk polymorphs. We have developed a method to generate a wide range of new low energy nanofilm and bulk polymorphs using nets as a basis, and showed that there exist at least three nanofilm structures with trigonal basal plane symmetry compatible epitaxial growth on fcc metal (111) surfaces that are more stable than layered-ZnO. While confirming the previous theoretical studies predicting the BCT-ZnO phase as being the lowest energy free-standing nanofilm for small thicknesses, we obtained a range of structurally related and near energetically degenerate phases, indicating there exists BCT polytypism. With increasing thickness we found that atomically reconstructed wz-ZnO becomes more stable than BCT-ZnO for ~ 14 MLs, and is always more stable than non-reconstructed

wz-ZnO. We have also stressed the influence of strain on polymorphism by showing that BCT-ZnO and layered-ZnO nanofilms are unstable to novel polymorphs under in-plane strain. Together with the T1 structures and BCT structures which were also predicted as reconstructions on island corners in the previous chapter, our results strongly suggest that many new nanofilm polymorphs should be experimentally accessible, and in some cases, may have even already been observed.

In chapter 7, we focused on bulk polymorphism and, specifically, investigated the effect of nanoporosity. Our results showed that both energetic instability and band gap increase with nanoporosity and we predicted that nanoporosity could induce band gap increases of up to ~ 1.5 eV relative to wurtzite ZnO. We showed that the band gap increase is related with bandwidth changes in the conduction band and the valance band. We suggested that the underlying physical mechanism for this effect is that introducing nanoporosity, and thus periodic internal void space, restricts extended orbital overlaps and thus decreases bandwidths. Due to the generality of this argument, we expect that nanoporosity could similarly affect bandgap values in a wide range of materials and could be employed as a band gap engineering method.



Summary in Catalan

**Efecte de la dimensionalitat i del polimorfisme
en les propietats de l'òxid de zinc (ZnO)**

Nom del Programa de Doctorat:

QUIMICA TEORICA I COMPUTACIONAL DELS MATERIALS

Nom i cognom del doctorand:

ILKER DEMIROGLU

Nom i cognom i filiació dels directors de la Tesi:

STEFAN THOMAS BROMLEY

QUIMICA FISICA

FACULTAT DE QUIMICA

FRANCESC ILLAS RIERA

QUIMICA FISICA

FACULTAT DE QUIMICA

Resum:

Els elements metàl·lics de la taula periòdica poden donar lloc a una varietat d'òxids que tenen una gran importància en la física, la química i la ciència dels materials. Entre els varis materials inorgànics que presenten a la actualitat interès tecnològic, els òxids metàl·lics tenen un paper preponderant. Degut a l'ampli ventall d'estructures i propietats, aquests compostos tenen també un gran nombre d'aplicacions. En la química industrial una gran part dels catalitzadors són òxids metàl·lics o empen òxids metàl·lics com a suports. En geologia, una gran part dels minerals esta constituïda per òxids metàl·lics. Els òxids metàl·lics apareixen també quan es parla de moltes propietats o fenòmens en física d'estat sòlid com son el ferromagnetisme i l'antiferromagnetisme, la

ferroelectricitat d'alta temperatura, la conductivitat d'ions ràpids, i la superconductivitat d'alta temperatura crítica. La rica varietat de propietats dels òxids metàl·lics, que va des dels sistemes metàl·lics fins a la superconductivitat, és una font constant de noves perspectives per l'aplicació d'aquests materials en les indústries de l'electrònica i de l'optoelectrònica.

La possibilitat de que un compost determinat es trobi en més d'una forma cristal·lina, o fase sòlida ordenada, representa un fenomen prou conegut anomenat polimorfisme. Aquest té una importància crucial en moltes branques de la ciència i de la tecnologia ja que els polimorfs sovint presenten diferències en les seves propietats físiques i químiques. L'avanç continu en el desenvolupament de dispositius que requereixen nanomaterials de baixa dimensionalitat com les nanopartícules, els nanofil·ls i les nanocapes, que tenen dimensionalitat 0, 1, i 2, respectivament, fa que assolir un coneixement profund i més general sobre les relacions entre l'estabilitat relativa de fases cristal·lines (polimorfs) amb diferent grandària i/o dimensionalitat que competeixen en estabilitat s'hagi convertit gairebé en una necessitat. El polimorfisme que exhibeix un determinat material es molt sensible a l'escala en grandària i a la dimensionalitat. Aquest fenomen es troba particularment amplificat quan es comparen polimorfs del material tridimensional (3D o *bulk*) amb el sistema corresponent a la nanoescala i per tant de dimensions reduïdes.

El treball de recerca desenvolupat en aquesta tesi es centra en ZnO, un dels semiconductors de tipus II-VI amb un ampli ventall d'aplicacions. El ZnO és un component clau en molts processos de manufactura en pintures, cosmètics, fàrmacs, plàstics, bateries, equipament elèctric, gomes, sabons, tèxtil, recobriments de sols i molt més. Apart de la seva aplicació en moltes indústries amb el conseqüent impacte social, el desenvolupament de tecnologies de creixement de monocristalls d'alta qualitat i de capes epitaxials, ha crescut considerablement l'interès purament científic. Els estudis en aquest tipus de mostres de ZnO ben caracteritzades i ben definides son prometedors en quan el potencial per a moltes aplicacions en nanotecnologia com poden ser la spintrònica o com a font de recolliment d'energia. En aquest sentit, el ZnO es pot considerar com un material amb futur, el que explica l'interès creixent que té el ZnO en la comunitat científica (veure Figure 1)

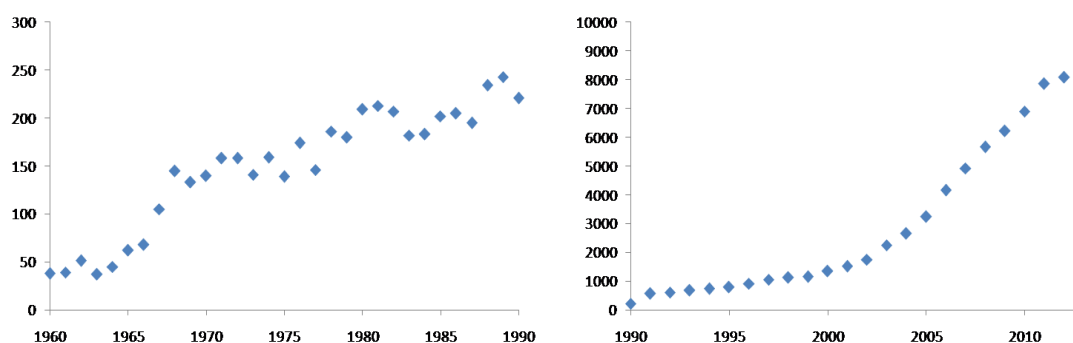


Figura 1 Nombre de vegades en les que “ZnO” apareix cada any desde 1960 fins 2013 (dades extretes de *web of science*).

En el capítol 1 es dona una introducció detallada dels conceptes més importants relacionats amb el present treball com són l'estructura cristal·logràfica, propietats semiconductores, polimorfisme i nanoescala. Tanmateix, es descriuen en detall les propietats més importants d'aquest material. Les propietats dels materials es troben íntimament lligades a la seva estructura a nivell atòmic. Totes les substàncies. Excepte l'heli, formen una o més fases sòlides si se les refreda suficientment. Així, la majoria de compostos químics exhibeixen fases sòlides, normalment, cristal·lines, on els àtoms, molècules i ions es troben empaquetats de manera regular amb un ordre a llarg abast. Si, però, hi ha només ordre a curt abast, el sòlid en qüestió es diu que és amorf (Figura 2)

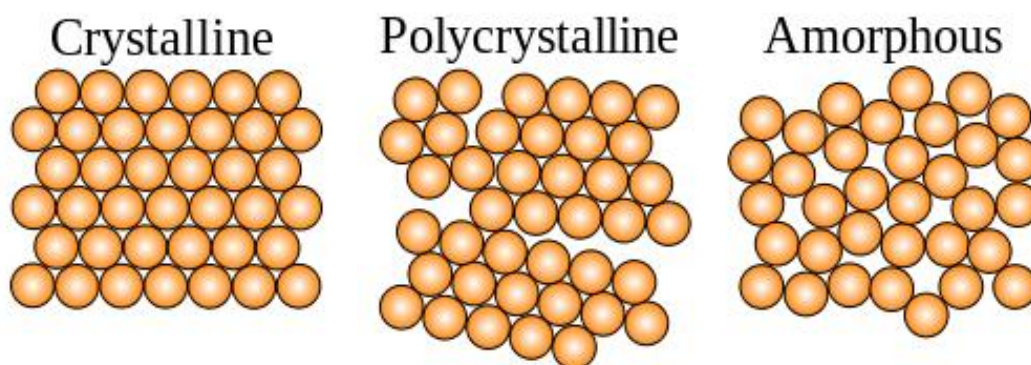


Figura 2. Exemples il·lustratius de sòlids cristal·lins i amorfs.

Per entendre les propietats d'un material cal conèixer la seva estructura a nivell atòmic. Un dels problemes més simples de descriure i alhora més difícils de resoldre en química computacional és precisament la determinació de l'estructura atòmica. L'aplicació de

qualsevol mètode computacional per estudiar un sistema químic requereix un model matemàtic a través del qual es pugui calcular l'energia del sistema en funció de la seva configuració atòmica, i.e. en funció de la posició dels àtoms que el defineixen. Òbviament, l'èxit del camí escollit dependrà de la qualitat del model matemàtic que s'empri. Per a sistemes petits, constituïts per un nombre limitat d'àtoms, és possible emprar mètodes basats en la mecànica quàntica (QM). Walther Kohn i John Ople varen guanyar el premi Noble de Química el 1988 pel desenvolupament de la teoria del funcional de la densitat (DFT) i dels mètodes computacionals de la química quàntica. Malauradament, l'aplicació dels mètodes del tipus QM, precisos i computacionalment costosos, estan limitats a sistemes que continguin com a màxim uns pocs centenars d'àtoms, si bé hi ha desenvolupaments en curs que pretenen superar aquesta barrera. D'altra banda, cal considerar també l'escala temporal. Alguns processos químics i molts processos biològics es belluguen en una escala temporal que va del microsegon al milisegon però els mètodes computacionals actuals permeten anar en petites etapes de l'ordre del femtosegon. Així, és possible que fins i tot una única simulació requereixi avaluar l'energia del sistema de l'ordre de 10^8 vegades. Un gran nombre d'avaluacions de l'energia del sistema és també necessari quan hom pretén emprar mètodes d'optimització global per explorar els espais configuracionals amb un cert detall. Clarament els mètodes de tipus QM no són adequats per aquest tipus d'estudis, els temps de càlcul serien massa llargs, inclús pels superordinadors moderns. Els models anomenats "atomístics" són adequats per estudis que requereixen un gran nombre d'avaluacions de l'energia del sistema o simulacions molt llargues. Els models atomístics empenyen camps de força en els que els àtoms, i no els electrons o els nuclis que són els ingredients necessaris quan s'empren mètodes QM, constitueixen les partícules més petites del sistema. Les equacions matemàtiques que lliguen els camps de força amb l'energia del sistema, inclouen termes relativament senzills per a descriure les interaccions físiques que determinen l'estructura i governen les propietats dinàmiques. Aquestes simplificacions són les que permeten accelerar enormement el càlcul de l'energia, de manera que se'n poden fer moltíssimes amb un cost computacional raonable. Al llarg d'aquest treball s'han emprat tant mètodes atomístics basats en camps de força clàssics com mètodes mecanoquàntics basats en la teoria del funcional de la densitat. El capítol 2 inclou una descripció prou detallada d'aquests dos tipus de tècniques computacionals.

En el capítol 3 es comencen a descriure els resultats de la recerca que s'ha duta terme i que s'inicia amb l'estudi dels sistemes amb dimensionalitat zero (0D) ja que els nanoclusters i les nanopartícules constitueixen un dels millors exemples de materials nanoestructurats que mostren propietats inusuals i que, a més, poden ser variades per ajustar-les als valors necessaris per algunes aplicacions. Encara que hi ha alguns estudis previs sobre nanoclusters de ZnO aïllats, en fase gas, és important entendre com canvien les seves propietats quan es troben suportat. Tanmateix, l'adsorció de nanoclusters de ZnO en superfícies metàl·liques constitueix una de les etapes inicial del creixement de capes de ZnO suportades en metalls pel que el seu estudi pot donar també informació important.

En aquesta part de l'estudi s'ha dut a terme una cerca sistemàtica de estructures corresponents als mínims globals per a nanoclusters $(\text{ZnO})_n$ sobre la superfície Ag(111) amb $n = 1-16, 20$ i 24 . En una primera etapa s'ha emprat el mètode anomenat "*Monte Carlo Basin Hopping*" avaluant l'energia amb potencials interatòmics (camps de força) i, posteriorment, s'han refinat els resultats emprant càlculs de tipus DFT aplicats a les estructures candidates a ser mínims globals. Aquest estudi ha predit varies estructures de baixa energies pels nanoclusters $(\text{ZnO})_n$, tant en fase gas com sobre el suport metàl·lic de plata. A través d'una comparació amb un estudi previ corresponents mínims locals de nanoclusters de ZnO s'observa que els mínims locals de mínima energia es troben ràpidament emprant el codi d'optimització KLMC. A més el codi es mostra altament eficient en l'ordre de les estructures tant en rang com en diversitat.

En les estructures $(\text{ZnO})_n$ suportes, s'observa que la presència del suport afecta l'ordre d'estabilitats dels mateixos però de manera molt més dràstica afecta selectivament les estructures bidimensionals (2D) que, a partir d'una certa grandària, en fase gas són menys estables que les tridimensionals (3D). Per tant, tenir en compte la presència del suport durant la optimització de la nanoestructura resulta crucial.

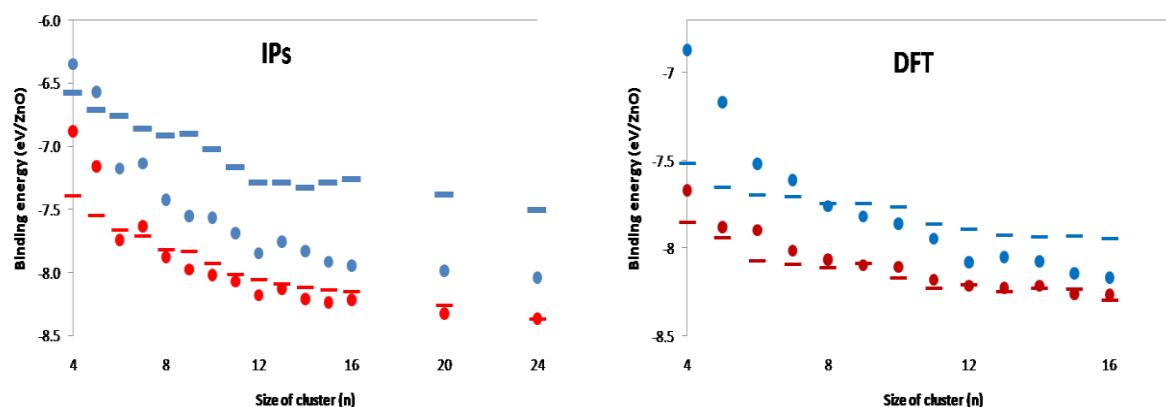


Figura 3 Energia relativaper a les estructures 2D i 3D en funció de la grandària i tant en fase gas com sobre el suport.

D'acord amb el nostres resultats, obtinguts amb els potencial interatòmics, els clústers 2D aïllats i en fase gas són menys estables que els clústers 3D, especialment quan més gran es la grandària del sistema (Figura 3). Conseqüentment, per a valors de n superiors a 8 no es trobaran estructures 2D es fase gas indicant, de nou, la gran importància del suport en la determinació de l'estructura final. La separació energètica entre les estructures 2D i 3D esdevé més petita quan l'energia s'obté de càlculs mecanoquantics DFT però apareix clarament si bé per a valors de n superiors a 12.

La figura 4 mostra les diferències energètiques dels millors clústers, 3D i 2D, suportats per a cada tamany de cluster, ambdós potencials interatòmics i el DFT. D'acord amb els potencials interatòmics, per tamany $n = 4, 5$ i 7 les estructures bidimensionals son preferides, i les majors diferencies en estabilitat son per a les de mida $n = 9, 12$ i 15 . A partir de la mida $n = 8$ els clústers 3D presenten estabilitats mes elevades, per tant, la diferència disminueix lleugerament a mida que la grandària augmenta. Els clústers bidimensionals resten en $0,1\text{eV/ZnO}$ fins els clústers considerats de mida $n = 24$ on les estructures 2D de nou tornen a ser més estables. Els resultats del DFT semblen qualitativament similars als resultats dels potencials interatòmics a partir de la mida $n=7$, mentre que les estructures tridimensionals estan més afavorides en IPs, els calculs DFT tendeixen a afavorir les estructures 2D. La figura 5 resumeix les estructures amb energia més baixa obtingudes amb DFT de per ambdós tipus de clústers, 2D i 3D.

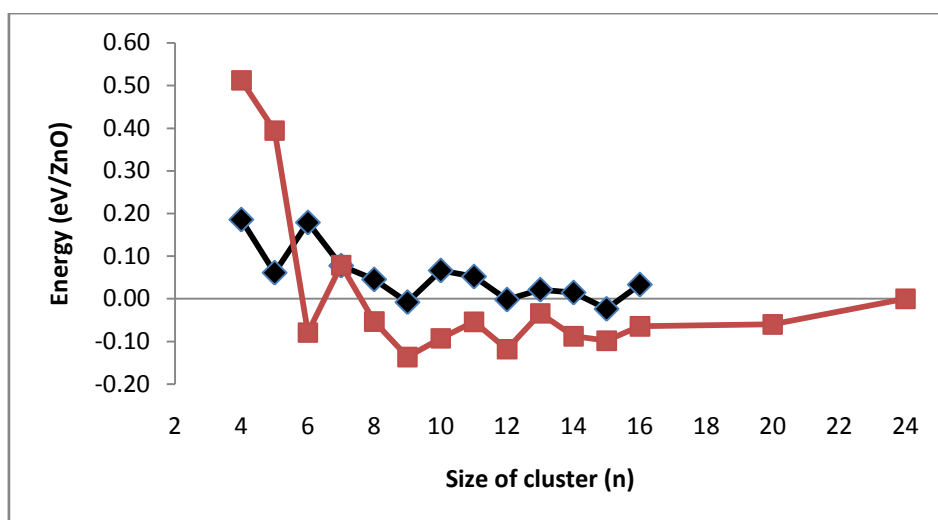


Figura 4. Diferència d'energies relatives entre clústers 2D i 3D de més baixa energia respecte la mida dels clústers.

Amb l'estabilització extra destacada, els clústers bidimensionals resten en el rang de les primeres estructures amb la energia més baixa competint amb els clústers 3D, en ambdós casos emprant potencials interatòmics i a nivell de càlcul DFT. Principalment l'estabilització extra s'atribueix principalment a l'àrea de contacte, que és evidentment més gran per clústers de dues dimensions on tots els àtoms poden interactuar amb la superfície. A més, l'àrea de contacte determina el rànquing dels clústers 3D suportats, el que resulta en que les bombolles el·lipsoïdes o bicapes inflades son suportades preferentment, mentre que clústers tridimensionals totalment simètrics són més estables en el buit. L'altre factor determinant es va trobar en l'encaix amb la morfologia de la superfície. L'anell de sis que és un dels patrons principals per tots dos tipus de clústers, 3D i 2D, encaixa millor amb la superfície Ag(111) ja que presenta la mateixa simetria radial d'ordre 6. Tanmateix, deguda la diferència de la cel·la, l'encaix no es vàlid cel·les grans. Mitjançant els potencials interatòmics, per a clústers 2D l'altre superfície plana Ag(100) s'ha trobat que és més adequada que no pas la superfície rugosa Ag(110); mentre els clústers tridimensionals poden encaixar millor en la superfície rugosa.

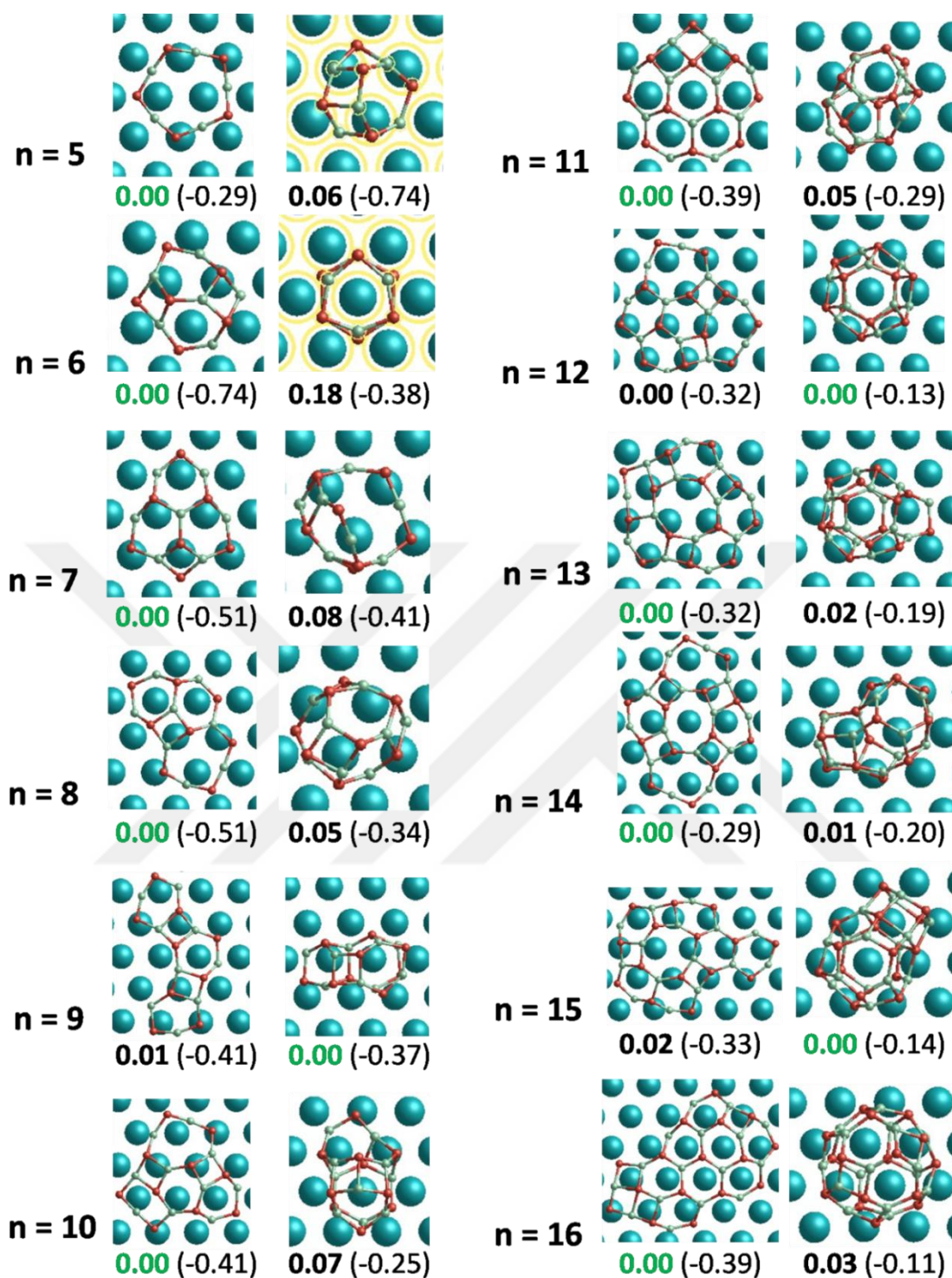


Figura 5. Estructures i energies dels nanoclusters 2D i 3D de menor energia $(\text{ZnO})_n$ suportats en $\text{Ag}(111)$. Les energies relatives estan sota les estructures i les energies d'estabilització degudes al suport es troben entre parèntesis.

Si considerem l'aproximació d'una monocapa dins d'unes condicions de contorn periòdiques, on els enllaços extra formen una estructura 2D, podem esperar el

creixement d'una monocapa completa. De fet, els nostres resultats preliminars obtinguts de l'optimització global per clústers de mides $n = 12-16$ utilitzant una cel·la unitària més petita, els quals permeten a les estructures bidimensionals sentir l'efecte de la seva imatge periòdica, mostrant que les estructures nanolaminars, que són periòdiques en una dimensió, esdevenen de més baixa energia que els clústers obtinguts amb la optimització global. Aquestes nanolàmines principalment consisteixen en anells de 4 i 6 membres. La diferència d'energia augmenta inclús en el cas del $(\text{ZnO})_{20}$, on la periodicitat es destacable en dues dimensions. Juntament amb la estabilitat relativa dels anells de 6 membres suportats, no seria sorprenent que la formació d'una monocapa uniforme de anells de sis membres fos possible a la superfície de plata ja que ambdós són proporcionals. En conclusió, les estabilitats preferents de les estructures 2D de clústers ZnO es poden veure com les etapes inicials del creixement de la capa fina i concorda amb els resultats experimentals observats de làmines grafitiques de ZnO en la superfície Ag(111).

En el capítol 4 hem continuat amb les nostres consideracions per a una sola làmina d'òxid de zinc (ZnO) basades en el mateix pla bidimensional (2D) de topologia hexagonal com el grafé, però alternant àtoms veïns de Zn o O enlloc d'àtoms de carboni. Emprant DFT i els potencials interatòmics hem investigat la força de la interacció d'un únic pla 2D-ZnO amb la superfície Ag(111) i com aquesta afecta a les propietats estructurals de la capa. Construint sobre les prediccions prèvies de l'enllaç multi-centre (MCB) assisteixen el transport d'hidrogen a través d'anells hexagonals de Zn_3O_3 en el sistema sodalita ZnO (SOD-ZnO), també hem investigat com els àtoms d'hidrogen interactuen amb una capa 2D-ZnO quan passen a través d'una apertura Zn_3O_3 .

Per al sistema més petit 1:1 2D-ZnO en Ag(111), les discrepàncies entre la cel·la unitat de la làmina de 2D-ZnO aïllada i la capa (111) de plata en la direcció A-B es troba que és entre +12 (DFT) i +14 (IP) per cent, el que ens diu que per poder acomodar la lamina 2D-ZnO en la cel·la unitat fixa de Ag(111), deu haver-hi una compressió significativa. Per aquesta raó la làmina 2D-ZnO suportada en plata per al sistema 1:1 està significativament torçada respecte l'estructura energèticament afavorida quan aquesta està lliure, on els àtoms de zinc estan orientats cap a la capa de plata i els àtoms

d'oxigen cap a fora, juntament amb això les distàncies d'enllaç Zn-O són relativament més curtes. Comparant aquest sistema combinat ZnO-Ag amb un model similar, però amb la làmina d'òxid de zinc torçada i lluny de la capa de plata (111), dona energies d'enllaç de la làmina d'entre 0.39 i 0.94 eV/ZnO, depenent del nivell de teoria emprat. No obstant això, fent servir l'energia de la cel·la unitat de la làmina 2D-ZnO completament optimitzada (és a dir, sense la restricció a-b de la capa Ag(111) de la cel·la unitat) i la cel·la unitat de la capa de plata (111) aïllada com a referències d'energies, es mostra que el sistema 1:1 és inestable respecte a la separació espontània de ZnO-Ag. Des de la optimització basada en IP sense aplicar-hi restriccions a la cel·la unitat de la làmina plana 2D-ZnO trobem que és energèticament més favorable en concordança amb la optimització completa de la làmina 2D-ZnO aïllada, en DFT sense restriccions. Diverses d'aquestes làmines planes optimitzades amb IP s'han fet servir per a calcular els valors de a_{ZnO} en exploracions IP per a una sèrie de sistemes X:Y partint des de $a_{\text{ZnO}}/a_{\text{Ag}}$ amb diferències menors que 1 i incrementant-les gradualment fins a la unitat. Trobem que, tot i que, com s'esperava, a menors diferències les energies de lligadura de els sistemes 2D-ZnO sobre Ag(111) sense restriccions són més grans, només quan la diferència és menor a un 1% l'energia de lligadura del sistema ZnO-en-Ag(111) amb restriccions es tornen molt semblants als casos amb restricció (és a dir, mostrant que el corresponent model X:Y no es exageradament restrictiu per a la relaxació dels subsistemes ZnO i Ag separats). Per els càlculs IP el millor model respecte aquest fet es va trobar el sistema 8:9 on la làmina 2D-ZnO s'estira en un 0.3%. En els càlculs DFT es va trobar que per el sistema 7:8 es requereixen compressions de la làmina 2D-ZnO de tan sols un 0.1%.

Es va estudiar també la interacció d'hidrogen atòmic amb el sistema de 2D-ZnO no suportat fent servir tant models periòdics com models de clúster a nivell DFT. En particular, ens centrem en la interacció de l'hidrogen amb un anell de Zn_3O_3 quan travessa la làmina. Es va trobar que els àtoms d'hidrogen s'uneixen d'una manera relativament feble a la part superior del Zn (0.32eV) i O (0.04eV) elevant així la possibilitat de transport a través de la làmina 2D-ZnO a altes temperatures. En apropar-se al centre d'un anell hexagonal Zn_3O_3 al llarg d'una línia perpendicular al pla de la làmina, l'àtom d'H esdevé primerament adsorbit de forma feble fins que assoleix una posició de mínima energia a una distància d'1 Å de la làmina 2D-ZnO (- 0.04 eV respecte

la làmina i l'àtom d'hidrogen per separat). Posteriorment, l'entrada a l'anell des de aquesta posició provoca un augment de l'energia relativa del sistema des de aquest mínim feble fins a un màxim de +0.11eV en el centre de l'anell de Zn_3O_3 . El cost d'energia només es degut a la distorsió estructural de la lamina de 2D-ZnO induïda per l'hidrogen i és de 1.27eV. Així, la interacció entre l'hidrogen i la làmina 2D-ZnO, on l'hidrogen es troba al centre de l'anell Zn_3O_3 ($\text{H}@\text{Zn}_3\text{O}_3$), es compensa per aquest efecte en 1.16 eV. Els càlculs per a la làmina 2D-ZnO aïllada interaccionant amb l'hidrogen proporcionen una forta evidència per a la formació d'un estat d'enllaços multi-centres de baixa energia ($\text{Zn } 4s\text{--H } 1s$) quan passa a través de l'anell de Zn_3O_3 de la làmina 2D-ZnO, permetent així de forma relativament fàcil el transport d'hidrogen a través de la làmina.

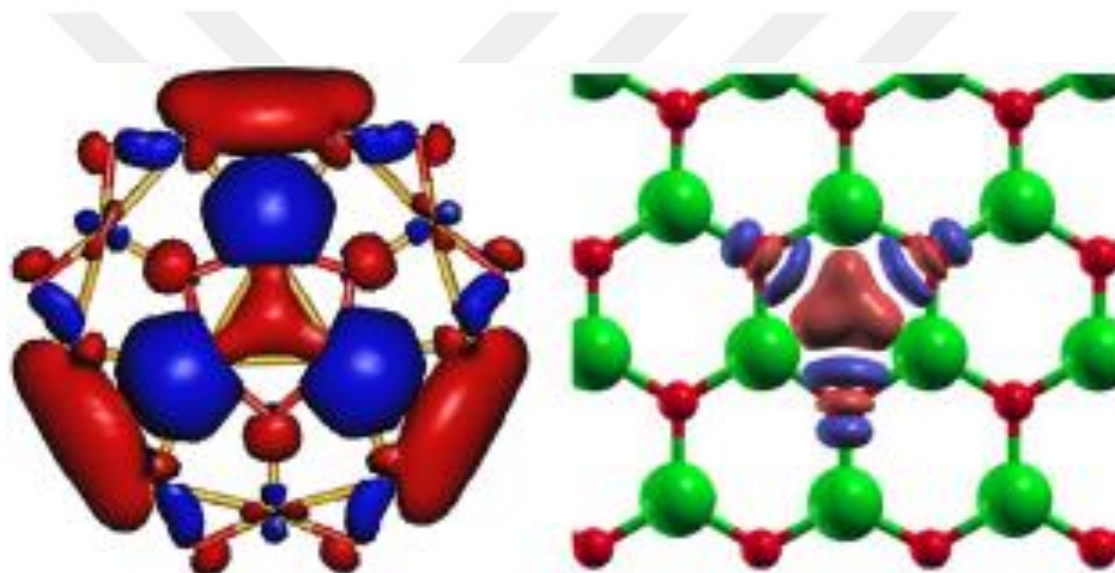


Figura 6. Orbital proposat per el $\text{Zn } 4s\text{--H } 1s$ MCB obtingut amb el model de cluster utilitzant el funcional B3LYP (dret). Increment de carrega relatiu observat al centre de l'anell i amb menor abast als oxigens (gris clar) mentre la carrega disminueix (gris fosc) als lobuls dels orbitals p dels oxigens.

Després de considerar una sola làmina de ZnO sobre la superfície d' Ag(111) i el cas específic de les propietats de transport d'H, es va passar a l'estudi de multicapes de ZnO al Capítol 5. Un cop obtinguts els informes experimentals, i en particular mesures de 2.7 ML d'una lamina de ZnO suportada sobre plata, s'ha dissenyat models teòrics entre 2 i 2.7 ML de recobriment a partir de la creació d'illes amb una tercera (i quarta) capes incompletes a la part superior d'un sistema bicapa complet de 2ML, per estudiar els

efectes de mida d'aquestes illes en l'estructura de ZnO. On computacionalment ha estat factible, s'ha inclòs explícitament la Ag (111) del substrat.

Per 2ML de ZnO sobre Ag (111), el desplaçament vertical d'una monocapa de ZnO es veu afectat per la capa de ZnO addicional, amb interaccions en la direcció de l'eix z més fortes que la interacció Ag-ZnO. També, a diferència del cas d'una monocapa, no es van trobar àtoms de Zn més propers a la superfície de plata en la pel·lícula de 2ML, mentre que les petites variacions en les separacions de capes intermèdies locals es van produir al llarg de tota la cel·la unitària per a un 13% de les connexions bicapa. Aquestes distorsions estructurals menors entre capes, no segueixen el patró d'una estructura tipus WZ o una ordenació BCT, però sembla ser que són perturbacions induïdes pel substrat a una lamina de 2ML perfecte.

A mesura que es treballava amb models d'illes de 2.2 ML, les variacions locals en la separació de les capes observades en el cas de 2ML quasi desapareixen, mentre que les separacions ordenades es troben a l'illa. A la Figura 7 es pot observar que el nucli hexagonal central de l'illa i la corresponent part dels dos primers ML sota aquest nucli convergeix per a mostrar l'estructura WZ, que a la vegada, queda rodejada de regions més petites que mostra una estructura similar al BCT. Si es compara el model de 2ML suportades sobre Ag (111) amb el seu homòleg lliure, la fase de WZ no es forma a l'illa i el nucli del sistema roman en fase de grafit. No obstant, els motius encara es troben a les cantonades de l'illa, que es més comprimit que en el cas amb plata suportada.

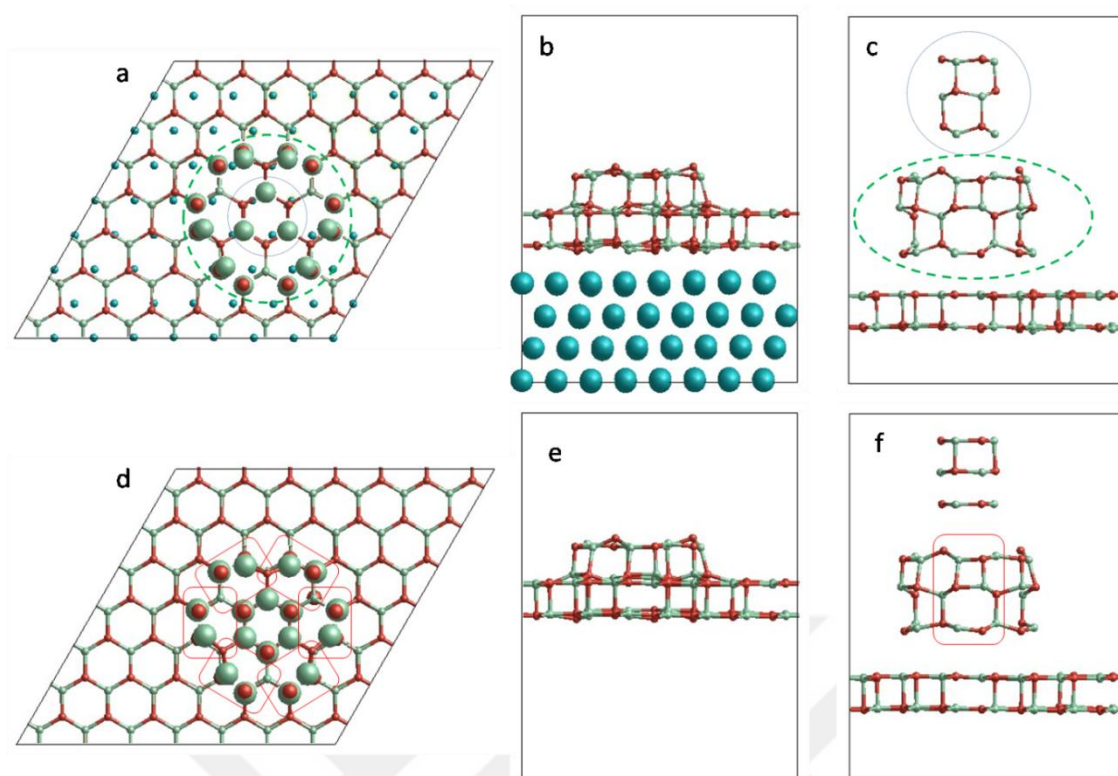


Figura 7: Estructures optimitzades de 2ML de ZnO amb suport (a,b,c) i sense suport (d,e,f). Les boles més grans s'utilitzen per a diferenciar la zona on es produeixen les separacions entre les capes en les principals figures de visualització (a i d). En c i f es mostren les parts cilíndriques separades entre sí, en vista lateral. El rectangle vermell indica les reconstruccions BCT que no estan en consonància amb la resta.

L'aparició de la fase de WZ també es veu afectada per l'addició d'una unitat hexagonal de Zn_3O_3 com a una quarta capa del nostre model 2.3 ML sobre Ag (111). En aquest cas, mentre que dues primeres capes sota el nucli de l'illa tenen estructura WZ, les altres dues capes que pertanyen a les capes adsorbides incompletes convergeixen en fase grafit. Els motius BTC es formen a les tres cantonades de l'illa hexagonal i a la part corresponent de les dues primeres capes immediatament inferiors a l'illa. Mentre que les fases de grafit i WZ tenen simetria trigonal, la fase BTC no, i per tant, aquestes tres regions BTC separades no es poden expandir i unir-se entre si, per a fer una fase BCT expandida en concordança amb la fase WZ, la fase grafit o fins i tot la superfície de plata (111). La barreja global d'estructures WZ i BCT en els models 2.2 ML i 2.3ML es també molt similar a l'estructura d'un polimorf hipotètic predit de ZnO que hem anomenat T1.

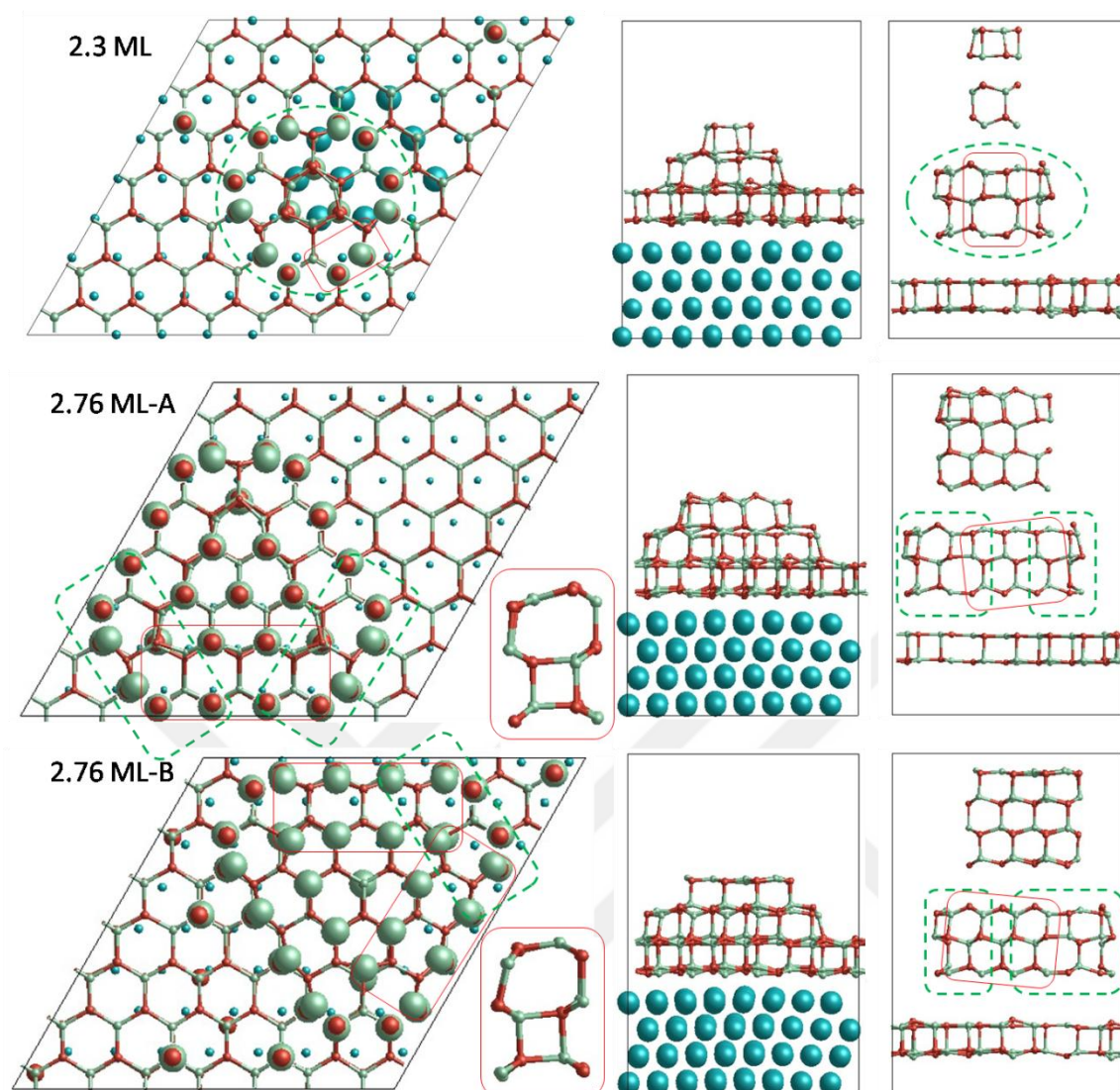


Figura 8: Vista superior i lateral de les estructures dels models 2.3ML, 2.76ML-A i 2.76ML-B. Els cercles vermells indiquen les reconstruccions BCT, mentre que els cercles verds indiquen les reconstruccions T1.

Quan canviem a models amb illes mes grans, observem reconstruccions estructurals similars a l'interior i sota l'illa formada per una nova capa incompleta com es veu als models 2.2 i 2.3. L'interior de les illes triangulars adopta estructura WZ i esta rodejada per vores amb estructures BCT i cantonades amb estructura T1, com es mostra a la Figura 8. S'ha observat que aquests models estan en un millor acord estructural amb les dades experimentals per el cas de les lamines formades per 2.7 ML que no pas respecte als models que assumeixen una estructura purament gràfica o purament WZ.

Per a les nano-lamines independents amb 2ML, totes dues estructures, WZ i BCT, es relaxen directament fins obtenir la doble capa perfectament plana de la fase laminada. Per al cas de 3 capes en el buit amb estructura WZ, succeeix la mateixa transformació espontània a una fase gràfica/laminada, mentre que la fase BCT pot conservar la seva estructura si comprimeix lleugerament. Es mes, es troba que l'estabilitat energètica de 3 capes de BCT-ZnO es gairebé la mateixa que per una lamina amb 3ML de la fase gràfica. Per el cas de lamines amb 4ML, mentre que la fase BCT esdevé en el polimorf mes estable al buit, tant mateix existeix un ampli rang de fases que competeixen energèticament, les quals tenen una energia inferior a la fase gràfica.

Al Capítol 6, hem continuat la nostra investigació comparant el polimorfisme de les nano-lamines de ZnO amb el sòlid bulk. Hem generat un ampli rang de polimorfs de ZnO basats en lamines hexagonals inspirades en l'enumeració de les seves xarxes subjacents característiques i evaluant l'estabilitat del sòlid "bulk" i les nano-lamines d'aquestes estructures mitjançant càlculs ab initio. Hem observat un ampli polimorfisme d'estructures de baixa energia en les nano-lamines amb un ordre d'estabilitat totalment diferent al del sòlid "bulk". A partir d'aquestes bases generals hem pogut tenir un millor coneixement de les transicions estructurals observades durant el creixement epitaxial i les prediccions d'estabilitat de les nano-lamines en variar-ne el gruix la pressió exercida. Inicialment ens hem centrat en les nano-lamines de 4 ML, on els experimentals no han pogut discernir una estructura atòmica preferent definida. Tant mateix el wz-ZnO no reconstruït es estructuralment inestable per aquest gruix (es converteix espontàniament en ZnO laminat) tots els altres polimorfs o be mantenen la seva estructura o convergeixen a altres estructures diferents a les del ZnO laminat. A diferència del wz-ZnO sense reconstrucció, tots els altres polimorfs considerats no presenten dipol en la direcció d'empaquetament [0001]. Les nano-lamines de WZ-ZnO amb 4 ML que presenten reconstrucció atòmica s'ha observat que son > 0.08 eV/ZnO menys estables que d'altres models de 4 ML considerats. Consistentment amb estudis previs s'ha observat que la nano-lamina amb 4 ML mes estable energèticament presenta una estructura BCT-ZnO. En un petit rang d'energies per sota el BCT-ZnO tant per la fase "bulk" (0.01 eV/ZnO) i les nano-lamines (0.0025 eV/ZnO) hem trobat 3 estructures mes, les quals presenten un caràcter politípic.

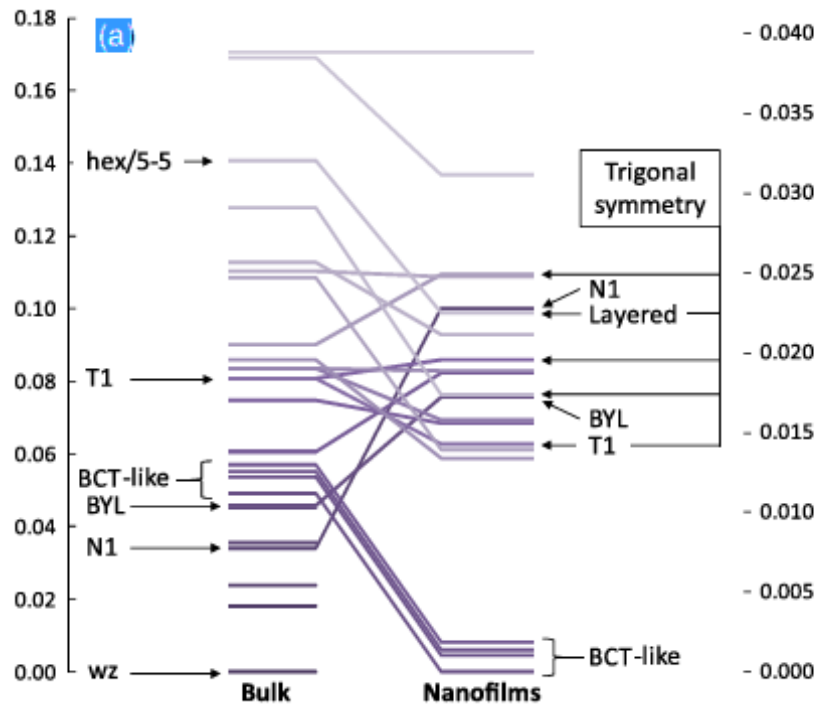


Figura 9 Comparació d'energies relatives (eV/ZnO) dels polimorfs de ZnO com a sòlid “bulk” i les nano-lamines amb 4 ML. Els eixos esquerre i dret fan referència a les energies del “bulk” i les nano-lamines, respectivament.

Per qualsevol polimorf l'estabilitat de les nano-lamines s'ha trobat típicament inferior a la del sòlid “bulk” amb diferències d'energia d'aproximadament 0.1 eV/ZnO. Hem destacat dos trets principals: (i) El rang d'energies que abasten les nano-lamines amb 4 ML (0.04 eV/ZnO) és més de 4 vegades més petit que el corresponent a les estructures del “bulk” (0.17 eV/ZnO), (ii) Te lloc un reordenament significatiu de les estructures corresponents entre les nano-lamines amb 4 ML i el sòlid “bulk”. Aquest fet suggereix que els intercanvis entre diferents polimorfs han de ser més assequibles en les nano-lamines que no pas en el sòlid bulk i això implica que les nano-lamines fines presenten major tendència a no presentar fases wz-ZnO. El reordenament energètic entre “bulk” i nano-lamines més dràstic ocorre en l'entrecreuament entre WZ a BCT. Fent us d'aquests dos polimorfs com a indicadors d'estabilitat del bulk i les nano-lamines, respectivament, hem predit que l'ordenament energètic del ZnO és general per altres materials, representant $\Delta E_{\text{bulk} \rightarrow \text{nano}}$ per a l'estructura BCT i wz per deu materials diferents. L'estructura BCT es troba sempre menys desestabilitzada que no pas l'estructura wz de tal manera que sempre succeeix una transició del “bulk” a nano-lamines. L'abast de l'entrecreuament s'ha vist que és específic per a cada material, amb

un valor de $\Delta E_{\text{bulk} \rightarrow \text{nano}}$ que creix linealment amb relació amb la càrrega iònica formal del material.

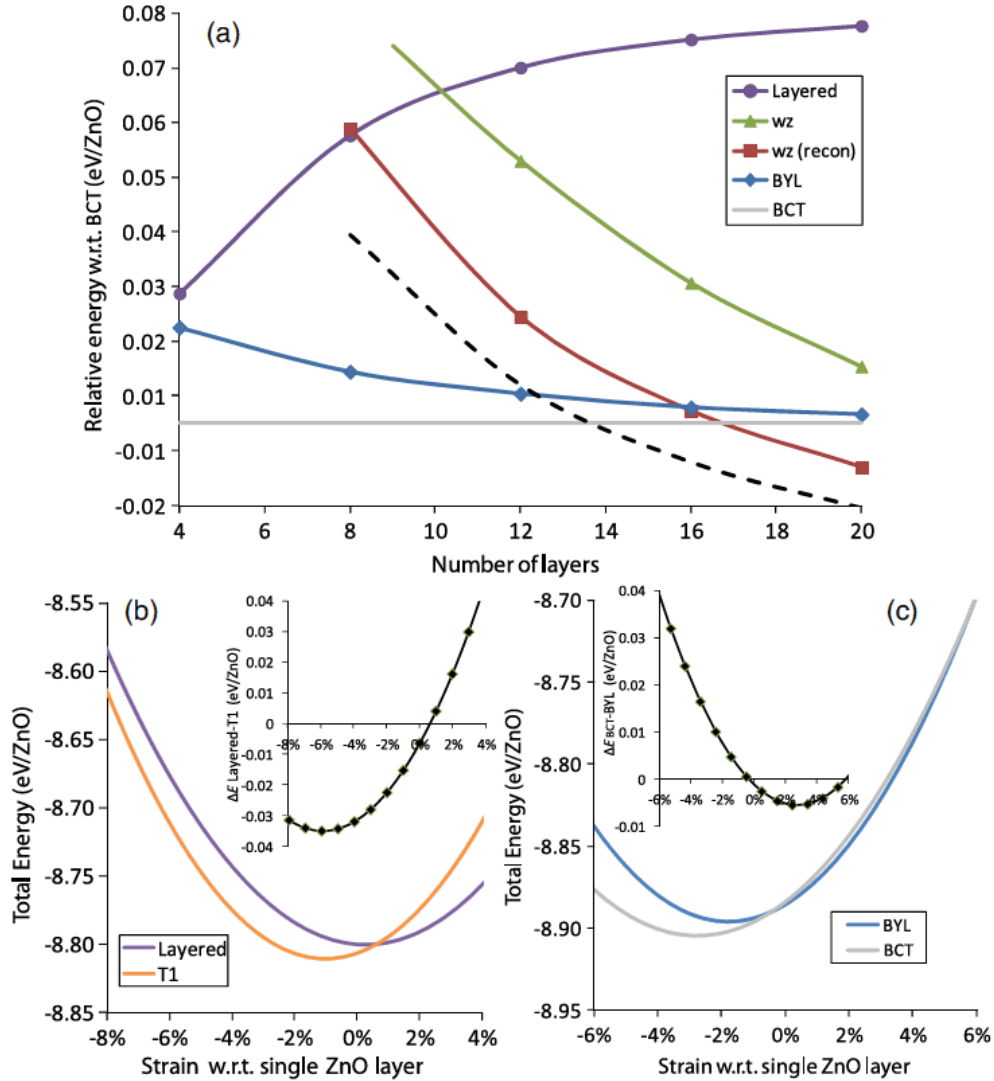


Figura 10 (a) Casos seleccionats de la variació d'estabilitat energètica de nanopel·lícules amb el gruix, (b) variació de l'energia amb la tensió dins el pla pel cas 4 ML layered-ZnO front T1-ZnO, (c) variació de l'energia amb la tensió dins el pla pel cas 8 ML BCT-ZnO front BYL-ZnO. Les tensions es mostren relatives al cas 1 ML layered-ZnO. Les imatges incrustades mostren les diferències d'energia entre polimorfs. Considerant el nostre conjunt de nanopel·lícules estequiomètriques apolars 4 ML, hem trobat que tres tenen una simetria trigonal en el pla basal (0001) i alhora són energèticament més estables que el layered-ZnO. Durant la comparació de les dades estructurals d'aquests polimorfs amb les mostres experimentals 3.5 i 4.5 ML s'ha trobat que les dades del més estable (T1) estan molt d'acord, particularment amb la mostra de

4.5 ML. Tot i considerar el error experimental estimat ($\pm 0.1 \text{ \AA}$) la interpretació de layered-ZnO o wz-ZnO és possible, i l'existència de que com a mínim una altra estructura de nanopel·lícula és completament compatible amb les dades experimentals obre la possibilitat a que aquests polimorfs juguin un paper important en la inestabilitat estructural observada en ZnO suportat en metalls per $>2\text{ML}$.

A més, hem estudiat la influència del gruix i tensió en la estabilitat estructural relativa de les nanopel·lícules. En augmentar el gruix, l'estabilitat del wz-ZnO amb reconstrucció atòmica creix ràpidament i esdevé la fase de ZnO més estable energèticament per $>16 \text{ ML}$ [línia vermella, Figura 10(a)], molt abans que les nanopel·lícules BYL-ZnO o wz-ZnO sense reconstrucció comencen a ésser energèticament competitives vers la BCT-ZnO. Per tal de considerar l'efecte de la tensió en l'estabilitat estructural relativa de les nanopel·lícules hem examinat dos sistemes: (i) T1-ZnO front layered-ZnO amb nanopel·lícules de 4 ML, i (ii) BYL-ZnO front BCT-ZnO amb nanopel·lícules de 8 ML. En el primer cas, el layered-ZnO està afavorit per les tensions positives més grans, mentre que entre tensions positives petites i tensions compressives moderades el T1-ZnO és energèticament favorable, que implica que els substrats amb discordances de dimensions en el pla de la cel·la indueixen petites tensions epitaxials compressives que podrien ajudar a estabilitzar el T1-ZnO. En el segon cas hem trobat que hi ha un petit ventall de estabilitat d'excés sota petites tensions positives per a la fase BYL-ZnO on l'estabilitat energètica de les dues nanopel·lícules s'inverteix. Aquests resultats corroboren altres estudis teòrics que suggereixen que les forces mecàniques aplicades en nanosistemes ZnO poden ésser una ruta fèrtil per l'accés a nous polimorfs.

En aquest últim capítol ens centrem en el polimorfisme de bulki hem investigat l'efecte de la nanoporositat. En aquesta part de l'estudi hem explorat bases de dades que contenen 4 xarxes connectades (4CNs) per obtenir topologies d'enllaços que produeixin un gran nombre d'estructures de ZnO. A més dels 26 polimorfs de ZnO de baixa densitat que ja es varen proposar¹⁵, hem inclòs 60 noves estructures basades en 4CN, i 19 estructures més basades en crear nanopors linears monodimensionals ($D_{\text{pore}} = 1$) orientats en la direcció [0001] amb diferents formes, diàmetres i disposició del espaiat entre pors en el bulk wz-ZnO (estructures wz-ZnO-NP).

Hem utilitzat càlculs DFT per estudiar l'estabilitat energètica (E_{rel}) i el band gap (ΔE_{gap}) relatiu al wz-ZnO d'aquests 105 polimorfs amb diferents graus i tipus de nanoporositat. Primer vam estimar la viabilitat sintètica dels nostres 105 polimorfs de ZnO a partir dels valors calculats de E_{rel} (energia relativa al wz-ZnO) agafant un límit superior de +0.3 eV/ZnO, corresponent a la E_{rel} del polimorf sintetitzat experimentalment rs-ZnO. A la Figura 11a es pot veure com la majoria (88%) de les estructures es troben al rang delimitat de E_{rel} viables juntament amb la tendència que presenta la E_{rel} a augmentar amb l'increment de la nanoporositat (proporció de volum buit, V_{pore}). A diferència dels polimorfs basats en 4CN, les estructures wz-ZnO-NP exhibeixen àtoms tricoordinats en les parets nanoporoses, però els seus valors de E_{rel} (punts oberts de la Figura 11a) segueixen el mateix patró general d'estabilitat relativa amb el V_{pore} . De fet, un nombre d'estructures de wz-ZnO-NP del nostre conjunt han estat trobades com els polimorfs més estables relatius als seus valors de V_{pore} .

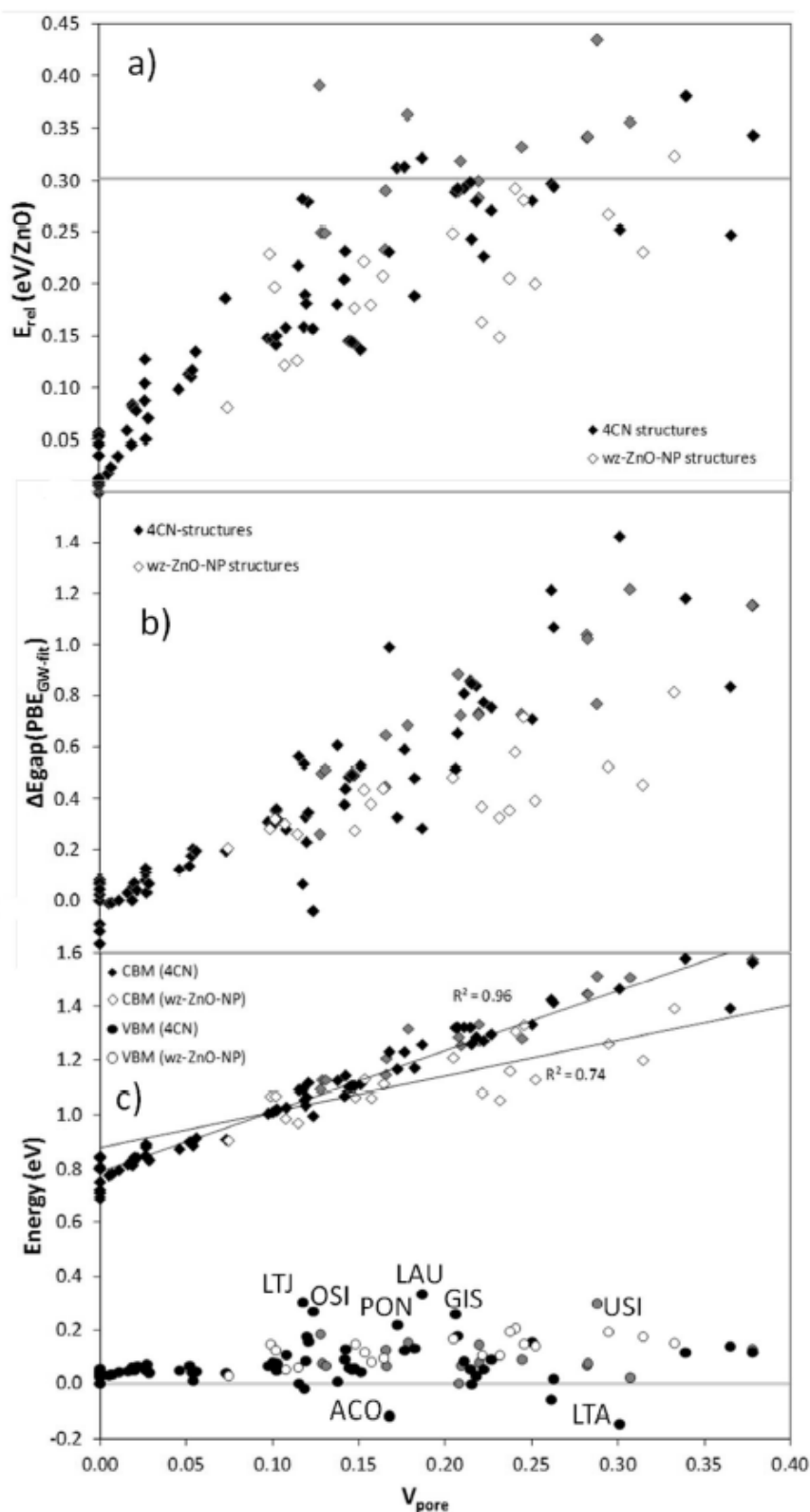


Figura 11. Variació relativa a V_{pore} de: a) E_{rel} (la línia gris indica la E_{rel} dels ZnO), b) $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$, c) Valors de VBM i de CBM de totes les estructures on es marquen els valors de VMD perifèrics.

En quant a l'estructura electrònica hem trobat que el $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ també augmenta generalment amb l'increment del V_{pore} (veure Figura 11b). Agafant l'energia mitjana dels estats 1s core del Zn com a valor de referència comú hem comparat les energies de la banda de valència màxima (VBM) i de la banda de conducció mínima (CBM), per a totes les estructures (relatives a la wz-ZnO) en front del V_{pore} (veure la Figura 11c). Aquesta comparació a revelat un important nombre de coneixements sobre la base física subjacent als resultats de la Figura 11b. Primer, els nivells VBM per a la majoria d'estructures s'estenen entre ± 0.2 eV sense una marcada tendència a incrementar o disminuir amb el V_{pore} . Segon, les energies VBM que difereixen més relativament a aquelles de la wz-ZnO tendeixen a correspondre a estructures que presenten grans distorsions estructurals locals. Tercer, la CBM mostra un increment lineal amb l'increment del V_{pore} , proporcionant una major comprensió del increment total en el ΔE_{gap} amb l'increment del V_{pore} de la Figura 11b. Els polimorfs basats en 4CN presenten valors de CBM compresos en una estreta (~ 0.2 eV) banda d'energia respecte al V_{pore} . Les estructures wz-ZnO-Np semblen seguir una tendència similar però lleugerament menys marcada, en línia amb el seu ΔE_{gap} menor a l'incrementar el V_{pore} .

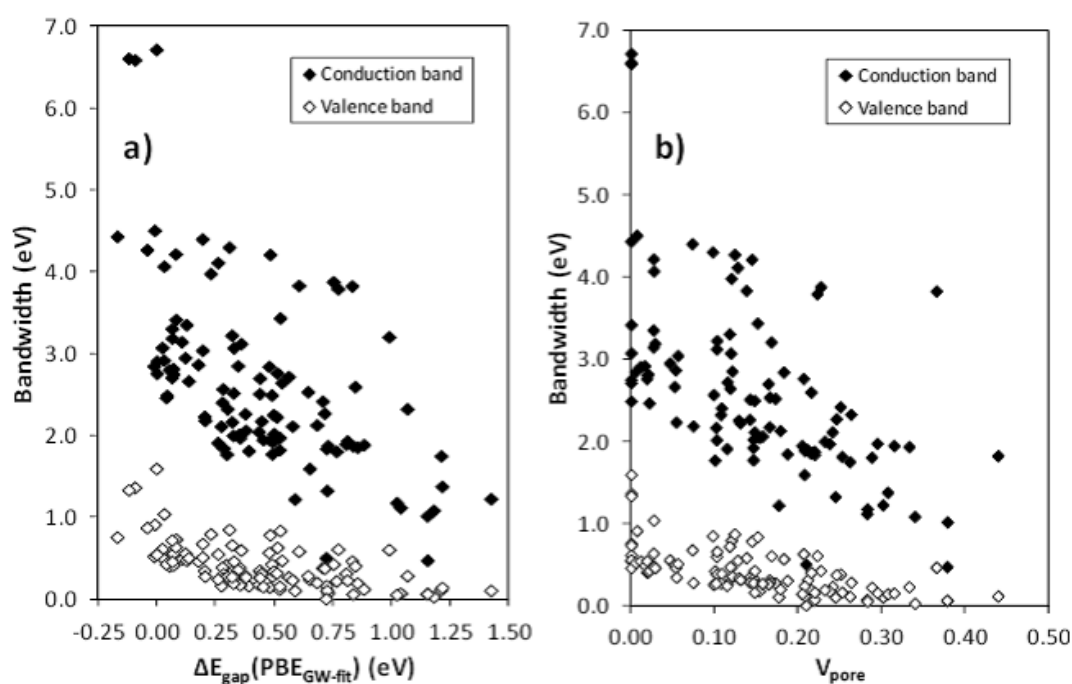


Figura 12. Gràfiques de les amplades de banda de les bandes de conducció i de valència en front de: a) $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ i b) V_{pore}

Hem investigat en detall les amplades de banda de la CB i de la VB per a cada polimorf nanoporós respecte al $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ (Figura 12a) i al V_{pore} (Figura 12b), els quals mostren una tendència general per reduir l'amplada de la banda tant en la CB com en la VB a l'incrementar el $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$ i el V_{pore} . Aquesta tendència confirma el mecanisme físic que hem suggerit referent a com canvia el ΔE_{gap} amb la nanoporositat desde la perspectiva de l'estructura de bandes.

Hem conclòs els nostres resultats explicant que la nanoporositat està inextricablement connectada tant amb la E_{rel} com amb el ΔE_{gap} i hem predit que la nanoporositat pot induir un increment en el band gap de fins a ~ 1.5 eV relatiu a la wurtzita ZnO. Comprovant també la generalitat d'aquest fenomen, pel CdS i pel CdSe suggerim que la nanoporositat pot ser emprada com un mètode genèric d'enginyeria de band gapper materials funcionals morfològicament i electrònicament.

Publications:

[1] Ilker Demiroglu, Daniele Stradi, Francesc Illas and Stefan T. Bromley, A theoretical study of a ZnO graphene analogue: adsorption on Ag(111) and hydrogen transport, J. Phys. Condens. Matter, 23 (2011) 334215.

[2] Ilker Demiroglu, Stefan T. Bromley, Nanofilm versus Bulk Polymorphism in Wurtzite Materials, Phys. Rev. Lett., 110 (2013) 245501.

[3] Ilker Demiroglu, Sergio Tosoni, Francesc Illas, Stefan T. Bromley, Bandgap engineering through nanoporosity, Nanoscale, 6 (2014) 1181.

[4] E. Mete, I. Demiroglu, M. F. Danisman and S. Ellialtioglu, Pentacene Multilayers on Ag(111), J. Phys. Chem C, 114 (2010) 2724.

[5] E. Mete, I. Demiroglu, E. Albayrak, G. Bracco, S. Ellialtioglu, M. F. Danisman, Influence of Steps on the Tilting and Adsorption Dynamics of Ordered Pentacene Films on Vicinal Ag(111) Surfaces, J. Phys. Chem C, 116 (2012) 19424.

[6] Ilker Demiroglu, Stefan T. Bromley, Comparison of structures and stabilities of free space and surface-supported ZnO nanoclusters, Submitted to Nanoscale.



Appendix

Calculated properties, cell parameters and fractional coordinates of all 105 considered bulk structures. Structures 1-86 are 4CN-based structures. Structures 87-105 are wz-ZnO-NP structures. Both sets are ordered with respect to increasing V_{pore} . When V_{pore} is the same for two or more structures, they are ordered relative to increasing E_{rel} .

Str 1 (WZ)	cell parameters
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.00 eV	3.271 3.271 15.970 90.00 90.00 120.00
E_{rel} : 0.00 eV/ZnO	fractional coordinates
Pore _{max} : 0.18 nm	Zn 0.000 0.000 1.000
V_{pore} : 0 %	Zn 0.333 0.667 0.833
D_{pore} : 0	Zn 0.667 0.333 0.667
cell parameters	Zn 0.000 0.000 0.500
3.280 3.280 5.300 90.00 90.00 120.00	Zn 0.667 0.333 0.333
fractional coordinates	Zn 0.333 0.667 0.167
Zn 0.646 0.376 0.852	O 0.000 0.000 0.875
Zn 0.312 0.709 0.352	O 0.333 0.667 0.708
O 0.312 0.709 0.730	O 0.667 0.333 0.541
O 0.646 0.376 0.230	O 0.000 0.000 0.375
	O 0.667 0.333 0.208
	O 0.333 0.667 0.041
Str 2 (4H)	Str 4 (ZB)
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.09 eV	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.17 eV
E_{rel} : 0.01 eV/ZnO	E_{rel} : 0.01 eV/ZnO
Pore _{max} : 0.18 nm	Pore _{max} : 0.18 nm
V_{pore} : 0 %	V_{pore} : 0 %
D_{pore} : 0	D_{pore} : 0
cell parameters	cell parameters
3.273 3.273 10.639 90.00 90.00 120.00	4.620 4.620 4.620 90.00 90.00 90.00
fractional coordinates	fractional coordinates
Zn 0.000 0.000 0.906	Zn 0.500 0.203 0.750
Zn 0.667 0.333 0.656	Zn 0.000 0.703 0.750
Zn 0.000 0.000 0.406	Zn 0.500 0.703 0.250
Zn 0.333 0.667 0.156	Zn 0.000 0.203 0.250
O 0.667 0.333 0.844	O 0.750 0.953 0.500
O 0.000 0.000 0.595	O 0.250 0.453 0.500
O 0.333 0.667 0.344	O 0.750 0.453 0.000
O 0.000 0.000 0.095	O 0.250 0.953 0.000
Str 3 (6H)	Str 5 (64_2_5204) ¹⁸
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.12 eV	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.02 eV
E_{rel} : 0.01 eV/ZnO	E_{rel} : 0.04 eV/ZnO
Pore _{max} : 0.18 nm	Pore _{max} : 0.18 nm
V_{pore} : 0 %	
D_{pore} : 0	

V _{pore} : 0 %	Zn 0.169 0.153 0.839
D _{pore} : 0	Zn 0.507 0.589 0.836
cell parameters	Zn 0.507 0.089 0.836
5.377 13.149 5.699 89.99 89.98 90.02	Zn 0.007 0.905 0.666
fractional coordinates	Zn 0.007 0.405 0.666
Zn 0.670 0.190 0.920	Zn 0.669 0.841 0.663
Zn 0.798 0.690 0.920	Zn 0.669 0.341 0.663
Zn 0.674 0.435 0.917	Zn 0.346 0.841 0.662
Zn 0.794 0.935 0.917	Zn 0.346 0.341 0.662
Zn 0.294 0.935 0.591	Zn 0.346 0.591 0.339
Zn 0.174 0.435 0.591	Zn 0.346 0.091 0.339
Zn 0.298 0.690 0.589	Zn 0.669 0.591 0.339
Zn 0.170 0.190 0.588	Zn 0.669 0.091 0.339
Zn 0.670 0.314 0.420	Zn 0.007 0.655 0.336
Zn 0.798 0.814 0.420	Zn 0.007 0.155 0.336
Zn 0.674 0.068 0.417	Zn 0.507 0.839 0.166
Zn 0.794 0.568 0.417	Zn 0.507 0.339 0.166
Zn 0.174 0.069 0.091	Zn 0.169 0.903 0.163
Zn 0.294 0.569 0.091	Zn 0.169 0.403 0.163
Zn 0.298 0.814 0.089	Zn 0.845 0.903 0.163
Zn 0.170 0.314 0.088	Zn 0.845 0.403 0.163
O 0.172 0.690 0.919	O 0.845 0.843 0.837
O 0.296 0.190 0.919	O 0.845 0.343 0.837
O 0.176 0.936 0.918	O 0.170 0.843 0.837
O 0.292 0.436 0.918	O 0.169 0.343 0.837
O 0.792 0.436 0.591	O 0.507 0.903 0.837
O 0.676 0.936 0.591	O 0.507 0.403 0.837
O 0.672 0.690 0.589	O 0.007 0.591 0.665
O 0.796 0.190 0.589	O 0.007 0.091 0.665
O 0.172 0.814 0.419	O 0.669 0.651 0.664
O 0.296 0.314 0.419	O 0.669 0.151 0.664
O 0.292 0.068 0.418	O 0.345 0.651 0.664
O 0.176 0.568 0.418	O 0.345 0.151 0.664
O 0.792 0.068 0.091	O 0.669 0.901 0.338
O 0.676 0.568 0.091	O 0.669 0.401 0.338
O 0.796 0.314 0.089	O 0.345 0.901 0.338
O 0.672 0.814 0.089	O 0.345 0.401 0.338
	O 0.007 0.341 0.337
Str 6 (BYL) ¹⁹	O 0.007 0.841 0.337
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.05 eV	O 0.507 0.653 0.165
E _{rel} : 0.05 eV/ZnO	O 0.507 0.153 0.165
Pore _{max} : 0.18 nm	O 0.845 0.593 0.165
V _{pore} : 0 %	O 0.845 0.093 0.165
D _{pore} : 0	O 0.169 0.593 0.165
cell parameters	O 0.169 0.093 0.165
9.858 10.831 5.707 90.00 90.02 90.00	
fractional coordinates	Str 7 (64_2_7625) ¹⁸
Zn 0.845 0.653 0.840	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.07 eV
Zn 0.845 0.153 0.840	E _{rel} : 0.05 eV/ZnO
Zn 0.169 0.653 0.839	Pore _{max} : 0.17 nm

V_{pore} : 0 %
 D_{pore} : 0
 cell parameters
 5.585 6.513 11.371 90.00 90.01 89.99
 fractional coordinates
 Zn 0.304 0.321 0.924
 Zn 0.167 0.821 0.924
 Zn 0.667 0.049 0.833
 Zn 0.804 0.549 0.833
 Zn 0.304 0.549 0.673
 Zn 0.167 0.049 0.673
 Zn 0.667 0.821 0.583
 Zn 0.804 0.321 0.583
 Zn 0.167 0.795 0.424
 Zn 0.304 0.295 0.424
 Zn 0.804 0.066 0.333
 Zn 0.667 0.567 0.333
 Zn 0.167 0.566 0.173
 Zn 0.304 0.066 0.173
 Zn 0.667 0.795 0.083
 Zn 0.804 0.295 0.083
 O 0.801 0.817 0.923
 O 0.670 0.317 0.923
 O 0.301 0.052 0.833
 O 0.170 0.552 0.833
 O 0.670 0.552 0.673
 O 0.801 0.052 0.673
 O 0.301 0.818 0.583
 O 0.170 0.318 0.583
 O 0.802 0.798 0.423
 O 0.670 0.298 0.423
 O 0.301 0.564 0.333
 O 0.170 0.064 0.333
 O 0.801 0.564 0.173
 O 0.670 0.064 0.173
 O 0.301 0.798 0.083
 O 0.170 0.298 0.083

Str 8

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.07 eV

E_{rel} : 0.05 eV/ZnO

Pore_{max} : 0.17 nm

V_{pore} : 0 %

D_{pore} : 0

cell parameters

6.516 19.702 5.578 90.00 90.00 60.06

fractional coordinates

Zn 0.660 0.058 0.729

Zn 0.160 0.558 0.728

Zn 0.666 0.224 0.728

Zn 0.166 0.724 0.728

Zn 0.644 0.391 0.728

Zn 0.144 0.891 0.728

Zn 0.144 0.391 0.593

Zn 0.644 0.891 0.593

Zn 0.166 0.224 0.593

Zn 0.666 0.724 0.593

Zn 0.160 0.058 0.593

Zn 0.660 0.558 0.593

Zn 0.805 0.285 0.229

Zn 0.305 0.785 0.228

Zn 0.799 0.118 0.228

Zn 0.299 0.618 0.228

Zn 0.322 0.451 0.228

Zn 0.822 0.951 0.228

Zn 0.822 0.451 0.093

Zn 0.322 0.951 0.093

Zn 0.299 0.118 0.093

Zn 0.799 0.618 0.093

Zn 0.305 0.285 0.093

Zn 0.805 0.785 0.093

O 0.306 0.285 0.726

O 0.302 0.118 0.726

O 0.802 0.618 0.726

O 0.806 0.785 0.726

O 0.820 0.451 0.726

O 0.320 0.951 0.726

O 0.320 0.452 0.595

O 0.820 0.951 0.595

O 0.806 0.285 0.595

O 0.802 0.118 0.595

O 0.302 0.618 0.594

O 0.306 0.785 0.594

O 0.164 0.224 0.227

O 0.664 0.724 0.227

O 0.159 0.058 0.226

O 0.659 0.558 0.226

O 0.146 0.391 0.226

O 0.646 0.891 0.226

O 0.646 0.391 0.095

O 0.659 0.058 0.095

O 0.146 0.891 0.095

O 0.159 0.558 0.095

O 0.663 0.225 0.094

O 0.163 0.725 0.094

Str 9 (64_1_1)¹⁸

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.08 eV

E_{rel} : 0.06 eV/ZnO

Pore_{max} : 0.17 nm

V_{pore} : 0 %
 D_{pore} : 0
 cell parameters
 5.706 6.513 5.566 90.00 90.00 90.00
 fractional coordinates
 Zn 0.555 0.813 0.715
 Zn 0.055 0.045 0.715
 Zn 0.555 0.313 0.582
 Zn 0.055 0.545 0.582
 Zn 0.875 0.813 0.215
 Zn 0.375 0.045 0.215
 Zn 0.875 0.313 0.082
 Zn 0.375 0.545 0.082
 O 0.874 0.312 0.714
 O 0.374 0.546 0.714
 O 0.874 0.812 0.582
 O 0.374 0.046 0.582
 O 0.055 0.546 0.214
 O 0.555 0.312 0.214
 O 0.055 0.046 0.082
 O 0.555 0.812 0.082

Str 10 (59_4_253337)¹⁸

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.01 eV

E_{rel} : 0.02 eV/ZnO

Pore_{max} : 0.18 nm

V_{pore} : 1 %

D_{pore} : 1

cell parameters

22.770 5.328 6.577 90.00 90.00 90.00

fractional coordinates

Zn 0.669 0.175 0.754

Zn 0.834 0.675 0.754

Zn 0.334 0.806 0.754

Zn 0.169 0.306 0.754

Zn 0.918 0.177 0.754

Zn 0.585 0.677 0.754

Zn 0.418 0.305 0.754

Zn 0.085 0.805 0.754

Zn 0.793 0.177 0.504

Zn 0.957 0.680 0.504

Zn 0.710 0.677 0.504

Zn 0.457 0.801 0.504

Zn 0.046 0.301 0.504

Zn 0.546 0.180 0.504

Zn 0.293 0.305 0.504

Zn 0.210 0.805 0.504

Zn 0.669 0.175 0.254

Zn 0.169 0.306 0.254

Zn 0.918 0.177 0.254

Zn 0.834 0.675 0.254

Zn 0.334 0.806 0.254

Zn 0.585 0.677 0.254

Zn 0.418 0.305 0.254

Zn 0.085 0.805 0.254

Zn 0.957 0.680 0.004

Zn 0.793 0.177 0.004

Zn 0.710 0.677 0.004

Zn 0.457 0.801 0.004

Zn 0.046 0.301 0.004

Zn 0.293 0.305 0.004

Zn 0.210 0.805 0.004

Zn 0.546 0.180 0.004

O 0.586 0.299 0.754

O 0.335 0.183 0.754

O 0.169 0.683 0.754

O 0.917 0.799 0.754

O 0.835 0.299 0.754

O 0.669 0.799 0.754

O 0.417 0.682 0.754

O 0.086 0.182 0.754

O 0.545 0.795 0.504

O 0.710 0.299 0.504

O 0.458 0.187 0.504

O 0.293 0.683 0.504

O 0.210 0.182 0.504

O 0.793 0.799 0.504

O 0.958 0.294 0.504

O 0.045 0.687 0.504

O 0.586 0.299 0.254

O 0.335 0.183 0.254

O 0.169 0.683 0.254

O 0.917 0.799 0.254

O 0.835 0.299 0.254

O 0.669 0.799 0.254

O 0.417 0.682 0.254

O 0.086 0.182 0.254

O 0.545 0.795 0.004

O 0.710 0.299 0.004

O 0.458 0.187 0.004

O 0.293 0.683 0.004

O 0.210 0.182 0.004

O 0.793 0.799 0.004

O 0.958 0.294 0.004

O 0.045 0.687 0.004

Str 11 (59_3_250)¹⁸

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.01 eV

E_{rel} : 0.02 eV/ZnO

Pore_{max} : 0.18 nm

V _{pore} : 1 %	Zn 0.165 0.689 0.250
D _{pore} : 1	Zn 0.911 0.818 0.000
cell parameters	Zn 0.589 0.318 0.000
17.069 5.342 3.288 90.00 90.00 90.00	Zn 0.411 0.694 0.000
fractional coordinates	Zn 0.089 0.194 0.000
Zn 0.443 0.793 0.771	O 0.833 0.696 0.750
Zn 0.114 0.797 0.770	O 0.668 0.196 0.750
Zn 0.226 0.300 0.770	O 0.333 0.815 0.750
Zn 0.891 0.167 0.770	O 0.168 0.315 0.750
Zn 0.779 0.665 0.770	O 0.913 0.200 0.500
Zn 0.561 0.172 0.770	O 0.587 0.700 0.500
Zn 0.279 0.800 0.271	O 0.413 0.311 0.500
Zn 0.391 0.298 0.271	O 0.087 0.811 0.500
Zn 0.943 0.672 0.270	O 0.833 0.696 0.250
Zn 0.061 0.292 0.270	O 0.668 0.196 0.250
Zn 0.614 0.668 0.270	O 0.333 0.815 0.250
Zn 0.725 0.165 0.270	O 0.168 0.315 0.250
O 0.225 0.676 0.771	O 0.913 0.200 0.000
O 0.444 0.178 0.771	O 0.587 0.700 0.000
O 0.890 0.791 0.770	O 0.413 0.311 0.000
O 0.114 0.173 0.770	O 0.087 0.811 0.000
O 0.561 0.787 0.770	
O 0.780 0.289 0.770	Str 13 ()
O 0.390 0.674 0.271	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.03 eV
O 0.061 0.677 0.270	E _{rel} : 0.06 eV/ZnO
O 0.280 0.176 0.270	Pore _{max} : 0.19 nm
O 0.944 0.287 0.270	V _{pore} : 2 %
O 0.725 0.789 0.270	D _{pore} : 1
O 0.614 0.291 0.270	cell parameters
	6.601 13.178 5.389 89.86 90.00 59.94
Str 12 (59_4_280312) ¹⁸	fractional coordinates
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.00 eV	Zn 0.149 0.591 0.726
E _{rel} : 0.03 eV/ZnO	Zn 0.148 0.841 0.725
Pore _{max} : 0.18 nm	Zn 0.649 0.841 0.725
V _{pore} : 1 %	Zn 0.653 0.586 0.606
D _{pore} : 1	Zn 0.644 0.096 0.599
cell parameters	Zn 0.145 0.338 0.599
11.372 5.375 6.586 90.00 90.00 90.00	Zn 0.659 0.338 0.599
fractional coordinates	Zn 0.146 0.094 0.598
Zn 0.835 0.322 0.750	Zn 0.819 0.920 0.223
Zn 0.665 0.822 0.750	Zn 0.306 0.676 0.222
Zn 0.335 0.189 0.750	Zn 0.820 0.677 0.222
Zn 0.165 0.689 0.750	Zn 0.322 0.918 0.222
Zn 0.911 0.818 0.500	Zn 0.312 0.428 0.215
Zn 0.589 0.318 0.500	Zn 0.316 0.173 0.096
Zn 0.411 0.694 0.500	Zn 0.817 0.173 0.096
Zn 0.089 0.194 0.500	Zn 0.816 0.424 0.095
Zn 0.835 0.322 0.250	O 0.316 0.173 0.721
Zn 0.665 0.822 0.250	O 0.818 0.173 0.721
Zn 0.335 0.189 0.250	O 0.817 0.422 0.721

O 0.313 0.427 0.614
 O 0.820 0.676 0.605
 O 0.307 0.676 0.605
 O 0.819 0.921 0.605
 O 0.321 0.919 0.604
 O 0.644 0.096 0.217
 O 0.146 0.093 0.216
 O 0.145 0.338 0.216
 O 0.658 0.338 0.216
 O 0.652 0.587 0.208
 O 0.148 0.592 0.100
 O 0.650 0.841 0.100
 O 0.148 0.841 0.100

Str 14 (59_4_253313)¹⁸

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.00 eV

E_{rel} : 0.05 eV/ZnO

Pore_{max}: 0.18 nm

V_{pore}: 2 %

D_{pore}: 1

cell parameters

22.669 5.462 6.584 90.02 89.99 89.99

fractional coordinates

Zn 0.078 0.683 0.752

Zn 0.417 0.183 0.752

Zn 0.578 0.812 0.752

Zn 0.917 0.312 0.752

Zn 0.668 0.185 0.752

Zn 0.327 0.811 0.752

Zn 0.168 0.311 0.752

Zn 0.827 0.684 0.752

Zn 0.452 0.682 0.502

Zn 0.042 0.182 0.502

Zn 0.290 0.313 0.502

Zn 0.952 0.813 0.502

Zn 0.790 0.182 0.502

Zn 0.705 0.682 0.502

Zn 0.205 0.813 0.502

Zn 0.543 0.313 0.502

Zn 0.078 0.683 0.252

Zn 0.417 0.183 0.252

Zn 0.917 0.312 0.252

Zn 0.578 0.812 0.252

Zn 0.668 0.185 0.252

Zn 0.327 0.811 0.252

Zn 0.168 0.311 0.252

Zn 0.827 0.684 0.252

Zn 0.452 0.682 0.002

Zn 0.042 0.182 0.002

Zn 0.290 0.313 0.002

Zn 0.205 0.813 0.002

Zn 0.952 0.813 0.002

Zn 0.790 0.182 0.002

Zn 0.705 0.682 0.002

Zn 0.543 0.313 0.002

O 0.416 0.809 0.752

O 0.079 0.308 0.752

O 0.667 0.810 0.752

O 0.828 0.309 0.752

O 0.916 0.687 0.752

O 0.328 0.186 0.752

O 0.167 0.686 0.752

O 0.579 0.187 0.752

O 0.042 0.808 0.502

O 0.453 0.309 0.502

O 0.542 0.687 0.502

O 0.953 0.186 0.502

O 0.706 0.313 0.502

O 0.289 0.682 0.502

O 0.789 0.813 0.502

O 0.206 0.182 0.502

O 0.416 0.809 0.252

O 0.079 0.308 0.252

O 0.828 0.309 0.252

O 0.667 0.810 0.252

O 0.916 0.687 0.252

O 0.328 0.186 0.252

O 0.167 0.686 0.252

O 0.579 0.187 0.252

O 0.042 0.808 0.002

O 0.453 0.309 0.002

O 0.542 0.687 0.002

O 0.953 0.186 0.002

O 0.706 0.313 0.002

O 0.289 0.682 0.002

O 0.789 0.813 0.002

O 0.206 0.182 0.002

Str 15 ()

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.06 eV

E_{rel} : 0.08 eV/ZnO

Pore_{max}: 0.19 nm

V_{pore}: 2 %

D_{pore}: 1

cell parameters

9.962 9.921 5.371 89.63 90.00 120.14

fractional coordinates

Zn 0.895 0.441 0.817

Zn 0.561 0.441 0.817

Zn 0.228 0.441 0.817

Zn 0.558 0.101 0.703
 Zn 0.891 0.101 0.702
 Zn 0.224 0.101 0.702
 Zn 0.896 0.778 0.690
 Zn 0.563 0.778 0.690
 Zn 0.230 0.778 0.690
 Zn 0.780 0.545 0.315
 Zn 0.446 0.545 0.315
 Zn 0.113 0.545 0.315
 Zn 0.785 0.222 0.302
 Zn 0.452 0.222 0.302
 Zn 0.118 0.222 0.302
 Zn 0.782 0.882 0.188
 Zn 0.115 0.882 0.188
 Zn 0.448 0.882 0.188
 O 0.781 0.881 0.811
 O 0.114 0.881 0.811
 O 0.448 0.881 0.811
 O 0.785 0.221 0.709
 O 0.451 0.221 0.709
 O 0.118 0.222 0.709
 O 0.780 0.545 0.698
 O 0.447 0.545 0.698
 O 0.113 0.545 0.698
 O 0.896 0.778 0.307
 O 0.563 0.778 0.307
 O 0.230 0.778 0.307
 O 0.558 0.101 0.297
 O 0.891 0.102 0.296
 O 0.225 0.102 0.296
 O 0.895 0.442 0.194
 O 0.562 0.442 0.194
 O 0.228 0.442 0.193

Str 16 (189_3_1615)¹⁸
 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.07 eV
 E_{rel} : 0.08 eV/ZnO
 Pore_{max} : 0.23 nm
 V_{pore} : 2 %
 D_{pore} : 1
 cell parameters
 9.924 9.925 5.395 90.00 90.00 120.00
 fractional coordinates
 Zn 0.888 0.437 0.817
 Zn 0.563 0.437 0.817
 Zn 0.563 0.111 0.817
 Zn 0.890 0.766 0.805
 Zn 0.890 0.109 0.805
 Zn 0.233 0.109 0.805
 Zn 0.558 0.771 0.689

Zn 0.228 0.771 0.689
 Zn 0.228 0.442 0.689
 Zn 0.781 0.548 0.319
 Zn 0.781 0.218 0.319
 Zn 0.452 0.218 0.319
 Zn 0.776 0.881 0.203
 Zn 0.119 0.881 0.203
 Zn 0.119 0.223 0.203
 Zn 0.446 0.878 0.192
 Zn 0.446 0.553 0.192
 Zn 0.121 0.553 0.192
 O 0.447 0.879 0.811
 O 0.447 0.553 0.811
 O 0.121 0.553 0.811
 O 0.119 0.881 0.800
 O 0.119 0.223 0.800
 O 0.776 0.881 0.800
 O 0.781 0.548 0.694
 O 0.781 0.218 0.694
 O 0.452 0.218 0.694
 O 0.558 0.771 0.315
 O 0.228 0.771 0.315
 O 0.228 0.442 0.315
 O 0.890 0.766 0.208
 O 0.890 0.109 0.208
 O 0.233 0.109 0.208
 O 0.563 0.437 0.198
 O 0.889 0.437 0.198
 O 0.563 0.111 0.198

Str 17 ()
 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.04 eV
 E_{rel} : 0.08 eV/ZnO
 Pore_{max} : 0.19 nm
 V_{pore} : 2 %
 D_{pore} : 1
 cell parameters
 22.823 5.416 6.631 90.02 89.99 90.33
 fractional coordinates
 Zn 0.422 0.303 0.754
 Zn 0.582 0.679 0.754
 Zn 0.837 0.696 0.754
 Zn 0.332 0.674 0.754
 Zn 0.919 0.181 0.754
 Zn 0.084 0.814 0.754
 Zn 0.671 0.311 0.754
 Zn 0.167 0.297 0.754
 Zn 0.547 0.176 0.505
 Zn 0.294 0.177 0.504
 Zn 0.212 0.694 0.504

Zn 0.791 0.297 0.504	O 0.045 0.692 0.004
Zn 0.958 0.683 0.504	O 0.709 0.185 0.004
Zn 0.046 0.312 0.504	O 0.212 0.291 0.004
Zn 0.709 0.811 0.504	
Zn 0.457 0.805 0.504	Str 18 (SSCCCC) ¹⁶
Zn 0.422 0.303 0.255	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.08 eV
Zn 0.582 0.679 0.254	E_{rel} : 0.09 eV/ZnO
Zn 0.837 0.696 0.254	Pore _{max} : 0.19 nm
Zn 0.332 0.674 0.254	V _{pore} : 3 %
Zn 0.919 0.181 0.254	D _{pore} : 0
Zn 0.084 0.814 0.254	cell parameters
Zn 0.671 0.311 0.254	11.462 5.320 3.331 89.99 90.00 90.00
Zn 0.167 0.297 0.254	fractional coordinates
Zn 0.547 0.176 0.005	Zn 0.278 0.187 0.920
Zn 0.294 0.177 0.004	Zn 0.615 0.804 0.919
Zn 0.212 0.694 0.004	Zn 0.778 0.285 0.919
Zn 0.958 0.683 0.004	Zn 0.115 0.667 0.919
Zn 0.791 0.297 0.004	Zn 0.370 0.785 0.420
Zn 0.046 0.312 0.004	Zn 0.533 0.304 0.420
Zn 0.709 0.811 0.004	Zn 0.033 0.168 0.419
Zn 0.457 0.805 0.004	Zn 0.870 0.687 0.419
O 0.583 0.300 0.755	O 0.279 0.778 0.920
O 0.333 0.297 0.754	O 0.613 0.183 0.919
O 0.167 0.701 0.754	O 0.114 0.289 0.919
O 0.919 0.807 0.754	O 0.779 0.694 0.919
O 0.837 0.292 0.754	O 0.369 0.193 0.419
O 0.084 0.187 0.754	O 0.535 0.683 0.419
O 0.421 0.682 0.754	O 0.869 0.278 0.419
O 0.670 0.688 0.754	O 0.035 0.789 0.419
O 0.545 0.799 0.505	
O 0.458 0.183 0.504	Str 19 ()
O 0.791 0.701 0.504	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.11 eV
O 0.295 0.802 0.504	E_{rel} : 0.10 eV/ZnO
O 0.958 0.304 0.504	Pore _{max} : 0.23 nm
O 0.045 0.692 0.504	V _{pore} : 3 %
O 0.709 0.185 0.504	D _{pore} : 1
O 0.212 0.291 0.504	cell parameters
O 0.583 0.300 0.255	8.769 6.624 5.461 89.98 90.03 79.20
O 0.333 0.297 0.254	fractional coordinates
O 0.167 0.701 0.254	Zn 0.556 0.617 0.996
O 0.919 0.807 0.254	Zn 0.889 0.294 0.994
O 0.837 0.292 0.254	Zn 0.560 0.116 0.873
O 0.084 0.187 0.254	Zn 0.217 0.943 0.873
O 0.421 0.682 0.254	Zn 0.218 0.457 0.872
O 0.670 0.688 0.254	Zn 0.889 0.792 0.861
O 0.545 0.799 0.005	Zn 0.773 0.553 0.495
O 0.458 0.183 0.004	Zn 0.444 0.887 0.482
O 0.791 0.701 0.004	Zn 0.102 0.228 0.481
O 0.295 0.802 0.004	Zn 0.445 0.401 0.481
O 0.958 0.304 0.004	Zn 0.773 0.050 0.361

Zn 0.106 0.727 0.359
 O 0.106 0.727 0.988
 O 0.775 0.055 0.986
 O 0.445 0.401 0.879
 O 0.445 0.887 0.878
 O 0.103 0.229 0.878
 O 0.773 0.557 0.870
 O 0.889 0.787 0.486
 O 0.559 0.116 0.476
 O 0.217 0.457 0.475
 O 0.217 0.943 0.475
 O 0.887 0.290 0.369
 O 0.556 0.617 0.366

Str 20 ()

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.13 eV

E_{rel} : 0.13 eV/ZnO

Pore_{max}: 0.22 nm

V_{pore}: 3 %

D_{pore}: 1

cell parameters

6.671 6.671 5.373 90.00 90.00 120.00

fractional coordinates

Zn 0.825 0.648 0.961

Zn 0.825 0.158 0.961

Zn 0.335 0.158 0.961

Zn 0.655 0.818 0.562

Zn 0.165 0.818 0.562

Zn 0.165 0.328 0.562

Zn 0.662 0.321 0.446

Zn 0.329 0.655 0.077

O 0.655 0.818 0.967

O 0.166 0.818 0.967

O 0.166 0.329 0.967

O 0.825 0.647 0.555

O 0.825 0.158 0.555

O 0.336 0.158 0.555

O 0.329 0.655 0.454

O 0.662 0.321 0.068

Str 21 (BCT)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.03 eV

E_{rel} : 0.05 eV/ZnO

Pore_{max}: 0.16 nm

V_{pore}: 3 %

D_{pore}: 1

cell parameters

7.925 7.925 3.287 90.00 90.00 90.00

fractional coordinates

Zn 0.503 0.818 0.500

Zn 0.503 0.182 0.500

Zn 0.003 0.682 0.500

Zn 0.003 0.318 0.500

Zn 0.821 0.000 0.000

Zn 0.685 0.500 0.000

Zn 0.321 0.500 0.000

Zn 0.185 0.000 0.000

O 0.821 0.500 0.500

O 0.685 0.000 0.500

O 0.321 0.000 0.500

O 0.185 0.500 0.500

O 0.503 0.682 0.000

O 0.503 0.318 0.000

O 0.003 0.818 0.000

O 0.003 0.182 0.000

Str 22 ()

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.07 eV

E_{rel} : 0.07 eV/ZnO

Pore_{max}: 0.19 nm

V_{pore}: 3 %

D_{pore}: 1

cell parameters

8.711 6.587 5.484 90.16 90.17 79.25

fractional coordinates

Zn 0.780 0.034 0.874

Zn 0.780 0.534 0.874

Zn 0.458 0.856 0.874

Zn 0.340 0.154 0.507

Zn 0.017 0.976 0.507

Zn 0.018 0.475 0.506

Zn 0.347 0.654 0.380

Zn 0.686 0.307 0.378

Zn 0.678 0.810 0.371

Zn 0.119 0.199 0.009

Zn 0.112 0.702 0.003

Zn 0.451 0.357 0.001

O 0.345 0.649 0.993

O 0.339 0.149 0.881

O 0.015 0.474 0.881

O 0.015 0.977 0.881

O 0.782 0.032 0.500

O 0.459 0.862 0.500

O 0.783 0.536 0.500

O 0.453 0.361 0.388

O 0.114 0.702 0.380

O 0.120 0.199 0.377

O 0.678 0.810 0.003

O 0.684 0.308 0.001

Str 23 (-LIT) ¹⁷	Zn 0.173 0.503 0.586
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.12 eV	Zn 0.803 0.489 0.414
E_{rel} : 0.10 eV/ZnO	Zn 0.673 0.989 0.414
Pore _{max} : 0.20 nm	Zn 0.307 0.260 0.330
V _{pore} : 5 %	Zn 0.169 0.760 0.330
D _{pore} : 1	Zn 0.807 0.260 0.169
cell parameters	Zn 0.669 0.760 0.169
9.891 5.586 5.716 90.00 90.00 90.00	Zn 0.303 0.489 0.086
fractional coordinates	Zn 0.173 0.989 0.086
Zn 0.994 0.935 0.840	O 0.296 0.497 0.915
Zn 0.670 0.933 0.831	O 0.180 0.997 0.915
Zn 0.332 0.065 0.817	O 0.803 0.735 0.829
Zn 0.832 0.435 0.683	O 0.674 0.235 0.829
Zn 0.170 0.567 0.669	O 0.303 0.735 0.671
Zn 0.494 0.565 0.660	O 0.174 0.235 0.671
Zn 0.506 0.065 0.340	O 0.796 0.497 0.585
Zn 0.830 0.067 0.331	O 0.680 0.997 0.585
Zn 0.168 0.935 0.317	O 0.296 0.994 0.415
Zn 0.668 0.565 0.183	O 0.180 0.494 0.415
Zn 0.330 0.433 0.169	O 0.803 0.757 0.329
Zn 0.006 0.435 0.160	O 0.674 0.257 0.329
O 0.995 0.563 0.838	O 0.303 0.757 0.171
O 0.668 0.558 0.834	O 0.174 0.257 0.171
O 0.332 0.436 0.818	O 0.796 0.994 0.085
O 0.832 0.064 0.682	O 0.680 0.494 0.085
O 0.168 0.942 0.666	
O 0.495 0.937 0.662	Str 25 (64_2_5457) ¹⁸
O 0.505 0.437 0.338	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.18 eV
O 0.832 0.442 0.334	E_{rel} : 0.11 eV/ZnO
O 0.168 0.564 0.318	Pore _{max} : 0.20 nm
O 0.668 0.936 0.182	V _{pore} : 5 %
O 0.332 0.058 0.166	D _{pore} : 2
O 0.005 0.063 0.162	cell parameters
	5.647 13.252 5.680 90.00 90.00 90.00
Str 24 (64_2_7619) ¹⁸	fractional coordinates
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.14 eV	Zn 0.305 0.691 0.907
E_{rel} : 0.11 eV/ZnO	Zn 0.173 0.191 0.907
Pore _{max} : 0.20 nm	Zn 0.170 0.935 0.902
V _{pore} : 5 %	Zn 0.308 0.435 0.902
D _{pore} : 2	Zn 0.808 0.435 0.595
cell parameters	Zn 0.670 0.935 0.595
5.630 6.563 11.501 90.00 90.00 90.00	Zn 0.673 0.191 0.591
fractional coordinates	Zn 0.805 0.692 0.591
Zn 0.803 0.003 0.914	Zn 0.305 0.806 0.407
Zn 0.673 0.503 0.914	Zn 0.173 0.306 0.407
Zn 0.307 0.231 0.830	Zn 0.308 0.062 0.402
Zn 0.169 0.731 0.830	Zn 0.171 0.562 0.402
Zn 0.807 0.231 0.669	Zn 0.807 0.062 0.095
Zn 0.669 0.731 0.669	Zn 0.671 0.562 0.095
Zn 0.303 0.003 0.586	Zn 0.673 0.306 0.091

Zn 0.805 0.806 0.091
 O 0.807 0.191 0.911
 O 0.671 0.691 0.910
 O 0.797 0.935 0.910
 O 0.681 0.435 0.910
 O 0.297 0.935 0.587
 O 0.181 0.435 0.587
 O 0.307 0.191 0.587
 O 0.171 0.691 0.587
 O 0.807 0.306 0.411
 O 0.671 0.806 0.411
 O 0.798 0.562 0.410
 O 0.680 0.062 0.410
 O 0.180 0.062 0.087
 O 0.297 0.562 0.087
 O 0.171 0.806 0.087
 O 0.307 0.306 0.087

Str 26 (AEN)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.21 eV

E_{rel} : 0.12 eV/ZnO

Pore_{max}: 0.24 nm

V_{pore}: 5 %

D_{pore}: 1

cell parameters

6.690 8.692 10.869 90.00 90.01 90.00

fractional coordinates

Zn 0.872 0.509 0.938
 Zn 0.372 0.509 0.938
 Zn 0.622 0.821 0.836
 Zn 0.122 0.821 0.836
 Zn 0.622 0.197 0.836
 Zn 0.122 0.197 0.836
 Zn 0.872 0.697 0.645
 Zn 0.372 0.697 0.645
 Zn 0.872 0.321 0.645
 Zn 0.372 0.321 0.645
 Zn 0.622 0.009 0.544
 Zn 0.122 0.009 0.544
 Zn 0.622 0.509 0.438
 Zn 0.122 0.509 0.438
 Zn 0.872 0.197 0.336
 Zn 0.372 0.197 0.336
 Zn 0.872 0.821 0.336
 Zn 0.372 0.821 0.336
 Zn 0.622 0.321 0.145
 Zn 0.122 0.321 0.145
 Zn 0.622 0.697 0.145
 Zn 0.122 0.697 0.145
 Zn 0.872 0.009 0.044

Zn 0.372 0.009 0.044
 O 0.622 0.009 0.936
 O 0.122 0.009 0.936
 O 0.872 0.697 0.837
 O 0.872 0.321 0.837
 O 0.372 0.697 0.837
 O 0.372 0.321 0.837
 O 0.122 0.821 0.644
 O 0.622 0.821 0.644
 O 0.622 0.197 0.644
 O 0.122 0.197 0.644
 O 0.872 0.509 0.545
 O 0.372 0.509 0.545
 O 0.872 0.009 0.436
 O 0.372 0.009 0.436
 O 0.622 0.321 0.337
 O 0.122 0.321 0.337
 O 0.622 0.697 0.337
 O 0.122 0.697 0.337
 O 0.872 0.197 0.144
 O 0.372 0.197 0.144
 O 0.872 0.821 0.144
 O 0.372 0.821 0.144
 O 0.622 0.509 0.045
 O 0.122 0.509 0.045

Str 27 (ATV)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.20 eV

E_{rel} : 0.13 eV/ZnO

Pore_{max}: 0.23 nm

V_{pore}: 6 %

D_{pore}: 1

cell parameters

5.280 10.095 5.895 90.00 90.00 90.00

fractional coordinates

Zn 0.811 0.250 0.840
 Zn 0.311 0.750 0.840
 Zn 0.811 0.906 0.666
 Zn 0.811 0.594 0.666
 Zn 0.311 0.406 0.666
 Zn 0.311 0.094 0.666
 Zn 0.811 0.406 0.334
 Zn 0.811 0.094 0.334
 Zn 0.311 0.906 0.334
 Zn 0.311 0.594 0.334
 Zn 0.811 0.750 0.160
 Zn 0.311 0.250 0.160
 O 0.692 0.750 0.837
 O 0.192 0.250 0.837
 O 0.688 0.406 0.671

O 0.688 0.094 0.671	Str 30 (ABW) ¹⁷
O 0.188 0.906 0.671	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.30 eV
O 0.188 0.594 0.671	E_{rel} : 0.15 eV/ZnO
O 0.688 0.906 0.329	Pore _{max} : 0.22 nm
O 0.688 0.594 0.329	V _{pore} : 10 %
O 0.188 0.406 0.329	D _{pore} : 1
O 0.188 0.094 0.329	cell parameters
O 0.692 0.250 0.163	12.188 6.707 11.061 90.00 90.00 90.00
O 0.192 0.750 0.163	fractional coordinates
	Zn 0.912 0.500 0.998
	Zn 0.912 0.000 0.998
	Zn 0.412 0.500 0.998
	Zn 0.412 0.000 0.998
	Zn 0.585 0.750 0.899
	Zn 0.585 0.250 0.899
	Zn 0.085 0.750 0.899
	Zn 0.085 0.250 0.899
	Zn 0.835 0.750 0.748
	Zn 0.835 0.250 0.748
	Zn 0.335 0.750 0.748
	Zn 0.335 0.250 0.748
	Zn 0.662 0.500 0.649
	Zn 0.662 0.000 0.649
	Zn 0.162 0.500 0.649
	Zn 0.162 0.000 0.649
	Zn 0.912 0.500 0.498
	Zn 0.912 0.000 0.498
	Zn 0.412 0.500 0.498
	Zn 0.412 0.000 0.498
	Zn 0.585 0.750 0.399
	Zn 0.585 0.250 0.399
	Zn 0.085 0.750 0.399
	Zn 0.085 0.250 0.399
	Zn 0.835 0.750 0.248
	Zn 0.835 0.250 0.248
	Zn 0.335 0.750 0.248
	Zn 0.335 0.250 0.248
	Zn 0.662 0.500 0.149
	Zn 0.662 0.000 0.149
	Zn 0.162 0.500 0.149
	Zn 0.162 0.000 0.149
	O 0.585 0.500 0.997
	O 0.585 0.000 0.997
	O 0.085 0.500 0.997
	O 0.085 0.000 0.997
	O 0.912 0.750 0.900
	O 0.912 0.250 0.900
	O 0.412 0.750 0.900
	O 0.412 0.250 0.900
	O 0.662 0.750 0.747
Str 28 (JBW) ¹⁷	
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.20 eV	
E_{rel} : 0.19 eV/ZnO	
Pore _{max} : 0.21 nm	
V _{pore} : 7 %	
D _{pore} : 1	
cell parameters	
3.353 10.166 4.751 90.00 90.00 90.00	
fractional coordinates	
Zn 0.750 0.608 0.893	
Zn 0.750 0.904 0.893	
Zn 0.750 0.256 0.610	
Zn 0.250 0.756 0.389	
Zn 0.250 0.405 0.106	
Zn 0.250 0.108 0.106	
O 0.750 0.408 0.871	
O 0.750 0.104 0.871	
O 0.750 0.756 0.626	
O 0.250 0.256 0.374	
O 0.250 0.604 0.128	
O 0.250 0.908 0.128	
Str 29 (SSCSSC) ¹⁶	
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.31 eV	
E_{rel} : 0.15 eV/ZnO	
Pore _{max} : 0.22 nm	
V _{pore} : 10 %	
D _{pore} : 1	
cell parameters	
5.534 3.365 6.051 90.00 89.99 89.99	
fractional coordinates	
Zn 0.062 0.108 0.727	
Zn 0.562 0.608 0.573	
Zn 0.363 0.108 0.227	
Zn 0.863 0.608 0.073	
O 0.869 0.608 0.725	
O 0.369 0.108 0.576	
O 0.557 0.608 0.225	
O 0.056 0.108 0.076	

O 0.662 0.250 0.747	O 0.383 0.124 0.865
O 0.162 0.750 0.747	O 0.997 0.011 0.865
O 0.162 0.250 0.747	O 0.496 0.511 0.865
O 0.835 0.500 0.650	O 0.536 0.624 0.519
O 0.835 0.000 0.650	O 0.036 0.124 0.519
O 0.335 0.500 0.650	O 0.649 0.011 0.519
O 0.335 0.000 0.650	O 0.149 0.511 0.519
O 0.585 0.500 0.497	O 0.823 0.837 0.365
O 0.585 0.000 0.497	O 0.323 0.337 0.365
O 0.085 0.500 0.497	O 0.709 0.450 0.365
O 0.085 0.000 0.497	O 0.209 0.951 0.365
O 0.912 0.750 0.400	O 0.824 0.184 0.019
O 0.912 0.250 0.400	O 0.324 0.684 0.019
O 0.412 0.750 0.400	O 0.710 0.797 0.019
O 0.412 0.250 0.400	O 0.210 0.297 0.019
O 0.662 0.750 0.247	
O 0.662 0.250 0.247	Str 32 (SSSCSC) ¹⁶
O 0.162 0.750 0.247	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.36 eV
O 0.162 0.250 0.247	E_{rel} : 0.14 eV/ZnO
O 0.835 0.500 0.150	Pore _{max} : 0.23 nm
O 0.835 0.000 0.150	V _{pore} : 10 %
O 0.335 0.500 0.150	D _{pore} : 1
O 0.335 0.000 0.150	cell parameters
	5.714 6.466 6.134 90.02 90.02 89.96
Str 31 (DFT) ¹⁷	fractional coordinates
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.35 eV	Zn 0.037 0.071 0.727
E_{rel} : 0.14 eV/ZnO	Zn 0.537 0.787 0.727
Pore _{max} : 0.23 nm	Zn 0.537 0.287 0.568
V _{pore} : 10 %	Zn 0.037 0.571 0.568
D _{pore} : 1	Zn 0.887 0.287 0.227
cell parameters	Zn 0.387 0.570 0.227
8.631 8.631 8.907 57.08 122.92 96.99	Zn 0.387 0.070 0.068
fractional coordinates	Zn 0.887 0.787 0.068
Zn 0.710 0.449 0.862	O 0.386 0.066 0.725
Zn 0.210 0.949 0.862	O 0.886 0.792 0.725
Zn 0.818 0.840 0.862	O 0.886 0.292 0.570
Zn 0.318 0.340 0.862	O 0.386 0.566 0.570
Zn 0.715 0.795 0.521	O 0.538 0.292 0.225
Zn 0.323 0.686 0.521	O 0.037 0.565 0.224
Zn 0.823 0.186 0.521	O 0.037 0.065 0.070
Zn 0.215 0.295 0.521	O 0.537 0.792 0.070
Zn 0.494 0.516 0.362	
Zn 0.994 0.016 0.362	Str 33 (135_1_4) ¹⁸
Zn 0.885 0.624 0.362	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.32 eV
Zn 0.385 0.124 0.362	E_{rel} : 0.15 eV/ZnO
Zn 0.539 0.619 0.021	Pore _{max} : 0.28 nm
Zn 0.039 0.119 0.021	V _{pore} : 10 %
Zn 0.648 0.011 0.021	D _{pore} : 1
Zn 0.148 0.511 0.021	cell parameters
O 0.883 0.624 0.865	6.471 6.471 5.285 90.00 90.00 90.00

fractional coordinates
 Zn 0.832 0.148 0.700
 Zn 0.633 0.648 0.700
 Zn 0.332 0.347 0.700
 Zn 0.133 0.847 0.700
 Zn 0.832 0.847 0.200
 Zn 0.633 0.347 0.200
 Zn 0.332 0.648 0.200
 Zn 0.133 0.148 0.200
 O 0.633 0.347 0.821
 O 0.833 0.847 0.821
 O 0.333 0.648 0.821
 O 0.133 0.148 0.821
 O 0.133 0.848 0.321
 O 0.332 0.348 0.321
 O 0.832 0.148 0.321
 O 0.633 0.648 0.321

Str 34 (AEL)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.28 eV

E_{rel} : 0.16 eV/ZnO

Pore_{max}: 0.32 nm

V_{pore} : 11 %

D_{pore} : 1

cell parameters

8.832 11.915 5.285 90.01 90.02 89.99

fractional coordinates

Zn 0.526 0.115 0.810
 Zn 0.438 0.615 0.810
 Zn 0.526 0.393 0.810
 Zn 0.438 0.893 0.810
 Zn 0.119 0.754 0.810
 Zn 0.844 0.254 0.810
 Zn 0.835 0.966 0.808
 Zn 0.835 0.542 0.808
 Zn 0.128 0.466 0.808
 Zn 0.128 0.042 0.808
 Zn 0.938 0.115 0.310
 Zn 0.026 0.615 0.310
 Zn 0.026 0.893 0.310
 Zn 0.938 0.393 0.310
 Zn 0.619 0.254 0.310
 Zn 0.344 0.754 0.310
 Zn 0.335 0.466 0.308
 Zn 0.335 0.042 0.308
 Zn 0.628 0.966 0.308
 Zn 0.628 0.542 0.308
 O 0.341 0.754 0.691
 O 0.622 0.254 0.691
 O 0.939 0.116 0.687

O 0.939 0.392 0.687
 O 0.024 0.892 0.687
 O 0.024 0.616 0.687
 O 0.628 0.542 0.686
 O 0.334 0.466 0.686
 O 0.334 0.042 0.686
 O 0.628 0.966 0.686
 O 0.841 0.254 0.191
 O 0.122 0.754 0.191
 O 0.439 0.616 0.187
 O 0.524 0.392 0.187
 O 0.439 0.892 0.187
 O 0.524 0.116 0.187
 O 0.128 0.042 0.186
 O 0.834 0.966 0.186
 O 0.835 0.542 0.186
 O 0.128 0.466 0.186

Str 35 (APD)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.56 eV

E_{rel} : 0.22 eV/ZnO

Pore_{max}: 0.27 nm

V_{pore} : 12 %

D_{pore} : 1

cell parameters

5.281 13.064 6.545 90.00 90.00 90.00

fractional coordinates

Zn 0.312 0.202 0.902
 Zn 0.188 0.702 0.902
 Zn 0.801 0.052 0.897
 Zn 0.699 0.552 0.897
 Zn 0.301 0.052 0.603
 Zn 0.199 0.552 0.603
 Zn 0.812 0.202 0.598
 Zn 0.688 0.702 0.598
 Zn 0.312 0.298 0.402
 Zn 0.188 0.798 0.402
 Zn 0.801 0.448 0.397
 Zn 0.699 0.948 0.397
 Zn 0.301 0.448 0.103
 Zn 0.199 0.948 0.103
 Zn 0.812 0.298 0.098
 Zn 0.688 0.798 0.098
 O 0.809 0.701 0.899
 O 0.691 0.201 0.899
 O 0.301 0.553 0.898
 O 0.199 0.053 0.898
 O 0.801 0.553 0.602
 O 0.699 0.053 0.602
 O 0.309 0.701 0.601

O 0.191 0.201 0.601
 O 0.809 0.799 0.399
 O 0.691 0.299 0.399
 O 0.301 0.947 0.398
 O 0.199 0.447 0.398
 O 0.801 0.947 0.102
 O 0.699 0.447 0.102
 O 0.309 0.799 0.101
 O 0.191 0.299 0.101

Str 36 (LTJ)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.07 eV

E_{rel} : 0.28 eV/ZnO

Pore_{max}: 0.24 nm

V_{pore}: 12 %

D_{pore}: 3

cell parameters

5.798 5.817 6.785 90.00 90.00 90.00

fractional coordinates

Zn 0.580 0.089 0.902

Zn 0.080 0.411 0.848

Zn 0.597 0.563 0.648

Zn 0.903 0.063 0.602

Zn 0.420 0.911 0.402

Zn 0.920 0.589 0.348

Zn 0.403 0.437 0.148

Zn 0.097 0.937 0.102

O 0.931 0.099 0.903

O 0.431 0.401 0.847

O 0.589 0.914 0.652

O 0.911 0.414 0.598

O 0.069 0.901 0.403

O 0.569 0.599 0.347

O 0.411 0.086 0.152

O 0.089 0.586 0.098

Str 37 (hUMQ)²⁰

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.54 eV

E_{rel} : 0.16 eV/ZnO

Pore_{max}: 0.26 nm

V_{pore}: 12 %

D_{pore}: 1

cell parameters

9.024 9.021 5.652 90.00 89.97 90.01

fractional coordinates

Zn 0.246 0.905 0.816

Zn 0.100 0.242 0.816

Zn 0.763 0.096 0.816

Zn 0.909 0.759 0.815

Zn 0.600 0.742 0.670

Zn 0.409 0.259 0.670

Zn 0.263 0.596 0.670

Zn 0.746 0.405 0.670

Zn 0.246 0.096 0.316

Zn 0.100 0.759 0.316

Zn 0.763 0.905 0.316

Zn 0.909 0.241 0.316

Zn 0.409 0.742 0.170

Zn 0.600 0.259 0.170

Zn 0.263 0.405 0.170

Zn 0.746 0.596 0.170

O 0.407 0.742 0.814

O 0.602 0.258 0.814

O 0.262 0.403 0.814

O 0.747 0.598 0.814

O 0.102 0.758 0.672

O 0.907 0.242 0.672

O 0.247 0.098 0.672

O 0.762 0.903 0.672

O 0.407 0.258 0.314

O 0.262 0.598 0.314

O 0.602 0.742 0.314

O 0.747 0.403 0.314

O 0.102 0.242 0.172

O 0.247 0.903 0.172

O 0.907 0.758 0.172

O 0.762 0.098 0.172

Str 38 (AFO)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.33 eV

E_{rel} : 0.19 eV/ZnO

Pore_{max}: 0.35 nm

V_{pore}: 12 %

D_{pore}: 1

cell parameters

6.268 9.045 5.264 90.00 90.00 110.27

fractional coordinates

Zn 0.559 0.118 0.599

Zn 0.588 0.739 0.598

Zn 0.151 0.739 0.598

Zn 0.177 0.355 0.592

Zn 0.721 0.442 0.591

Zn 0.452 0.905 0.099

Zn 0.860 0.284 0.098

Zn 0.424 0.284 0.098

Zn 0.834 0.668 0.092

Zn 0.291 0.582 0.091

O 0.560 0.121 0.980

O 0.593 0.745 0.976

O 0.178 0.356 0.976

O 0.152 0.745 0.976
 O 0.722 0.445 0.970
 O 0.451 0.902 0.480
 O 0.418 0.278 0.476
 O 0.833 0.667 0.476
 O 0.860 0.278 0.476
 O 0.289 0.578 0.470

Str 39 (ATO)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.23 eV

E_{rel} : 0.18 eV/ZnO

Pore_{max}: 0.34 nm

V_{pore}: 12 %

D_{pore}: 1

cell parameters

13.460 13.460 3.213 90.00 90.00

120.00

fractional coordinates

Zn 0.529 0.619 0.925

Zn 0.381 0.910 0.925

Zn 0.090 0.471 0.925

Zn 0.952 0.757 0.742

Zn 0.804 0.048 0.742

Zn 0.243 0.196 0.742

Zn 0.862 0.286 0.591

Zn 0.714 0.577 0.591

Zn 0.423 0.138 0.591

Zn 0.577 0.862 0.408

Zn 0.286 0.423 0.408

Zn 0.138 0.714 0.408

Zn 0.757 0.804 0.258

Zn 0.196 0.952 0.258

Zn 0.048 0.243 0.258

Zn 0.910 0.529 0.075

Zn 0.619 0.090 0.075

Zn 0.471 0.381 0.075

O 0.528 0.911 0.910

O 0.383 0.472 0.910

O 0.089 0.617 0.910

O 0.950 0.194 0.757

O 0.806 0.756 0.757

O 0.244 0.050 0.757

O 0.861 0.578 0.577

O 0.717 0.139 0.577

O 0.422 0.283 0.577

O 0.578 0.717 0.423

O 0.283 0.861 0.423

O 0.139 0.422 0.423

O 0.756 0.950 0.243

O 0.194 0.244 0.243

O 0.050 0.806 0.243

O 0.911 0.383 0.090

O 0.617 0.528 0.090

O 0.472 0.089 0.090

Str 40 (JRY)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.35 eV

E_{rel} : 0.28 eV/ZnO

Pore_{max}: 0.25 nm

V_{pore}: 12 %

D_{pore}: 1

cell parameters

5.328 5.868 10.876 90.00 90.00 90.00

fractional coordinates

Zn 0.583 0.595 0.981

Zn 0.133 0.374 0.922

Zn 0.581 0.091 0.824

Zn 0.419 0.591 0.676

Zn 0.867 0.874 0.578

Zn 0.417 0.095 0.519

Zn 0.917 0.405 0.481

Zn 0.367 0.626 0.422

Zn 0.919 0.909 0.324

Zn 0.081 0.409 0.176

Zn 0.633 0.126 0.078

Zn 0.083 0.905 0.019

O 0.439 0.904 0.975

O 0.896 0.127 0.916

O 0.441 0.416 0.826

O 0.559 0.916 0.674

O 0.104 0.627 0.584

O 0.561 0.404 0.525

O 0.061 0.096 0.475

O 0.604 0.873 0.416

O 0.059 0.584 0.326

O 0.941 0.084 0.174

O 0.396 0.373 0.084

O 0.939 0.596 0.025

Str 41 (OSI)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: -0.04 eV

E_{rel} : 0.16 eV/ZnO

Pore_{max}: 0.39 nm

V_{pore}: 12 %

D_{pore}: 1

cell parameters

11.732 11.602 3.376 90.00 90.00 90.00

fractional coordinates

Zn 0.715 0.848 0.500

Zn 0.715 0.157 0.500

Zn 0.619 0.502 0.500
 Zn 0.381 0.502 0.500
 Zn 0.285 0.848 0.500
 Zn 0.285 0.157 0.500
 Zn 0.000 0.786 0.500
 Zn 0.000 0.219 0.500
 Zn 0.881 0.002 0.000
 Zn 0.785 0.657 0.000
 Zn 0.785 0.348 0.000
 Zn 0.500 0.719 0.000
 Zn 0.500 0.286 0.000
 Zn 0.215 0.657 0.000
 Zn 0.215 0.348 0.000
 Zn 0.119 0.002 0.000
 O 0.847 0.714 0.500
 O 0.847 0.291 0.500
 O 0.788 0.002 0.500
 O 0.500 0.626 0.500
 O 0.500 0.379 0.500
 O 0.212 0.002 0.500
 O 0.153 0.714 0.500
 O 0.153 0.291 0.500
 O 0.712 0.502 0.000
 O 0.653 0.791 0.000
 O 0.653 0.214 0.000
 O 0.347 0.791 0.000
 O 0.347 0.214 0.000
 O 0.288 0.502 0.000
 O 0.000 0.879 0.000
 O 0.000 0.126 0.000

Str 42 (MVY)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.26 eV

E_{rel} : 0.39 eV/ZnO

Pore_{max}: 0.25 nm

V_{pore}: 13 %

D_{pore}: 1

cell parameters

3.190 5.734 9.195 90.00 90.00 90.00

fractional coordinates

Zn 0.603 0.678 0.796
 Zn 0.897 0.178 0.704
 Zn 0.233 0.894 0.500
 Zn 0.897 0.178 0.296
 Zn 0.603 0.678 0.204
 Zn 0.267 0.394 0.000
 O 0.392 0.317 0.795
 O 0.108 0.817 0.705
 O 0.718 0.118 0.500
 O 0.108 0.817 0.295

O 0.392 0.317 0.205

O 0.782 0.618 0.000

Str 43 AWO)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.50 eV

E_{rel} : 0.25 eV/ZnO

Pore_{max}: 0.27 nm

V_{pore}: 13 %

D_{pore}: 3

cell parameters

5.832 10.117 11.881 90.00 90.00 90.20

fractional coordinates

Zn 0.690 0.506 0.919
 Zn 0.190 0.006 0.919
 Zn 0.674 0.141 0.829
 Zn 0.174 0.641 0.829
 Zn 0.835 0.844 0.820
 Zn 0.335 0.344 0.820
 Zn 0.835 0.344 0.680
 Zn 0.335 0.844 0.680
 Zn 0.674 0.641 0.671
 Zn 0.174 0.141 0.671
 Zn 0.690 0.006 0.581
 Zn 0.190 0.506 0.581
 Zn 0.810 0.494 0.419
 Zn 0.310 0.994 0.419
 Zn 0.826 0.859 0.329
 Zn 0.326 0.359 0.329
 Zn 0.665 0.156 0.320
 Zn 0.165 0.656 0.320
 Zn 0.665 0.656 0.180
 Zn 0.165 0.156 0.180
 Zn 0.826 0.359 0.171
 Zn 0.326 0.859 0.171
 Zn 0.810 0.994 0.081
 Zn 0.310 0.494 0.081
 O 0.815 0.002 0.917
 O 0.315 0.502 0.917
 O 0.688 0.341 0.829
 O 0.188 0.841 0.829
 O 0.827 0.643 0.828
 O 0.327 0.143 0.828
 O 0.827 0.143 0.672
 O 0.327 0.643 0.672
 O 0.688 0.841 0.671
 O 0.188 0.341 0.671
 O 0.815 0.502 0.583
 O 0.315 0.002 0.583
 O 0.685 0.998 0.417
 O 0.185 0.498 0.417

O 0.812 0.659 0.329
 O 0.312 0.159 0.329
 O 0.673 0.357 0.328
 O 0.173 0.857 0.328
 O 0.673 0.857 0.172
 O 0.173 0.357 0.172
 O 0.812 0.159 0.171
 O 0.312 0.659 0.171
 O 0.685 0.498 0.083
 O 0.185 0.998 0.083

Str 44 (UEI)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.51 eV

E_{rel} : 0.25 eV/ZnO

Pore_{max}: 0.30 nm

V_{pore}: 13 %

D_{pore}: 3

cell parameters

11.887 5.859 10.095 90.00 90.00 90.00

fractional coordinates

Zn 0.821 0.333 0.840

Zn 0.679 0.833 0.840

Zn 0.321 0.167 0.840

Zn 0.179 0.667 0.840

Zn 0.828 0.672 0.636

Zn 0.672 0.172 0.636

Zn 0.328 0.828 0.636

Zn 0.172 0.328 0.636

Zn 0.919 0.189 0.501

Zn 0.581 0.689 0.501

Zn 0.419 0.311 0.501

Zn 0.081 0.811 0.501

Zn 0.821 0.833 0.340

Zn 0.679 0.333 0.340

Zn 0.321 0.667 0.340

Zn 0.179 0.167 0.340

Zn 0.828 0.172 0.136

Zn 0.672 0.672 0.136

Zn 0.328 0.328 0.136

Zn 0.172 0.828 0.136

Zn 0.919 0.689 0.001

Zn 0.581 0.189 0.001

Zn 0.419 0.811 0.001

Zn 0.081 0.311 0.001

O 0.917 0.315 0.999

O 0.583 0.815 0.999

O 0.417 0.185 0.999

O 0.083 0.685 0.999

O 0.828 0.684 0.837

O 0.672 0.184 0.837

O 0.328 0.816 0.837

O 0.172 0.316 0.837

O 0.828 0.327 0.639

O 0.672 0.827 0.639

O 0.328 0.173 0.639

O 0.172 0.673 0.639

O 0.917 0.815 0.499

O 0.583 0.315 0.499

O 0.417 0.685 0.499

O 0.083 0.185 0.499

O 0.828 0.184 0.337

O 0.672 0.684 0.337

O 0.328 0.316 0.337

O 0.172 0.816 0.337

O 0.828 0.827 0.139

O 0.672 0.327 0.139

O 0.328 0.673 0.139

O 0.172 0.173 0.139

Str 45 (ATN)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.61 eV

E_{rel} : 0.18 eV/ZnO

Pore_{max}: 0.34 nm

V_{pore}: 14 %

D_{pore}: 1

cell parameters

8.312 8.312 3.392 90.00 90.00 90.00

fractional coordinates

Zn 0.902 0.731 0.500

Zn 0.727 0.137 0.500

Zn 0.309 0.906 0.500

Zn 0.133 0.313 0.500

Zn 0.809 0.406 0.000

Zn 0.633 0.813 0.000

Zn 0.402 0.231 0.000

Zn 0.227 0.637 0.000

O 0.902 0.310 0.500

O 0.729 0.905 0.500

O 0.306 0.138 0.500

O 0.134 0.733 0.500

O 0.806 0.638 0.000

O 0.634 0.233 0.000

O 0.402 0.810 0.000

O 0.229 0.405 0.000

Str 46 (SAF)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.38 eV

E_{rel} : 0.20 eV/ZnO

Pore_{max}: 0.41 nm

V_{pore}: 14 %

D _{pore} : 1	O 0.402 0.833 0.808
cell parameters	O 0.098 0.333 0.808
9.513 18.309 5.260 90.00 90.00 90.00	O 0.897 0.778 0.315
fractional coordinates	O 0.603 0.278 0.315
Zn 0.902 0.777 0.695	O 0.397 0.722 0.315
Zn 0.598 0.277 0.695	O 0.103 0.222 0.315
Zn 0.402 0.723 0.695	O 0.893 0.949 0.308
Zn 0.098 0.223 0.695	O 0.606 0.449 0.308
Zn 0.786 0.136 0.692	O 0.394 0.551 0.308
Zn 0.714 0.636 0.692	O 0.106 0.051 0.308
Zn 0.286 0.364 0.692	O 0.787 0.137 0.308
Zn 0.214 0.864 0.692	O 0.713 0.637 0.308
Zn 0.895 0.948 0.688	O 0.287 0.363 0.308
Zn 0.605 0.448 0.688	O 0.213 0.863 0.308
Zn 0.395 0.552 0.688	O 0.902 0.333 0.308
Zn 0.105 0.052 0.688	O 0.598 0.833 0.308
Zn 0.899 0.330 0.686	O 0.402 0.167 0.308
Zn 0.601 0.830 0.686	O 0.098 0.667 0.308
Zn 0.399 0.170 0.686	
Zn 0.101 0.670 0.686	Str 47 (APC) ¹⁷
Zn 0.902 0.223 0.195	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.44 eV
Zn 0.598 0.723 0.195	E _{rel} : 0.23 eV/ZnO
Zn 0.402 0.277 0.195	Pore _{max} : 0.26 nm
Zn 0.098 0.777 0.195	V _{pore} : 14 %
Zn 0.786 0.864 0.192	D _{pore} : 3
Zn 0.714 0.364 0.192	cell parameters
Zn 0.286 0.636 0.192	5.788 12.765 6.464 90.00 90.00 90.00
Zn 0.214 0.136 0.192	fractional coordinates
Zn 0.895 0.052 0.188	Zn 0.328 0.711 0.895
Zn 0.605 0.552 0.188	Zn 0.172 0.211 0.895
Zn 0.395 0.448 0.188	Zn 0.824 0.048 0.881
Zn 0.105 0.948 0.188	Zn 0.676 0.548 0.881
Zn 0.899 0.670 0.186	Zn 0.324 0.048 0.619
Zn 0.601 0.170 0.186	Zn 0.176 0.548 0.619
Zn 0.399 0.830 0.186	Zn 0.828 0.711 0.605
Zn 0.101 0.330 0.186	Zn 0.672 0.211 0.605
O 0.897 0.222 0.815	Zn 0.328 0.789 0.395
O 0.603 0.722 0.815	Zn 0.172 0.289 0.395
O 0.397 0.278 0.815	Zn 0.824 0.452 0.381
O 0.103 0.778 0.815	Zn 0.676 0.952 0.381
O 0.893 0.051 0.808	Zn 0.324 0.452 0.119
O 0.606 0.551 0.808	Zn 0.176 0.952 0.119
O 0.394 0.449 0.808	Zn 0.828 0.789 0.105
O 0.106 0.949 0.808	Zn 0.672 0.289 0.105
O 0.787 0.863 0.808	O 0.317 0.549 0.890
O 0.713 0.363 0.808	O 0.183 0.049 0.890
O 0.287 0.637 0.808	O 0.822 0.211 0.888
O 0.213 0.137 0.808	O 0.678 0.711 0.888
O 0.902 0.667 0.808	O 0.322 0.211 0.612
O 0.598 0.167 0.808	O 0.178 0.711 0.612

O 0.817 0.549 0.610
 O 0.683 0.049 0.610
 O 0.317 0.951 0.390
 O 0.183 0.451 0.390
 O 0.822 0.289 0.388
 O 0.678 0.789 0.388
 O 0.322 0.289 0.112
 O 0.178 0.789 0.112
 O 0.817 0.951 0.110
 O 0.683 0.451 0.110

Str 48 (CAN)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.48 eV

E_{rel} : 0.15 eV/ZnO

Pore_{max}: 0.33 nm

V_{pore}: 14 %

D_{pore}: 1

cell parameters

7.817 7.817 3.368 90.00 90.00 120.00

fractional coordinates

Zn 0.611 0.686 0.750

Zn 0.340 0.933 0.750

Zn 0.094 0.416 0.750

Zn 0.936 0.607 0.250

Zn 0.690 0.090 0.250

Zn 0.419 0.337 0.250

O 0.610 0.932 0.750

O 0.341 0.417 0.750

O 0.094 0.686 0.750

O 0.936 0.337 0.250

O 0.689 0.606 0.250

O 0.420 0.091 0.250

Str 49 (AFG)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.50 eV

E_{rel} : 0.14 eV/ZnO

Pore_{max}: 0.33 nm

V_{pore}: 15 %

D_{pore}: 3

cell parameters

7.848 7.849 13.415 90.00 90.00 120.00

fractional coordinates

Zn 0.844 0.426 0.875

Zn 0.573 0.670 0.875

Zn 0.328 0.155 0.875

Zn 0.654 0.076 0.750

Zn 0.168 0.345 0.750

Zn 0.923 0.831 0.750

Zn 0.838 0.417 0.625

Zn 0.582 0.673 0.625

Zn 0.326 0.161 0.625

Zn 0.241 0.489 0.500

Zn 0.995 0.758 0.500

Zn 0.509 0.003 0.500

Zn 0.835 0.408 0.375

Zn 0.590 0.679 0.375

Zn 0.320 0.164 0.375

Zn 0.995 0.758 0.251

Zn 0.509 0.003 0.251

Zn 0.241 0.489 0.250

Zn 0.838 0.417 0.125

Zn 0.582 0.673 0.125

Zn 0.326 0.161 0.125

Zn 0.923 0.831 0.000

Zn 0.654 0.076 0.000

Zn 0.168 0.345 0.000

O 0.842 0.670 0.875

O 0.575 0.157 0.875

O 0.328 0.424 0.875

O 0.923 0.345 0.751

O 0.654 0.831 0.751

O 0.168 0.075 0.751

O 0.836 0.672 0.625

O 0.582 0.162 0.625

O 0.327 0.417 0.625

O 0.510 0.759 0.500

O 0.240 0.003 0.500

O 0.995 0.489 0.500

O 0.835 0.677 0.375

O 0.589 0.164 0.375

O 0.321 0.410 0.375

O 0.995 0.489 0.251

O 0.240 0.003 0.251

O 0.510 0.759 0.251

O 0.836 0.672 0.125

O 0.582 0.162 0.125

O 0.327 0.417 0.125

O 0.168 0.075 0.000

O 0.654 0.831 0.000

O 0.923 0.345 0.000

Str 50 (TOL)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.49 eV

E_{rel} : 0.14 eV/ZnO

Pore_{max}: 0.33 nm

V_{pore}: 15 %

D_{pore}: 3

cell parameters

7.863 7.863 20.073 90.00 90.00 120.00

fractional coordinates

Zn 0.748 0.746 1.000	O 0.003 0.747 0.666
Zn 0.258 0.002 1.000	O 0.589 0.660 0.583
Zn 0.003 0.257 1.000	O 0.345 0.929 0.583
Zn 0.588 0.928 0.917	O 0.076 0.416 0.583
Zn 0.344 0.416 0.917	O 0.750 0.009 0.500
Zn 0.077 0.661 0.917	O 0.263 0.254 0.500
Zn 0.748 0.747 0.833	O 0.996 0.742 0.500
Zn 0.258 0.002 0.833	O 0.589 0.660 0.417
Zn 0.003 0.257 0.833	O 0.345 0.929 0.417
Zn 0.930 0.587 0.750	O 0.076 0.416 0.417
Zn 0.662 0.075 0.750	O 0.257 0.256 0.333
Zn 0.418 0.343 0.750	O 0.003 0.748 0.333
Zn 0.748 0.747 0.666	O 0.749 0.002 0.333
Zn 0.258 0.002 0.666	O 0.662 0.587 0.250
Zn 0.003 0.257 0.666	O 0.930 0.343 0.250
Zn 0.344 0.416 0.583	O 0.417 0.074 0.250
Zn 0.589 0.929 0.583	O 0.743 0.995 0.167
Zn 0.076 0.661 0.583	O 0.010 0.749 0.167
Zn 0.750 0.740 0.500	O 0.256 0.262 0.167
Zn 0.995 0.255 0.500	O 0.930 0.343 0.083
Zn 0.265 0.010 0.500	O 0.417 0.074 0.083
Zn 0.589 0.929 0.417	O 0.662 0.587 0.083
Zn 0.344 0.416 0.417	
Zn 0.076 0.661 0.417	Str 51 (LIO) ¹⁷
Zn 0.748 0.746 0.333	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.50 eV
Zn 0.259 0.002 0.333	E_{rel} : 0.14 eV/ZnO
Zn 0.003 0.257 0.333	Pore _{max} : 0.33 nm
Zn 0.930 0.588 0.250	V _{pore} : 15 %
Zn 0.662 0.075 0.250	D _{pore} : 3
Zn 0.417 0.343 0.250	cell parameters
Zn 0.742 0.749 0.167	7.857 7.857 10.050 90.00 90.00 120.01
Zn 0.256 0.993 0.167	fractional coordinates
Zn 0.011 0.263 0.167	Zn 0.080 0.411 0.833
Zn 0.662 0.074 0.083	Zn 0.336 0.921 0.833
Zn 0.930 0.588 0.083	Zn 0.590 0.666 0.833
Zn 0.417 0.343 0.083	Zn 0.921 0.593 0.667
O 0.257 0.256 1.000	Zn 0.677 0.080 0.667
O 0.749 0.002 1.000	Zn 0.408 0.324 0.667
O 0.003 0.748 1.000	Zn 0.597 0.674 0.500
O 0.589 0.660 0.917	Zn 0.327 0.919 0.500
O 0.345 0.930 0.917	Zn 0.082 0.404 0.500
O 0.075 0.416 0.917	Zn 0.677 0.080 0.334
O 0.257 0.256 0.833	Zn 0.408 0.324 0.334
O 0.749 0.002 0.833	Zn 0.921 0.593 0.334
O 0.003 0.747 0.833	Zn 0.590 0.666 0.167
O 0.661 0.587 0.750	Zn 0.336 0.921 0.167
O 0.417 0.074 0.750	Zn 0.080 0.411 0.167
O 0.931 0.344 0.750	Zn 0.994 0.740 0.000
O 0.257 0.256 0.666	Zn 0.750 0.007 0.000
O 0.749 0.002 0.666	Zn 0.262 0.251 0.000

O 0.081 0.666 0.834
 O 0.590 0.920 0.833
 O 0.335 0.411 0.833
 O 0.922 0.325 0.666
 O 0.677 0.593 0.666
 O 0.408 0.080 0.666
 O 0.596 0.919 0.500
 O 0.082 0.673 0.500
 O 0.328 0.405 0.500
 O 0.677 0.593 0.334
 O 0.408 0.080 0.334
 O 0.922 0.325 0.334
 O 0.335 0.411 0.167
 O 0.590 0.920 0.167
 O 0.081 0.666 0.167
 O 0.994 0.252 0.000
 O 0.264 0.008 0.000
 O 0.749 0.738 0.000

Str 52 (LOS)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.49 eV

E_{rel} : 0.14 eV/ZnO

Pore_{max}: 0.34 nm

V_{pore}: 15 %

D_{pore}: 3

cell parameters

7.887 7.887 6.670 90.00 90.00 120.00

fractional coordinates

Zn 0.587 0.935 0.750

Zn 0.344 0.424 0.750

Zn 0.076 0.667 0.750

Zn 0.748 0.755 0.500

Zn 0.256 0.009 0.500

Zn 0.002 0.263 0.500

Zn 0.928 0.594 0.250

Zn 0.660 0.083 0.250

Zn 0.417 0.350 0.250

Zn 0.748 0.755 0.000

Zn 0.256 0.009 0.000

Zn 0.002 0.263 0.000

O 0.587 0.667 0.750

O 0.344 0.936 0.750

O 0.075 0.424 0.750

O 0.748 0.009 0.500

O 0.256 0.263 0.500

O 0.002 0.755 0.500

O 0.929 0.351 0.250

O 0.660 0.594 0.250

O 0.417 0.082 0.250

O 0.748 0.009 0.000

O 0.256 0.263 0.000

O 0.002 0.755 0.000

Str 53 (SOD)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.53 eV

E_{rel} : 0.14 eV/ZnO

Pore_{max}: 0.35 nm

V_{pore}: 15 %

D_{pore}: 3

cell parameters

5.663 5.663 5.663 90.00 90.00 90.00

fractional coordinates

Zn 0.000 0.500 0.750

Zn 0.750 0.000 0.500

Zn 0.250 0.000 0.500

Zn 0.000 0.500 0.250

Zn 0.500 0.750 0.000

Zn 0.500 0.250 0.000

O 0.500 0.000 0.750

O 0.000 0.750 0.500

O 0.000 0.250 0.500

O 0.500 0.000 0.250

O 0.750 0.500 0.000

O 0.250 0.500 0.000

Str 54 (AET)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.45 eV

E_{rel} : 0.23 eV/ZnO

Pore_{max}: 0.41 nm

V_{pore}: 17 %

D_{pore}: 1

cell parameters

21.516 9.431 5.296 90.00 90.00 90.00

fractional coordinates

Zn 0.500 0.352 0.583

Zn 0.000 0.852 0.583

Zn 0.819 0.399 0.563

Zn 0.681 0.899 0.563

Zn 0.319 0.899 0.563

Zn 0.181 0.399 0.563

Zn 0.921 0.111 0.563

Zn 0.579 0.611 0.563

Zn 0.421 0.611 0.563

Zn 0.079 0.111 0.563

Zn 0.846 0.790 0.560

Zn 0.654 0.290 0.560

Zn 0.346 0.290 0.560

Zn 0.154 0.790 0.560

Zn 0.772 0.099 0.554

Zn 0.728 0.599 0.554

Zn 0.272 0.599 0.554	O 0.500 0.680 0.437
Zn 0.228 0.099 0.554	O 0.000 0.180 0.437
Zn 0.500 0.648 0.083	O 0.772 0.897 0.431
Zn 0.000 0.148 0.083	O 0.728 0.397 0.431
Zn 0.819 0.601 0.063	O 0.272 0.397 0.431
Zn 0.681 0.101 0.063	O 0.228 0.897 0.431
Zn 0.319 0.101 0.063	
Zn 0.181 0.601 0.063	Str 55 (ATT) ¹⁷
Zn 0.921 0.889 0.063	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.65 eV
Zn 0.579 0.389 0.063	E_{rel} : 0.29 eV/ZnO
Zn 0.421 0.389 0.063	Pore _{max} : 0.28 nm
Zn 0.079 0.889 0.063	V _{pore} : 17 %
Zn 0.846 0.210 0.060	D _{pore} : 2
Zn 0.654 0.710 0.060	cell parameters
Zn 0.346 0.710 0.060	6.223 10.376 5.707 90.00 90.00 90.00
Zn 0.154 0.210 0.060	fractional coordinates
Zn 0.772 0.901 0.054	Zn 0.926 0.750 0.858
Zn 0.728 0.401 0.054	Zn 0.574 0.250 0.858
Zn 0.272 0.401 0.054	Zn 0.910 0.401 0.641
Zn 0.228 0.901 0.054	Zn 0.910 0.099 0.641
O 0.920 0.102 0.940	Zn 0.590 0.901 0.641
O 0.580 0.602 0.940	Zn 0.590 0.599 0.641
O 0.420 0.602 0.940	Zn 0.410 0.401 0.359
O 0.080 0.102 0.940	Zn 0.410 0.099 0.359
O 0.845 0.790 0.939	Zn 0.090 0.901 0.359
O 0.655 0.290 0.939	Zn 0.090 0.599 0.359
O 0.345 0.290 0.939	Zn 0.426 0.750 0.142
O 0.155 0.790 0.939	Zn 0.074 0.250 0.142
O 0.822 0.401 0.939	O 0.920 0.250 0.851
O 0.678 0.901 0.939	O 0.580 0.750 0.851
O 0.322 0.901 0.939	O 0.923 0.904 0.653
O 0.178 0.401 0.939	O 0.923 0.596 0.653
O 0.500 0.320 0.937	O 0.577 0.404 0.653
O 0.000 0.820 0.937	O 0.577 0.096 0.653
O 0.772 0.103 0.931	O 0.423 0.904 0.347
O 0.728 0.603 0.931	O 0.423 0.596 0.347
O 0.272 0.603 0.931	O 0.077 0.404 0.347
O 0.228 0.103 0.931	O 0.077 0.096 0.347
O 0.920 0.898 0.440	O 0.420 0.250 0.149
O 0.580 0.398 0.440	O 0.080 0.750 0.149
O 0.420 0.398 0.440	
O 0.080 0.898 0.440	Str 56 (ACO) ¹⁷
O 0.845 0.210 0.439	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.99 eV
O 0.655 0.710 0.439	E_{rel} : 0.23 eV/ZnO
O 0.345 0.710 0.439	Pore _{max} : 0.23 nm
O 0.155 0.210 0.439	V _{pore} : 17 %
O 0.822 0.599 0.439	D _{pore} : 3
O 0.678 0.099 0.439	cell parameters
O 0.322 0.099 0.439	6.278 6.278 6.278 90.00 90.00 90.00
O 0.178 0.599 0.439	fractional coordinates

Zn 0.835 0.165 0.835
 Zn 0.165 0.835 0.835
 Zn 0.665 0.665 0.665
 Zn 0.335 0.335 0.665
 Zn 0.665 0.335 0.335
 Zn 0.335 0.665 0.335
 Zn 0.835 0.835 0.165
 Zn 0.165 0.165 0.165
 O 0.838 0.838 0.838
 O 0.162 0.162 0.838
 O 0.662 0.338 0.662
 O 0.338 0.662 0.662
 O 0.662 0.662 0.338
 O 0.338 0.338 0.338
 O 0.838 0.162 0.162
 O 0.162 0.838 0.162

Str 57 (PON)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.33 eV

E_{rel} : 0.31 eV/ZnO

Pore_{max}: 0.30 nm

V_{pore}: 17 %

D_{pore}: 2

cell parameters

5.881 5.945 10.455 90.00 90.00 90.00

fractional coordinates

Zn 0.838 0.142 0.894
 Zn 0.338 0.858 0.894
 Zn 0.812 0.605 0.836
 Zn 0.312 0.395 0.836
 Zn 0.971 0.358 0.578
 Zn 0.471 0.642 0.578
 Zn 0.662 0.142 0.394
 Zn 0.162 0.858 0.394
 Zn 0.688 0.605 0.336
 Zn 0.188 0.395 0.336
 Zn 0.529 0.358 0.078
 Zn 0.029 0.642 0.078
 O 0.990 0.858 0.910
 O 0.490 0.142 0.910
 O 0.507 0.654 0.761
 O 0.007 0.346 0.761
 O 0.675 0.417 0.503
 O 0.175 0.583 0.503
 O 0.510 0.858 0.410
 O 0.010 0.142 0.410
 O 0.993 0.654 0.261
 O 0.493 0.346 0.261
 O 0.825 0.417 0.003
 O 0.325 0.583 0.003

Str 58 (ZON)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.59 eV

E_{rel} : 0.31 eV/ZnO

Pore_{max}: 0.32 nm

V_{pore}: 18 %

D_{pore}: 2

cell parameters

9.108 9.988 10.863 90.00 90.00 90.00

fractional coordinates

Zn 0.769 0.341 0.965
 Zn 0.731 0.841 0.965
 Zn 0.927 0.098 0.929
 Zn 0.573 0.598 0.929
 Zn 0.425 0.901 0.924
 Zn 0.075 0.401 0.924
 Zn 0.433 0.273 0.834
 Zn 0.067 0.773 0.834
 Zn 0.933 0.273 0.666
 Zn 0.567 0.773 0.666
 Zn 0.925 0.901 0.576
 Zn 0.575 0.401 0.576
 Zn 0.427 0.098 0.571
 Zn 0.073 0.598 0.571
 Zn 0.270 0.341 0.535
 Zn 0.231 0.841 0.535
 Zn 0.769 0.159 0.465
 Zn 0.731 0.659 0.465
 Zn 0.927 0.402 0.429
 Zn 0.573 0.902 0.429
 Zn 0.425 0.599 0.424
 Zn 0.075 0.099 0.424
 Zn 0.433 0.227 0.334
 Zn 0.067 0.727 0.334
 Zn 0.933 0.227 0.166
 Zn 0.567 0.727 0.166
 Zn 0.925 0.599 0.076
 Zn 0.575 0.099 0.076
 Zn 0.427 0.402 0.071
 Zn 0.073 0.902 0.071
 Zn 0.270 0.159 0.035
 Zn 0.231 0.659 0.035
 O 0.272 0.339 0.949
 O 0.228 0.839 0.949
 O 0.434 0.098 0.924
 O 0.066 0.598 0.924
 O 0.921 0.904 0.918
 O 0.579 0.404 0.918
 O 0.935 0.271 0.842
 O 0.565 0.771 0.842

O 0.435 0.271 0.658	O 0.979 0.750 0.824
O 0.065 0.771 0.658	O 0.521 0.250 0.824
O 0.421 0.904 0.582	O 0.863 0.398 0.661
O 0.079 0.404 0.582	O 0.863 0.102 0.661
O 0.934 0.098 0.576	O 0.637 0.898 0.661
O 0.566 0.598 0.576	O 0.637 0.602 0.661
O 0.772 0.339 0.551	O 0.349 0.750 0.625
O 0.728 0.839 0.551	O 0.151 0.250 0.625
O 0.272 0.161 0.449	O 0.849 0.750 0.375
O 0.228 0.661 0.449	O 0.651 0.250 0.375
O 0.434 0.402 0.424	O 0.363 0.398 0.339
O 0.066 0.902 0.424	O 0.363 0.102 0.339
O 0.921 0.596 0.418	O 0.137 0.898 0.339
O 0.579 0.096 0.418	O 0.137 0.602 0.339
O 0.935 0.229 0.342	O 0.479 0.750 0.176
O 0.565 0.729 0.342	O 0.021 0.250 0.176
O 0.435 0.229 0.158	
O 0.065 0.729 0.158	Str 60 (AFI) ¹⁷
O 0.421 0.596 0.082	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.48 eV
O 0.079 0.096 0.082	E_{rel} : 0.19 eV/ZnO
O 0.934 0.402 0.076	Pore _{max} : 0.48 nm
O 0.566 0.902 0.076	V _{pore} : 18 %
O 0.772 0.161 0.051	D _{pore} : 1
O 0.728 0.661 0.051	cell parameters
	8.925 8.925 5.298 90.00 90.00 120.00
Str 59 (OWE) ¹⁷	fractional coordinates
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.68 eV	Zn 0.877 0.326 0.688
E_{rel} : 0.36 eV/ZnO	Zn 0.674 0.551 0.688
Pore _{max} : 0.30 nm	Zn 0.551 0.877 0.688
V _{pore} : 18 %	Zn 0.449 0.123 0.688
D _{pore} : 2	Zn 0.326 0.449 0.688
cell parameters	Zn 0.123 0.674 0.688
9.477 9.404 5.534 90.00 90.00 90.00	Zn 0.877 0.551 0.188
fractional coordinates	Zn 0.674 0.123 0.188
Zn 0.981 0.250 0.833	Zn 0.551 0.674 0.188
Zn 0.519 0.750 0.833	Zn 0.449 0.326 0.188
Zn 0.861 0.899 0.645	Zn 0.326 0.877 0.188
Zn 0.861 0.601 0.645	Zn 0.123 0.449 0.188
Zn 0.639 0.399 0.645	O 0.878 0.552 0.812
Zn 0.639 0.101 0.645	O 0.674 0.122 0.812
Zn 0.355 0.250 0.620	O 0.552 0.674 0.812
Zn 0.145 0.750 0.620	O 0.448 0.326 0.812
Zn 0.855 0.250 0.380	O 0.326 0.878 0.812
Zn 0.645 0.750 0.380	O 0.122 0.448 0.812
Zn 0.361 0.899 0.355	O 0.878 0.326 0.312
Zn 0.361 0.601 0.355	O 0.674 0.552 0.312
Zn 0.139 0.399 0.355	O 0.552 0.878 0.312
Zn 0.139 0.101 0.355	O 0.448 0.122 0.312
Zn 0.481 0.250 0.167	O 0.326 0.448 0.312
Zn 0.019 0.750 0.167	O 0.122 0.674 0.312

Str 61 (LAU)¹⁷ $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.29 eV E_{rel} : 0.32 eV/ZnOPore_{max}: 0.33 nm V_{pore} : 19 % D_{pore} : 2

cell parameters

9.018 8.426 10.503 90.00 112.56 90.00

fractional coordinates

Zn 0.614 0.377 0.944

Zn 0.114 0.877 0.944

Zn 0.881 0.185 0.869

Zn 0.381 0.685 0.869

Zn 0.742 0.618 0.826

Zn 0.242 0.118 0.826

Zn 0.758 0.882 0.674

Zn 0.258 0.382 0.674

Zn 0.619 0.315 0.631

Zn 0.119 0.815 0.631

Zn 0.886 0.123 0.556

Zn 0.386 0.623 0.556

Zn 0.614 0.623 0.444

Zn 0.114 0.123 0.444

Zn 0.881 0.815 0.369

Zn 0.381 0.315 0.369

Zn 0.742 0.382 0.326

Zn 0.242 0.882 0.326

Zn 0.758 0.118 0.174

Zn 0.258 0.618 0.174

Zn 0.619 0.685 0.131

Zn 0.119 0.185 0.131

Zn 0.886 0.877 0.056

Zn 0.386 0.377 0.056

O 0.612 0.622 0.943

O 0.112 0.122 0.943

O 0.879 0.809 0.870

O 0.379 0.309 0.870

O 0.742 0.381 0.828

O 0.242 0.881 0.828

O 0.758 0.119 0.672

O 0.258 0.619 0.672

O 0.621 0.691 0.630

O 0.121 0.191 0.630

O 0.888 0.878 0.557

O 0.388 0.378 0.557

O 0.612 0.378 0.443

O 0.112 0.878 0.443

O 0.879 0.191 0.370

O 0.379 0.691 0.370

O 0.742 0.619 0.328

O 0.242 0.119 0.328

O 0.758 0.881 0.172

O 0.258 0.381 0.172

O 0.621 0.309 0.130

O 0.121 0.809 0.130

O 0.888 0.122 0.057

O 0.388 0.622 0.057

Str 62 (GIS)¹⁷ $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.52 eV E_{rel} : 0.29 eV/ZnOPore_{max}: 0.29 nm V_{pore} : 21 % D_{pore} : 3

cell parameters

6.409 6.409 6.327 90.00 90.00 88.87

fractional coordinates

Zn 0.837 0.413 0.875

Zn 0.163 0.087 0.875

Zn 0.663 0.087 0.625

Zn 0.337 0.413 0.625

Zn 0.663 0.587 0.375

Zn 0.337 0.913 0.375

Zn 0.837 0.913 0.125

Zn 0.163 0.587 0.125

O 0.838 0.088 0.875

O 0.162 0.412 0.875

O 0.662 0.412 0.625

O 0.338 0.088 0.625

O 0.662 0.912 0.375

O 0.338 0.588 0.375

O 0.838 0.588 0.125

O 0.162 0.912 0.125

Str 63 (SIV)¹⁷ $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.65 eV E_{rel} : 0.29 eV/ZnOPore_{max}: 0.32 nm V_{pore} : 21 % D_{pore} : 3

cell parameters

6.403 9.010 18.048 90.00 90.65 90.00

fractional coordinates

Zn 0.663 0.520 0.947

Zn 0.163 0.020 0.947

Zn 0.664 0.144 0.884

Zn 0.164 0.644 0.884

Zn 0.838 0.856 0.866

Zn 0.338 0.356 0.866

Zn 0.840 0.478 0.804	O 0.836 0.519 0.197
Zn 0.340 0.978 0.804	O 0.336 0.019 0.197
Zn 0.660 0.978 0.696	O 0.838 0.144 0.133
Zn 0.160 0.478 0.696	O 0.338 0.644 0.133
Zn 0.662 0.356 0.634	O 0.663 0.857 0.116
Zn 0.162 0.856 0.634	O 0.163 0.357 0.116
Zn 0.836 0.644 0.616	O 0.663 0.481 0.053
Zn 0.336 0.144 0.616	O 0.163 0.981 0.053
Zn 0.837 0.020 0.553	
Zn 0.337 0.520 0.553	Str 64 (OFF) ¹⁷
Zn 0.663 0.480 0.447	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.88 eV
Zn 0.163 0.980 0.447	E_{rel} : 0.29 eV/ZnO
Zn 0.664 0.856 0.384	Pore _{max} : 0.37 nm
Zn 0.164 0.356 0.384	V _{pore} : 21 %
Zn 0.838 0.144 0.366	D _{pore} : 3
Zn 0.338 0.644 0.366	cell parameters
Zn 0.840 0.522 0.304	8.036 8.036 10.395 90.00 90.00 120.00
Zn 0.340 0.022 0.304	fractional coordinates
Zn 0.660 0.022 0.196	Zn 0.998 0.249 0.902
Zn 0.160 0.522 0.196	Zn 0.751 0.749 0.902
Zn 0.662 0.644 0.134	Zn 0.251 0.002 0.902
Zn 0.162 0.144 0.134	Zn 0.582 0.931 0.750
Zn 0.836 0.356 0.116	Zn 0.348 0.418 0.750
Zn 0.336 0.856 0.116	Zn 0.069 0.652 0.750
Zn 0.837 0.980 0.053	Zn 0.998 0.249 0.598
Zn 0.337 0.480 0.053	Zn 0.751 0.749 0.598
O 0.837 0.019 0.947	Zn 0.251 0.002 0.598
O 0.337 0.519 0.947	Zn 0.998 0.749 0.402
O 0.837 0.643 0.884	Zn 0.751 0.002 0.402
O 0.337 0.143 0.884	Zn 0.251 0.249 0.402
O 0.662 0.356 0.867	Zn 0.582 0.652 0.250
O 0.162 0.856 0.867	Zn 0.348 0.931 0.250
O 0.664 0.981 0.803	Zn 0.069 0.418 0.250
O 0.164 0.481 0.803	Zn 0.998 0.749 0.098
O 0.836 0.481 0.697	Zn 0.751 0.002 0.098
O 0.336 0.981 0.697	Zn 0.251 0.249 0.098
O 0.838 0.856 0.633	O 0.993 0.741 0.904
O 0.338 0.356 0.633	O 0.748 0.007 0.904
O 0.663 0.143 0.616	O 0.259 0.252 0.904
O 0.163 0.643 0.616	O 0.582 0.660 0.750
O 0.663 0.519 0.553	O 0.340 0.922 0.750
O 0.163 0.019 0.553	O 0.078 0.418 0.750
O 0.837 0.981 0.447	O 0.993 0.741 0.596
O 0.337 0.481 0.447	O 0.748 0.007 0.596
O 0.837 0.357 0.384	O 0.259 0.252 0.596
O 0.337 0.857 0.384	O 0.993 0.252 0.404
O 0.662 0.644 0.367	O 0.748 0.741 0.404
O 0.162 0.144 0.367	O 0.259 0.007 0.404
O 0.664 0.019 0.303	O 0.582 0.922 0.250
O 0.164 0.519 0.303	O 0.340 0.418 0.250

O 0.078 0.660 0.250	Zn 0.055 0.835 0.750
O 0.993 0.252 0.096	Zn 0.906 0.298 0.598
O 0.748 0.741 0.096	Zn 0.702 0.608 0.598
O 0.259 0.007 0.096	Zn 0.608 0.906 0.598
Str 65 (MOZ) ¹⁷	Zn 0.392 0.094 0.598
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.72 eV	Zn 0.298 0.392 0.598
E_{rel} : 0.32 eV/ZnO	Zn 0.094 0.702 0.598
Pore _{max} : 0.65 nm	Zn 0.802 0.503 0.597
V _{pore} : 21 %	Zn 0.701 0.198 0.597
D _{pore} : 3	Zn 0.503 0.701 0.597
cell parameters	Zn 0.497 0.299 0.597
19.478 19.478 10.531 90.00 90.00	Zn 0.299 0.802 0.597
120.00	Zn 0.198 0.497 0.597
fractional coordinates	Zn 0.908 0.711 0.597
Zn 0.908 0.711 0.903	Zn 0.803 0.092 0.597
Zn 0.803 0.092 0.903	Zn 0.711 0.803 0.597
Zn 0.711 0.803 0.903	Zn 0.289 0.197 0.597
Zn 0.289 0.197 0.903	Zn 0.197 0.908 0.597
Zn 0.197 0.908 0.903	Zn 0.092 0.289 0.597
Zn 0.092 0.289 0.903	Zn 0.908 0.197 0.403
Zn 0.802 0.503 0.903	Zn 0.803 0.711 0.403
Zn 0.701 0.198 0.903	Zn 0.711 0.908 0.403
Zn 0.503 0.701 0.903	Zn 0.289 0.092 0.403
Zn 0.497 0.299 0.903	Zn 0.197 0.289 0.403
Zn 0.299 0.802 0.903	Zn 0.092 0.803 0.403
Zn 0.198 0.497 0.903	Zn 0.802 0.299 0.403
Zn 0.906 0.298 0.902	Zn 0.701 0.503 0.403
Zn 0.702 0.608 0.902	Zn 0.503 0.802 0.403
Zn 0.608 0.906 0.902	Zn 0.497 0.198 0.403
Zn 0.392 0.094 0.902	Zn 0.299 0.497 0.403
Zn 0.298 0.392 0.902	Zn 0.198 0.701 0.403
Zn 0.094 0.702 0.902	Zn 0.906 0.608 0.402
Zn 0.945 0.165 0.750	Zn 0.702 0.094 0.402
Zn 0.944 0.579 0.750	Zn 0.608 0.702 0.402
Zn 0.835 0.779 0.750	Zn 0.392 0.298 0.402
Zn 0.834 0.369 0.750	Zn 0.298 0.906 0.402
Zn 0.779 0.945 0.750	Zn 0.094 0.392 0.402
Zn 0.635 0.056 0.750	Zn 0.945 0.779 0.250
Zn 0.631 0.465 0.750	Zn 0.944 0.365 0.250
Zn 0.579 0.635 0.750	Zn 0.835 0.055 0.250
Zn 0.535 0.166 0.750	Zn 0.834 0.465 0.250
Zn 0.465 0.834 0.750	Zn 0.779 0.835 0.250
Zn 0.421 0.365 0.750	Zn 0.635 0.579 0.250
Zn 0.369 0.535 0.750	Zn 0.631 0.166 0.250
Zn 0.365 0.944 0.750	Zn 0.579 0.944 0.250
Zn 0.221 0.055 0.750	Zn 0.535 0.369 0.250
Zn 0.166 0.631 0.750	Zn 0.465 0.631 0.250
Zn 0.165 0.221 0.750	Zn 0.421 0.056 0.250
Zn 0.056 0.421 0.750	Zn 0.369 0.834 0.250
	Zn 0.365 0.421 0.250

Zn 0.221 0.165 0.250	O 0.470 0.632 0.750
Zn 0.166 0.535 0.250	O 0.426 0.058 0.750
Zn 0.165 0.945 0.250	O 0.368 0.838 0.750
Zn 0.056 0.635 0.250	O 0.367 0.426 0.750
Zn 0.055 0.221 0.250	O 0.219 0.159 0.750
Zn 0.906 0.608 0.098	O 0.162 0.530 0.750
Zn 0.702 0.094 0.098	O 0.159 0.941 0.750
Zn 0.608 0.702 0.098	O 0.059 0.219 0.750
Zn 0.392 0.298 0.098	O 0.058 0.633 0.750
Zn 0.298 0.906 0.098	O 0.800 0.302 0.596
Zn 0.094 0.392 0.098	O 0.698 0.499 0.596
Zn 0.802 0.299 0.097	O 0.501 0.200 0.596
Zn 0.701 0.503 0.097	O 0.499 0.800 0.596
Zn 0.503 0.802 0.097	O 0.302 0.501 0.596
Zn 0.497 0.198 0.097	O 0.200 0.698 0.596
Zn 0.299 0.497 0.097	O 0.911 0.199 0.595
Zn 0.198 0.701 0.097	O 0.801 0.712 0.595
Zn 0.908 0.197 0.097	O 0.712 0.911 0.595
Zn 0.803 0.711 0.097	O 0.288 0.089 0.595
Zn 0.711 0.908 0.097	O 0.199 0.288 0.595
Zn 0.289 0.092 0.097	O 0.089 0.801 0.595
Zn 0.197 0.289 0.097	O 0.908 0.610 0.594
Zn 0.092 0.803 0.097	O 0.702 0.092 0.594
O 0.908 0.610 0.906	O 0.610 0.702 0.594
O 0.702 0.092 0.906	O 0.390 0.298 0.594
O 0.610 0.702 0.906	O 0.298 0.908 0.594
O 0.390 0.298 0.906	O 0.092 0.390 0.594
O 0.298 0.908 0.906	O 0.908 0.298 0.406
O 0.092 0.390 0.906	O 0.702 0.610 0.406
O 0.911 0.199 0.905	O 0.610 0.908 0.406
O 0.801 0.712 0.905	O 0.390 0.092 0.406
O 0.712 0.911 0.905	O 0.298 0.390 0.406
O 0.288 0.089 0.905	O 0.092 0.702 0.406
O 0.199 0.288 0.905	O 0.911 0.712 0.405
O 0.089 0.801 0.905	O 0.801 0.089 0.405
O 0.800 0.302 0.904	O 0.712 0.801 0.405
O 0.698 0.499 0.904	O 0.288 0.199 0.405
O 0.501 0.200 0.904	O 0.199 0.911 0.405
O 0.499 0.800 0.904	O 0.089 0.288 0.405
O 0.302 0.501 0.904	O 0.800 0.499 0.404
O 0.200 0.698 0.904	O 0.698 0.200 0.404
O 0.942 0.367 0.750	O 0.501 0.302 0.404
O 0.941 0.781 0.750	O 0.499 0.698 0.404
O 0.841 0.059 0.750	O 0.302 0.800 0.404
O 0.838 0.470 0.750	O 0.200 0.501 0.404
O 0.781 0.841 0.750	O 0.942 0.574 0.250
O 0.633 0.574 0.750	O 0.941 0.159 0.250
O 0.632 0.162 0.750	O 0.841 0.781 0.250
O 0.574 0.942 0.750	O 0.838 0.368 0.250
O 0.530 0.368 0.750	O 0.781 0.941 0.250

O 0.633 0.058 0.250	Zn 0.337 0.394 0.483
O 0.632 0.470 0.250	Zn 0.840 0.273 0.358
O 0.574 0.633 0.250	Zn 0.340 0.773 0.358
O 0.530 0.162 0.250	Zn 0.660 0.773 0.142
O 0.470 0.838 0.250	Zn 0.160 0.273 0.142
O 0.426 0.367 0.250	Zn 0.663 0.394 0.017
O 0.368 0.530 0.250	Zn 0.163 0.894 0.017
O 0.367 0.942 0.250	O 0.663 0.607 0.986
O 0.219 0.059 0.250	O 0.163 0.107 0.986
O 0.162 0.632 0.250	O 0.664 0.230 0.857
O 0.159 0.219 0.250	O 0.165 0.730 0.857
O 0.059 0.841 0.250	O 0.835 0.730 0.643
O 0.058 0.426 0.250	O 0.336 0.230 0.643
O 0.800 0.499 0.096	O 0.837 0.107 0.514
O 0.698 0.200 0.096	O 0.337 0.607 0.514
O 0.501 0.302 0.096	O 0.663 0.393 0.486
O 0.499 0.698 0.096	O 0.163 0.893 0.486
O 0.302 0.800 0.096	O 0.664 0.770 0.357
O 0.200 0.501 0.096	O 0.165 0.270 0.357
O 0.911 0.712 0.095	O 0.835 0.270 0.143
O 0.801 0.089 0.095	O 0.336 0.770 0.143
O 0.712 0.801 0.095	O 0.837 0.893 0.014
O 0.288 0.199 0.095	O 0.337 0.393 0.014
O 0.199 0.911 0.095	
O 0.089 0.288 0.095	Str 67 (MER) ¹⁷
O 0.908 0.298 0.094	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.86 eV
O 0.702 0.610 0.094	E_{rel} : 0.30 eV/ZnO
O 0.610 0.908 0.094	Pore _{max} : 0.39 nm
O 0.390 0.092 0.094	V _{pore} : 21 %
O 0.298 0.390 0.094	D _{pore} : 3
O 0.092 0.702 0.094	cell parameters
	9.046 9.046 6.425 90.00 90.00 90.00
Str 66 (PHI) ¹⁷	fractional coordinates
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.81 eV	Zn 0.893 0.731 0.839
E_{rel} : 0.29 eV/ZnO	Zn 0.731 0.107 0.839
Pore _{max} : 0.32 nm	Zn 0.269 0.893 0.839
V _{pore} : 21 %	Zn 0.107 0.269 0.839
D _{pore} : 3	Zn 0.769 0.393 0.661
cell parameters	Zn 0.607 0.769 0.661
6.418 9.026 9.030 90.00 90.59 90.00	Zn 0.393 0.231 0.661
fractional coordinates	Zn 0.231 0.607 0.661
Zn 0.837 0.106 0.983	Zn 0.769 0.607 0.339
Zn 0.337 0.606 0.983	Zn 0.607 0.231 0.339
Zn 0.340 0.227 0.858	Zn 0.393 0.769 0.339
Zn 0.840 0.727 0.858	Zn 0.231 0.393 0.339
Zn 0.660 0.227 0.642	Zn 0.893 0.269 0.161
Zn 0.160 0.727 0.642	Zn 0.731 0.893 0.161
Zn 0.663 0.606 0.517	Zn 0.269 0.107 0.161
Zn 0.163 0.106 0.517	Zn 0.107 0.731 0.161
Zn 0.837 0.894 0.483	O 0.893 0.266 0.836

O 0.734 0.893 0.836
 O 0.266 0.107 0.836
 O 0.107 0.734 0.836
 O 0.766 0.607 0.664
 O 0.607 0.234 0.664
 O 0.393 0.766 0.664
 O 0.234 0.393 0.664
 O 0.766 0.393 0.336
 O 0.607 0.766 0.336
 O 0.393 0.234 0.336
 O 0.234 0.607 0.336
 O 0.893 0.734 0.164
 O 0.734 0.107 0.164
 O 0.266 0.893 0.164
 O 0.107 0.266 0.164

Str 68 (UMK)¹⁹

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.85 eV

E_{rel} : 0.24 eV/ZnO

Pore_{max}: 0.48 nm

V_{pore}: 22 %

D_{pore}: 1

cell parameters

8.947 8.948 5.559 90.00 90.00 120.00

fractional coordinates

Zn 0.321 0.451 0.934

Zn 0.127 0.668 0.934

Zn 0.538 0.862 0.934

Zn 0.864 0.536 0.570

Zn 0.669 0.125 0.570

Zn 0.453 0.320 0.570

Zn 0.127 0.451 0.434

Zn 0.538 0.668 0.434

Zn 0.321 0.862 0.434

Zn 0.864 0.320 0.070

Zn 0.669 0.536 0.070

Zn 0.453 0.125 0.070

O 0.867 0.538 0.936

O 0.667 0.122 0.935

O 0.451 0.322 0.935

O 0.323 0.450 0.569

O 0.123 0.666 0.569

O 0.539 0.866 0.569

O 0.867 0.322 0.436

O 0.667 0.538 0.436

O 0.451 0.122 0.435

O 0.123 0.450 0.069

O 0.323 0.866 0.069

O 0.539 0.666 0.069

Str 69 (LEV)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.84 eV

E_{rel} : 0.28 eV/ZnO

Pore_{max}: 0.37 nm

V_{pore}: 22 %

D_{pore}: 3

cell parameters

8.203 8.203 30.509 90.00 90.00 120.00

fractional coordinates

Zn 0.755 0.758 0.966

Zn 0.242 0.997 0.966

Zn 0.003 0.245 0.966

Zn 0.915 0.582 0.917

Zn 0.667 0.085 0.917

Zn 0.418 0.333 0.917

Zn 0.578 0.669 0.867

Zn 0.331 0.909 0.867

Zn 0.091 0.422 0.867

Zn 0.575 0.912 0.800

Zn 0.336 0.425 0.800

Zn 0.088 0.664 0.800

Zn 0.752 0.752 0.750

Zn 0.248 0.000 0.750

Zn 0.000 0.248 0.750

Zn 0.912 0.575 0.700

Zn 0.664 0.088 0.700

Zn 0.425 0.336 0.700

Zn 0.909 0.331 0.633

Zn 0.669 0.578 0.633

Zn 0.422 0.091 0.633

Zn 0.582 0.915 0.583

Zn 0.333 0.418 0.583

Zn 0.085 0.667 0.583

Zn 0.997 0.242 0.534

Zn 0.758 0.755 0.534

Zn 0.245 0.003 0.534

Zn 0.755 0.997 0.466

Zn 0.242 0.245 0.466

Zn 0.003 0.758 0.466

Zn 0.915 0.333 0.417

Zn 0.667 0.582 0.417

Zn 0.418 0.085 0.417

Zn 0.578 0.909 0.367

Zn 0.331 0.422 0.367

Zn 0.091 0.669 0.367

Zn 0.575 0.664 0.300

Zn 0.336 0.912 0.300

Zn 0.088 0.425 0.300

Zn 0.752 0.000 0.250

Zn 0.248 0.248 0.250

Zn 0.000 0.752 0.250	O 0.341 0.421 0.300
Zn 0.912 0.336 0.200	O 0.080 0.659 0.300
Zn 0.664 0.575 0.200	O 0.755 0.755 0.250
Zn 0.425 0.088 0.200	O 0.245 0.000 0.250
Zn 0.909 0.578 0.133	O 0.000 0.245 0.250
Zn 0.669 0.091 0.133	O 0.920 0.579 0.200
Zn 0.422 0.331 0.133	O 0.659 0.080 0.200
Zn 0.582 0.667 0.083	O 0.421 0.341 0.200
Zn 0.333 0.915 0.083	O 0.912 0.326 0.134
Zn 0.085 0.418 0.083	O 0.674 0.587 0.134
Zn 0.997 0.755 0.034	O 0.413 0.088 0.134
Zn 0.758 0.003 0.034	O 0.578 0.912 0.083
Zn 0.245 0.242 0.034	O 0.333 0.422 0.083
O 0.747 0.992 0.967	O 0.088 0.667 0.083
O 0.246 0.253 0.967	O 0.992 0.246 0.033
O 0.008 0.754 0.967	O 0.754 0.747 0.033
O 0.912 0.333 0.917	O 0.253 0.008 0.033
O 0.667 0.578 0.917	
O 0.422 0.088 0.917	Str 70 (EZT) ¹⁷
O 0.587 0.912 0.866	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.73 eV
O 0.326 0.413 0.866	E_{rel} : 0.30 eV/ZnO
O 0.088 0.674 0.866	Pore _{max} : 0.38 nm
O 0.579 0.659 0.800	V _{pore} : 22 %
O 0.341 0.920 0.800	D _{pore} : 3
O 0.080 0.421 0.800	cell parameters
O 0.755 0.000 0.750	6.893 8.088 13.962 89.45 90.00 90.00
O 0.245 0.245 0.750	fractional coordinates
O 0.000 0.755 0.750	Zn 0.500 0.133 0.926
O 0.920 0.341 0.700	Zn 0.759 0.875 0.884
O 0.659 0.579 0.700	Zn 0.241 0.875 0.884
O 0.421 0.080 0.700	Zn 0.500 0.540 0.823
O 0.912 0.587 0.634	Zn 0.000 0.616 0.807
O 0.674 0.088 0.634	Zn 0.500 0.884 0.693
O 0.413 0.326 0.634	Zn 0.000 0.960 0.677
O 0.578 0.667 0.583	Zn 0.741 0.625 0.616
O 0.333 0.912 0.583	Zn 0.259 0.625 0.616
O 0.088 0.422 0.583	Zn 0.000 0.367 0.574
O 0.992 0.747 0.533	Zn 0.793 0.000 0.500
O 0.754 0.008 0.533	Zn 0.207 0.000 0.500
O 0.253 0.246 0.533	Zn 0.000 0.633 0.426
O 0.747 0.754 0.467	Zn 0.741 0.375 0.384
O 0.246 0.992 0.467	Zn 0.259 0.375 0.384
O 0.008 0.253 0.467	Zn 0.000 0.040 0.323
O 0.912 0.578 0.417	Zn 0.500 0.116 0.307
O 0.667 0.088 0.417	Zn 0.000 0.384 0.193
O 0.422 0.333 0.417	Zn 0.500 0.460 0.177
O 0.587 0.674 0.366	Zn 0.759 0.125 0.116
O 0.326 0.912 0.366	Zn 0.241 0.125 0.116
O 0.088 0.413 0.366	Zn 0.500 0.867 0.074
O 0.579 0.920 0.300	Zn 0.707 0.500 0.000

Zn 0.293 0.500 0.000
 O 0.500 0.366 0.923
 O 0.760 0.625 0.885
 O 0.240 0.625 0.885
 O 0.500 0.954 0.824
 O 0.000 0.888 0.808
 O 0.500 0.612 0.692
 O 0.000 0.546 0.676
 O 0.740 0.875 0.615
 O 0.260 0.875 0.615
 O 0.000 0.134 0.577
 O 0.792 0.500 0.500
 O 0.208 0.500 0.500
 O 0.000 0.866 0.423
 O 0.740 0.125 0.385
 O 0.260 0.125 0.385
 O 0.000 0.454 0.324
 O 0.500 0.388 0.308
 O 0.000 0.112 0.192
 O 0.500 0.046 0.176
 O 0.760 0.375 0.115
 O 0.240 0.375 0.115
 O 0.500 0.634 0.077
 O 0.708 1.000 0.000
 O 0.292 1.000 0.000

Str 71 (EAB)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.73 eV

E_{rel} : 0.28 eV/ZnO

Pore_{max}: 0.37 nm

V_{pore} : 22 %

D_{pore} : 3

cell parameters

8.196 8.196 10.188 90.00 90.00 120.00

fractional coordinates

Zn 0.575 0.912 0.851

Zn 0.337 0.425 0.851

Zn 0.088 0.663 0.851

Zn 0.575 0.663 0.649

Zn 0.337 0.912 0.649

Zn 0.088 0.425 0.649

Zn 0.752 0.000 0.500

Zn 0.248 0.248 0.500

Zn 0.000 0.752 0.500

Zn 0.912 0.337 0.351

Zn 0.663 0.575 0.351

Zn 0.425 0.088 0.351

Zn 0.912 0.575 0.149

Zn 0.663 0.088 0.149

Zn 0.425 0.337 0.149

Zn 0.752 0.752 0.000

Zn 0.248 0.000 0.000

Zn 0.000 0.248 0.000

O 0.580 0.661 0.848

O 0.339 0.919 0.848

O 0.081 0.420 0.848

O 0.580 0.919 0.652

O 0.339 0.420 0.652

O 0.081 0.661 0.652

O 0.754 0.754 0.500

O 0.246 0.000 0.500

O 0.000 0.246 0.500

O 0.919 0.580 0.348

O 0.661 0.081 0.348

O 0.420 0.339 0.348

O 0.919 0.339 0.152

O 0.661 0.580 0.152

O 0.420 0.081 0.152

O 0.754 0.000 0.000

O 0.246 0.246 0.000

O 0.000 0.754 0.000

Str 72 (ATS)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.78 eV

E_{rel} : 0.23 eV/ZnO

Pore_{max}: 0.40 nm

V_{pore} : 22 %

D_{pore} : 1

cell parameters

8.430 13.663 3.391 90.00 90.00 89.72

fractional coordinates

Zn 0.872 0.527 0.750

Zn 0.689 0.164 0.750

Zn 0.616 0.750 0.750

Zn 0.372 0.027 0.750

Zn 0.189 0.664 0.750

Zn 0.116 0.250 0.750

Zn 0.889 0.731 0.250

Zn 0.815 0.317 0.250

Zn 0.633 0.954 0.250

Zn 0.389 0.231 0.250

Zn 0.315 0.817 0.250

Zn 0.133 0.454 0.250

O 0.888 0.248 0.750

O 0.810 0.663 0.750

O 0.634 0.028 0.750

O 0.388 0.748 0.750

O 0.310 0.163 0.750

O 0.134 0.528 0.750

O 0.695 0.818 0.250

O 0.616 0.233 0.250	Zn 0.624 0.718 0.750
O 0.370 0.954 0.250	Zn 0.376 0.282 0.750
O 0.195 0.318 0.250	Zn 0.282 0.905 0.750
O 0.116 0.733 0.250	Zn 0.095 0.376 0.750
O 0.870 0.454 0.250	Zn 0.844 0.335 0.597
	Zn 0.665 0.509 0.597
Str 73 (BCB) ¹⁹	Zn 0.509 0.844 0.597
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}}): 0.75 \text{ eV}$	Zn 0.491 0.156 0.597
$E_{\text{rel}}: 0.27 \text{ eV/ZnO}$	Zn 0.335 0.491 0.597
Pore _{max} : 0.47 nm	Zn 0.156 0.665 0.597
V _{pore} : 23 %	Zn 0.844 0.509 0.403
D _{pore} : 3	Zn 0.665 0.156 0.403
cell parameters	Zn 0.509 0.665 0.403
8.825 8.827 3.400 90.00 90.00 90.03	Zn 0.491 0.335 0.403
fractional coordinates	Zn 0.335 0.844 0.403
Zn 0.787 0.656 0.574	Zn 0.156 0.491 0.403
Zn 0.636 0.245 0.574	Zn 0.905 0.282 0.250
Zn 0.376 0.806 0.574	Zn 0.718 0.624 0.250
Zn 0.226 0.396 0.574	Zn 0.624 0.905 0.250
Zn 0.894 0.410 0.074	Zn 0.376 0.095 0.250
Zn 0.622 0.913 0.074	Zn 0.282 0.376 0.250
Zn 0.391 0.139 0.074	Zn 0.095 0.718 0.250
Zn 0.119 0.641 0.074	Zn 0.844 0.509 0.097
O 0.779 0.414 0.574	Zn 0.665 0.156 0.097
O 0.619 0.798 0.574	Zn 0.509 0.665 0.097
O 0.394 0.253 0.574	Zn 0.491 0.335 0.097
O 0.234 0.638 0.574	Zn 0.335 0.844 0.097
O 0.900 0.662 0.074	Zn 0.156 0.491 0.097
O 0.642 0.132 0.074	O 0.849 0.511 0.906
O 0.371 0.920 0.074	O 0.662 0.151 0.906
O 0.113 0.390 0.074	O 0.511 0.662 0.906
	O 0.489 0.338 0.906
Str 74 (LTL) ¹⁷	O 0.338 0.849 0.906
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}}): 0.73 \text{ eV}$	O 0.151 0.489 0.906
$E_{\text{rel}}: 0.33 \text{ eV/ZnO}$	O 0.899 0.272 0.750
Pore _{max} : 0.65 nm	O 0.728 0.627 0.750
V _{pore} : 24 %	O 0.627 0.899 0.750
D _{pore} : 3	O 0.373 0.101 0.750
cell parameters	O 0.272 0.373 0.750
11.418 11.418 10.623 90.00 90.00	O 0.101 0.728 0.750
120.00	O 0.849 0.511 0.594
fractional coordinates	O 0.662 0.151 0.594
Zn 0.844 0.335 0.903	O 0.511 0.662 0.594
Zn 0.665 0.509 0.903	O 0.489 0.338 0.594
Zn 0.509 0.844 0.903	O 0.338 0.849 0.594
Zn 0.491 0.156 0.903	O 0.151 0.489 0.594
Zn 0.335 0.491 0.903	O 0.849 0.338 0.406
Zn 0.156 0.665 0.903	O 0.662 0.511 0.406
Zn 0.905 0.624 0.750	O 0.511 0.849 0.406
Zn 0.718 0.095 0.750	O 0.489 0.151 0.406

O 0.338 0.489 0.406
 O 0.151 0.662 0.406
 O 0.899 0.627 0.250
 O 0.728 0.101 0.250
 O 0.627 0.728 0.250
 O 0.373 0.272 0.250
 O 0.272 0.899 0.250
 O 0.101 0.373 0.250
 O 0.849 0.338 0.094
 O 0.662 0.511 0.094
 O 0.511 0.849 0.094
 O 0.489 0.151 0.094
 O 0.338 0.489 0.094
 O 0.151 0.662 0.094

Str 75 (VFI)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.71 eV

E_{rel} : 0.28 eV/ZnO

Pore_{max}: 0.57 nm

V_{pore}: 25 %

D_{pore}: 1

cell parameters

11.552 11.552 5.372 90.00 90.00
 120.01

fractional coordinates

Zn 1.000 0.377 0.583

Zn 0.377 1.000 0.583

Zn 0.623 0.623 0.583

Zn 0.674 0.168 0.560

Zn 0.168 0.674 0.560

Zn 0.506 0.832 0.560

Zn 0.494 0.326 0.560

Zn 0.326 0.494 0.560

Zn 0.832 0.506 0.560

Zn 0.623 0.000 0.083

Zn 0.000 0.623 0.083

Zn 0.377 0.377 0.083

Zn 0.832 0.326 0.060

Zn 0.494 0.168 0.060

Zn 0.326 0.832 0.060

Zn 0.168 0.494 0.060

Zn 0.674 0.506 0.060

Zn 0.506 0.674 0.060

O 0.666 0.170 0.933

O 0.504 0.334 0.933

O 0.496 0.830 0.933

O 0.334 0.504 0.933

O 0.170 0.666 0.933

O 0.830 0.496 0.933

O 1.000 0.351 0.930

O 0.351 1.000 0.930

O 0.649 0.649 0.930

O 0.830 0.334 0.433

O 0.504 0.170 0.433

O 0.334 0.830 0.433

O 0.170 0.504 0.433

O 0.666 0.496 0.433

O 0.496 0.666 0.433

O 0.649 0.000 0.430

O 0.000 0.649 0.430

O 0.351 0.351 0.430

Str 76 (CHA)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.21 eV

E_{rel} : 0.30 eV/ZnO

Pore_{max}: 0.39 nm

V_{pore}: 26 %

D_{pore}: 3

cell parameters

8.575 8.577 9.857 90.00 90.00 120.00

fractional coordinates

Zn 0.566 0.919 0.962

Zn 0.092 0.672 0.962

Zn 0.340 0.446 0.962

Zn 0.326 0.912 0.752

Zn 0.573 0.686 0.752

Zn 0.099 0.439 0.752

Zn 0.899 0.586 0.629

Zn 0.673 0.112 0.629

Zn 0.426 0.339 0.629

Zn 0.907 0.353 0.419

Zn 0.659 0.579 0.419

Zn 0.433 0.105 0.419

Zn 0.007 0.779 0.296

Zn 0.759 0.005 0.295

Zn 0.233 0.253 0.295

Zn 0.992 0.246 0.086

Zn 0.240 0.019 0.086

Zn 0.766 0.772 0.086

O 0.093 0.446 0.961

O 0.566 0.673 0.961

O 0.339 0.919 0.961

O 0.100 0.685 0.753

O 0.573 0.912 0.753

O 0.326 0.439 0.753

O 0.899 0.339 0.628

O 0.426 0.112 0.628

O 0.672 0.585 0.627

O 0.906 0.579 0.420

O 0.660 0.106 0.420

O 0.433 0.352 0.420	fractional coordinates
O 0.233 0.006 0.294	Zn 0.816 0.622 0.938
O 0.006 0.252 0.294	Zn 0.684 0.878 0.938
O 0.760 0.779 0.294	Zn 0.483 0.860 0.923
O 0.993 0.773 0.087	Zn 0.017 0.640 0.923
O 0.766 0.019 0.087	Zn 0.412 0.454 0.922
O 0.239 0.246 0.087	Zn 0.088 0.046 0.922
	Zn 0.909 0.862 0.773
Str 77 (GME) ¹⁷	Zn 0.591 0.638 0.773
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.07 eV	Zn 0.409 0.138 0.727
E_{rel} : 0.29 eV/ZnO	Zn 0.091 0.362 0.727
Pore _{max} : 0.43 nm	Zn 0.912 0.546 0.578
V _{pore} : 26 %	Zn 0.588 0.954 0.578
D _{pore} : 3	Zn 0.983 0.140 0.577
cell parameters	Zn 0.517 0.360 0.577
8.670 8.670 6.440 90.00 90.00 120.00	Zn 0.316 0.378 0.562
fractional coordinates	Zn 0.184 0.122 0.562
Zn 0.571 0.673 0.910	Zn 0.816 0.878 0.438
Zn 0.327 0.898 0.910	Zn 0.684 0.622 0.438
Zn 0.102 0.429 0.910	Zn 0.483 0.640 0.423
Zn 0.571 0.898 0.590	Zn 0.017 0.860 0.423
Zn 0.327 0.429 0.590	Zn 0.412 0.046 0.422
Zn 0.102 0.673 0.590	Zn 0.088 0.454 0.422
Zn 0.898 0.327 0.410	Zn 0.909 0.638 0.273
Zn 0.673 0.571 0.410	Zn 0.591 0.862 0.273
Zn 0.429 0.102 0.410	Zn 0.409 0.362 0.227
Zn 0.898 0.571 0.090	Zn 0.091 0.138 0.227
Zn 0.673 0.102 0.090	Zn 0.912 0.954 0.078
Zn 0.429 0.327 0.090	Zn 0.588 0.546 0.078
O 0.569 0.896 0.910	Zn 0.983 0.360 0.077
O 0.327 0.431 0.910	Zn 0.517 0.140 0.077
O 0.104 0.673 0.910	Zn 0.316 0.122 0.062
O 0.569 0.673 0.590	Zn 0.184 0.378 0.062
O 0.327 0.896 0.590	O 0.817 0.879 0.940
O 0.104 0.431 0.590	O 0.683 0.621 0.940
O 0.896 0.569 0.410	O 0.486 0.642 0.929
O 0.673 0.104 0.410	O 0.014 0.858 0.929
O 0.431 0.327 0.410	O 0.412 0.048 0.920
O 0.896 0.327 0.090	O 0.088 0.452 0.920
O 0.673 0.569 0.090	O 0.907 0.630 0.774
O 0.431 0.104 0.090	O 0.592 0.870 0.774
	O 0.407 0.370 0.726
Str 78 (AFR) ¹⁷	O 0.092 0.130 0.726
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.04 eV	O 0.912 0.952 0.580
E_{rel} : 0.34 eV/ZnO	O 0.588 0.548 0.580
Pore _{max} : 0.48 nm	O 0.986 0.358 0.571
V _{pore} : 28 %	O 0.514 0.142 0.571
D _{pore} : 2	O 0.317 0.121 0.560
cell parameters	O 0.183 0.379 0.560
14.284 8.771 9.083 90.00 90.00 90.00	O 0.817 0.621 0.440

O 0.683 0.879 0.440
 O 0.486 0.858 0.429
 O 0.014 0.642 0.429
 O 0.412 0.452 0.420
 O 0.088 0.048 0.420
 O 0.907 0.870 0.274
 O 0.592 0.630 0.274
 O 0.407 0.130 0.226
 O 0.092 0.370 0.226
 O 0.912 0.548 0.080
 O 0.588 0.952 0.080
 O 0.986 0.142 0.071
 O 0.514 0.358 0.071
 O 0.317 0.379 0.060
 O 0.183 0.121 0.060

Str 79 (SFO)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.03 eV

E_{rel} : 0.34 eV/ZnO

Pore_{max}: 0.47 nm

V_{pore}: 28 %

D_{pore}: 2

cell parameters

14.435 8.766 9.091 90.00 98.36 90.00

fractional coordinates

Zn 0.934 0.873 0.980

Zn 0.434 0.373 0.980

Zn 0.733 0.890 0.919

Zn 0.233 0.390 0.919

Zn 0.662 0.297 0.903

Zn 0.162 0.797 0.903

Zn 0.341 0.612 0.793

Zn 0.841 0.112 0.793

Zn 0.659 0.612 0.707

Zn 0.159 0.112 0.707

Zn 0.838 0.797 0.597

Zn 0.338 0.297 0.597

Zn 0.767 0.390 0.581

Zn 0.267 0.890 0.581

Zn 0.566 0.373 0.520

Zn 0.066 0.873 0.520

Zn 0.934 0.127 0.480

Zn 0.434 0.627 0.480

Zn 0.733 0.110 0.419

Zn 0.233 0.610 0.419

Zn 0.662 0.703 0.403

Zn 0.162 0.203 0.403

Zn 0.841 0.888 0.293

Zn 0.341 0.388 0.293

Zn 0.659 0.388 0.207

Zn 0.159 0.888 0.207

Zn 0.838 0.203 0.097

Zn 0.338 0.703 0.097

Zn 0.767 0.610 0.081

Zn 0.267 0.110 0.081

Zn 0.566 0.627 0.020

Zn 0.066 0.127 0.020

O 0.933 0.129 0.981

O 0.433 0.629 0.981

O 0.736 0.108 0.925

O 0.236 0.608 0.925

O 0.663 0.702 0.900

O 0.163 0.202 0.900

O 0.843 0.880 0.795

O 0.343 0.380 0.795

O 0.657 0.380 0.705

O 0.157 0.880 0.705

O 0.837 0.202 0.600

O 0.337 0.702 0.600

O 0.764 0.608 0.575

O 0.264 0.108 0.575

O 0.567 0.629 0.519

O 0.067 0.129 0.519

O 0.933 0.871 0.481

O 0.433 0.371 0.481

O 0.736 0.892 0.425

O 0.236 0.392 0.425

O 0.663 0.298 0.400

O 0.163 0.798 0.400

O 0.843 0.120 0.295

O 0.343 0.620 0.295

O 0.657 0.620 0.205

O 0.157 0.120 0.205

O 0.837 0.798 0.100

O 0.337 0.298 0.100

O 0.764 0.392 0.075

O 0.264 0.892 0.075

O 0.567 0.371 0.019

O 0.067 0.871 0.019

Str 80 (USI)¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.77 eV

E_{rel} : 0.44 eV/ZnO

Pore_{max}: 0.42 nm

V_{pore}: 29 %

D_{pore}: 2

cell parameters

13.825 8.406 6.433 90.00 108.75 90.15

fractional coordinates

Zn 0.286 0.118 0.896

Zn 0.786 0.618 0.896	Zn 0.719 0.281 0.914
Zn 0.689 0.177 0.801	Zn 0.281 0.086 0.914
Zn 0.189 0.677 0.801	Zn 0.086 0.719 0.914
Zn 0.841 0.329 0.653	Zn 0.586 0.219 0.781
Zn 0.341 0.829 0.653	Zn 0.414 0.586 0.781
Zn 0.785 0.886 0.635	Zn 0.219 0.414 0.781
Zn 0.285 0.386 0.635	Zn 0.914 0.086 0.719
Zn 0.072 0.368 0.535	Zn 0.281 0.914 0.719
Zn 0.572 0.868 0.535	Zn 0.086 0.281 0.719
Zn 0.928 0.632 0.465	Zn 0.781 0.414 0.586
Zn 0.428 0.132 0.465	Zn 0.414 0.219 0.586
Zn 0.715 0.614 0.365	Zn 0.219 0.781 0.586
Zn 0.215 0.114 0.365	Zn 0.781 0.219 0.414
Zn 0.659 0.171 0.347	Zn 0.586 0.781 0.414
Zn 0.159 0.671 0.347	Zn 0.219 0.586 0.414
Zn 0.811 0.323 0.199	Zn 0.914 0.719 0.281
Zn 0.311 0.823 0.199	Zn 0.719 0.086 0.281
Zn 0.214 0.382 0.104	Zn 0.086 0.914 0.281
Zn 0.714 0.882 0.104	Zn 0.781 0.586 0.219
O 0.785 0.382 0.892	Zn 0.586 0.414 0.219
O 0.285 0.882 0.892	Zn 0.414 0.781 0.219
O 0.183 0.306 0.800	Zn 0.914 0.281 0.086
O 0.683 0.806 0.800	Zn 0.719 0.914 0.086
O 0.847 0.678 0.663	Zn 0.281 0.719 0.086
O 0.347 0.178 0.663	O 0.720 0.089 0.911
O 0.785 0.108 0.633	O 0.280 0.720 0.911
O 0.285 0.608 0.633	O 0.089 0.280 0.911
O 0.573 0.129 0.531	O 0.589 0.411 0.780
O 0.073 0.629 0.531	O 0.411 0.220 0.780
O 0.927 0.371 0.469	O 0.220 0.589 0.780
O 0.427 0.871 0.469	O 0.911 0.280 0.720
O 0.715 0.392 0.367	O 0.280 0.089 0.720
O 0.215 0.892 0.367	O 0.089 0.911 0.720
O 0.153 0.322 0.337	O 0.780 0.220 0.589
O 0.653 0.822 0.337	O 0.411 0.780 0.589
O 0.817 0.694 0.200	O 0.220 0.411 0.589
O 0.317 0.194 0.200	O 0.780 0.589 0.411
O 0.715 0.118 0.108	O 0.589 0.220 0.411
O 0.215 0.618 0.108	O 0.220 0.780 0.411
	O 0.911 0.089 0.280
Str 81 (LTA) ¹⁷	O 0.720 0.911 0.280
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.43 eV	O 0.089 0.720 0.280
E_{rel} : 0.25 eV/ZnO	O 0.780 0.411 0.220
Pore _{max} : 0.64 nm	O 0.589 0.780 0.220
V _{pore} : 30 %	O 0.411 0.589 0.220
D _{pore} : 3	O 0.911 0.720 0.089
cell parameters	O 0.720 0.280 0.089
10.759 10.759 10.759 60.00 60.00	O 0.280 0.911 0.089
60.00	
fractional coordinates	Str 82 (AFS) ¹⁷

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}}): 1.22 \text{ eV}$	O 0.333 0.667 0.440
$E_{\text{rel}}: 0.36 \text{ eV/ZnO}$	O 0.869 0.520 0.373
Pore _{max} : 0.56 nm	O 0.651 0.131 0.373
V _{pore} : 31 %	O 0.480 0.349 0.373
D _{pore} : 3	O 0.576 0.709 0.310
cell parameters	O 0.291 0.867 0.310
8.526 8.526 16.493 90.00 90.00 120.00	O 0.133 0.424 0.310
fractional coordinates	O 0.867 0.291 0.190
Zn 0.667 0.333 0.945	O 0.709 0.576 0.190
Zn 0.517 0.645 0.868	O 0.424 0.133 0.190
Zn 0.355 0.872 0.868	O 0.520 0.869 0.127
Zn 0.128 0.483 0.868	O 0.349 0.480 0.127
Zn 0.864 0.574 0.811	O 0.131 0.651 0.127
Zn 0.710 0.136 0.811	O 0.667 0.333 0.060
Zn 0.426 0.290 0.811	
Zn 0.574 0.864 0.689	Str 83 (SAO) ¹⁷
Zn 0.290 0.426 0.689	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}}): 1.18 \text{ eV}$
Zn 0.136 0.710 0.689	$E_{\text{rel}}: 0.38 \text{ eV/ZnO}$
Zn 0.872 0.355 0.632	Pore _{max} : 0.49 nm
Zn 0.645 0.517 0.632	V _{pore} : 34 %
Zn 0.483 0.128 0.632	D _{pore} : 3
Zn 0.333 0.667 0.555	cell parameters
Zn 0.667 0.333 0.445	8.925 8.925 13.591 90.00 90.00 90.00
Zn 0.517 0.872 0.368	fractional coordinates
Zn 0.355 0.483 0.368	Zn 0.606 0.877 0.948
Zn 0.128 0.645 0.368	Zn 0.394 0.123 0.948
Zn 0.864 0.290 0.311	Zn 0.896 0.878 0.874
Zn 0.710 0.574 0.311	Zn 0.104 0.122 0.874
Zn 0.426 0.136 0.311	Zn 0.700 0.117 0.807
Zn 0.574 0.710 0.189	Zn 0.300 0.883 0.807
Zn 0.290 0.864 0.189	Zn 0.617 0.800 0.693
Zn 0.136 0.426 0.189	Zn 0.383 0.200 0.693
Zn 0.872 0.517 0.132	Zn 0.622 0.396 0.626
Zn 0.645 0.128 0.132	Zn 0.378 0.604 0.626
Zn 0.483 0.355 0.132	Zn 0.623 0.106 0.552
Zn 0.333 0.667 0.055	Zn 0.377 0.894 0.552
O 0.333 0.667 0.940	Zn 0.704 0.704 0.500
O 0.869 0.349 0.873	Zn 0.296 0.296 0.500
O 0.651 0.520 0.873	Zn 0.894 0.377 0.448
O 0.480 0.131 0.873	Zn 0.106 0.623 0.448
O 0.576 0.867 0.810	Zn 0.604 0.378 0.374
O 0.291 0.424 0.810	Zn 0.396 0.622 0.374
O 0.133 0.709 0.810	Zn 0.800 0.617 0.307
O 0.867 0.576 0.690	Zn 0.200 0.383 0.307
O 0.709 0.133 0.690	Zn 0.883 0.300 0.193
O 0.424 0.291 0.690	Zn 0.117 0.700 0.193
O 0.520 0.651 0.627	Zn 0.878 0.896 0.126
O 0.349 0.869 0.627	Zn 0.122 0.104 0.126
O 0.131 0.480 0.627	Zn 0.877 0.606 0.052
O 0.667 0.333 0.560	Zn 0.123 0.394 0.052

Zn 0.796 0.204 0.000
 Zn 0.204 0.796 0.000
 O 0.607 0.121 0.947
 O 0.393 0.879 0.947
 O 0.894 0.127 0.876
 O 0.106 0.873 0.876
 O 0.703 0.885 0.807
 O 0.297 0.115 0.807
 O 0.615 0.203 0.693
 O 0.385 0.797 0.693
 O 0.627 0.606 0.624
 O 0.373 0.394 0.624
 O 0.621 0.893 0.553
 O 0.379 0.107 0.553
 O 0.704 0.296 0.500
 O 0.296 0.704 0.500
 O 0.893 0.621 0.447
 O 0.107 0.379 0.447
 O 0.606 0.627 0.376
 O 0.394 0.373 0.376
 O 0.797 0.385 0.307
 O 0.203 0.615 0.307
 O 0.885 0.703 0.193
 O 0.115 0.297 0.193
 O 0.873 0.106 0.124
 O 0.127 0.894 0.124
 O 0.879 0.393 0.053
 O 0.121 0.607 0.053
 O 0.796 0.796 0.000
 O 0.204 0.204 0.000

Str 84 (BBZ)¹⁹
 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.83 eV
 E_{rel} : 0.25 eV/ZnO
 Pore_{max}: 0.84 nm
 V_{pore}: 36 %
 D_{pore}: 3
 cell parameters
 12.902 12.901 3.370 90.00 90.00
 120.01
 fractional coordinates
 Zn 0.822 0.334 0.500
 Zn 0.673 0.512 0.500
 Zn 0.498 0.836 0.500
 Zn 0.495 0.185 0.500
 Zn 0.320 0.509 0.500
 Zn 0.172 0.687 0.500
 Zn 0.909 0.548 0.000
 Zn 0.622 0.099 0.000
 Zn 0.534 0.636 0.000

Zn 0.460 0.386 0.000
 Zn 0.372 0.923 0.000
 Zn 0.085 0.474 0.000
 O 0.819 0.503 0.500
 O 0.667 0.189 0.500
 O 0.504 0.340 0.500
 O 0.489 0.681 0.500
 O 0.326 0.832 0.500
 O 0.175 0.518 0.500
 O 0.912 0.375 0.000
 O 0.632 0.561 0.000
 O 0.547 0.926 0.000
 O 0.447 0.096 0.000
 O 0.362 0.461 0.000
 O 0.082 0.646 0.000

Str 85 (FAU)¹⁷
 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.16 eV
 E_{rel} : 0.34 eV/ZnO
 Pore_{max}: 0.67 nm
 V_{pore}: 38 %
 D_{pore}: 3
 cell parameters
 15.834 15.834 15.834 90.00 90.00
 90.00
 fractional coordinates
 Zn 0.880 0.196 0.965
 Zn 0.870 0.554 0.965
 Zn 0.380 0.696 0.965
 Zn 0.370 0.054 0.965
 Zn 0.715 0.120 0.946
 Zn 0.535 0.130 0.946
 Zn 0.215 0.620 0.946
 Zn 0.035 0.630 0.946
 Zn 0.696 0.465 0.880
 Zn 0.554 0.785 0.880
 Zn 0.196 0.965 0.880
 Zn 0.054 0.285 0.880
 Zn 0.696 0.285 0.870
 Zn 0.554 0.965 0.870
 Zn 0.196 0.785 0.870
 Zn 0.054 0.465 0.870
 Zn 0.715 0.630 0.804
 Zn 0.535 0.620 0.804
 Zn 0.215 0.130 0.804
 Zn 0.035 0.120 0.804
 Zn 0.880 0.554 0.785
 Zn 0.870 0.196 0.785
 Zn 0.380 0.054 0.785
 Zn 0.370 0.696 0.785

Zn 0.630 0.804 0.715	Zn 0.130 0.804 0.215
Zn 0.620 0.446 0.715	Zn 0.120 0.446 0.215
Zn 0.130 0.304 0.715	Zn 0.965 0.880 0.196
Zn 0.120 0.946 0.715	Zn 0.785 0.870 0.196
Zn 0.965 0.380 0.696	Zn 0.465 0.380 0.196
Zn 0.785 0.370 0.696	Zn 0.285 0.370 0.196
Zn 0.465 0.880 0.696	Zn 0.946 0.535 0.130
Zn 0.285 0.870 0.696	Zn 0.804 0.215 0.130
Zn 0.946 0.035 0.630	Zn 0.446 0.035 0.130
Zn 0.804 0.715 0.630	Zn 0.304 0.715 0.130
Zn 0.446 0.535 0.630	Zn 0.946 0.715 0.120
Zn 0.304 0.215 0.630	Zn 0.804 0.035 0.120
Zn 0.946 0.215 0.620	Zn 0.446 0.215 0.120
Zn 0.804 0.535 0.620	Zn 0.304 0.535 0.120
Zn 0.446 0.715 0.620	Zn 0.965 0.370 0.054
Zn 0.304 0.035 0.620	Zn 0.785 0.380 0.054
Zn 0.965 0.870 0.554	Zn 0.465 0.870 0.054
Zn 0.785 0.880 0.554	Zn 0.285 0.880 0.054
Zn 0.465 0.370 0.554	Zn 0.630 0.946 0.035
Zn 0.285 0.380 0.554	Zn 0.620 0.304 0.035
Zn 0.630 0.446 0.535	Zn 0.130 0.446 0.035
Zn 0.620 0.804 0.535	Zn 0.120 0.804 0.035
Zn 0.130 0.946 0.535	O 0.695 0.380 0.966
Zn 0.120 0.304 0.535	O 0.555 0.870 0.966
Zn 0.880 0.696 0.465	O 0.195 0.880 0.966
Zn 0.870 0.054 0.465	O 0.055 0.370 0.966
Zn 0.380 0.196 0.465	O 0.630 0.034 0.945
Zn 0.370 0.554 0.465	O 0.620 0.216 0.945
Zn 0.715 0.620 0.446	O 0.130 0.534 0.945
Zn 0.535 0.630 0.446	O 0.120 0.716 0.945
Zn 0.215 0.120 0.446	O 0.966 0.195 0.880
Zn 0.035 0.130 0.446	O 0.784 0.555 0.880
Zn 0.696 0.965 0.380	O 0.466 0.695 0.880
Zn 0.554 0.285 0.380	O 0.284 0.055 0.880
Zn 0.196 0.465 0.380	O 0.966 0.555 0.870
Zn 0.054 0.785 0.380	O 0.784 0.195 0.870
Zn 0.696 0.785 0.370	O 0.466 0.055 0.870
Zn 0.554 0.465 0.370	O 0.284 0.695 0.870
Zn 0.196 0.285 0.370	O 0.630 0.716 0.805
Zn 0.054 0.965 0.370	O 0.620 0.534 0.805
Zn 0.715 0.130 0.304	O 0.130 0.216 0.805
Zn 0.535 0.120 0.304	O 0.120 0.034 0.805
Zn 0.215 0.630 0.304	O 0.695 0.370 0.784
Zn 0.035 0.620 0.304	O 0.555 0.880 0.784
Zn 0.880 0.054 0.285	O 0.195 0.870 0.784
Zn 0.870 0.696 0.285	O 0.055 0.380 0.784
Zn 0.380 0.554 0.285	O 0.945 0.120 0.716
Zn 0.370 0.196 0.285	O 0.805 0.630 0.716
Zn 0.630 0.304 0.215	O 0.445 0.620 0.716
Zn 0.620 0.946 0.215	O 0.305 0.130 0.716

O 0.880 0.466 0.695	O 0.380 0.466 0.195
O 0.870 0.284 0.695	O 0.370 0.284 0.195
O 0.380 0.966 0.695	O 0.716 0.305 0.130
O 0.370 0.784 0.695	O 0.534 0.945 0.130
O 0.716 0.805 0.630	O 0.216 0.805 0.130
O 0.534 0.445 0.630	O 0.034 0.445 0.130
O 0.216 0.305 0.630	O 0.716 0.945 0.120
O 0.034 0.945 0.630	O 0.534 0.305 0.120
O 0.716 0.445 0.620	O 0.216 0.445 0.120
O 0.534 0.805 0.620	O 0.034 0.805 0.120
O 0.216 0.945 0.620	O 0.880 0.284 0.055
O 0.034 0.305 0.620	O 0.870 0.466 0.055
O 0.880 0.784 0.555	O 0.380 0.784 0.055
O 0.870 0.966 0.555	O 0.370 0.966 0.055
O 0.380 0.284 0.555	O 0.945 0.630 0.034
O 0.370 0.466 0.555	O 0.805 0.120 0.034
O 0.945 0.130 0.534	O 0.445 0.130 0.034
O 0.805 0.620 0.534	O 0.305 0.620 0.034
O 0.445 0.630 0.534	
O 0.305 0.120 0.534	Str 86 (EMT) ¹⁷
O 0.695 0.880 0.466	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 1.16 eV
O 0.555 0.370 0.466	E_{rel} : 0.34 eV/ZnO
O 0.195 0.380 0.466	Pore _{max} : 0.69 nm
O 0.055 0.870 0.466	V _{pore} : 38 %
O 0.630 0.534 0.445	D _{pore} : 3
O 0.620 0.716 0.445	cell parameters
O 0.130 0.034 0.445	11.201 11.201 18.270 89.99 90.00
O 0.120 0.216 0.445	120.00
O 0.966 0.695 0.380	fractional coordinates
O 0.784 0.055 0.380	Zn 0.261 0.213 0.945
O 0.466 0.195 0.380	Zn 0.799 0.561 0.945
O 0.284 0.555 0.380	Zn 0.451 0.751 0.945
O 0.966 0.055 0.370	Zn 0.345 0.015 0.911
O 0.784 0.695 0.370	Zn 0.168 0.667 0.911
O 0.466 0.555 0.370	Zn 0.998 0.844 0.911
O 0.284 0.195 0.370	Zn 0.569 0.272 0.857
O 0.630 0.216 0.305	Zn 0.202 0.443 0.857
O 0.620 0.034 0.305	Zn 0.740 0.810 0.857
O 0.130 0.716 0.305	Zn 0.105 0.078 0.816
O 0.120 0.534 0.305	Zn 0.472 0.907 0.816
O 0.695 0.870 0.284	Zn 0.934 0.540 0.816
O 0.555 0.380 0.284	Zn 0.329 0.335 0.762
O 0.195 0.370 0.284	Zn 0.677 0.506 0.762
O 0.055 0.880 0.284	Zn 0.506 0.683 0.762
O 0.945 0.620 0.216	Zn 0.413 0.137 0.727
O 0.805 0.130 0.216	Zn 0.223 0.599 0.727
O 0.445 0.120 0.216	Zn 0.875 0.789 0.727
O 0.305 0.630 0.216	Zn 0.167 0.023 0.642
O 0.880 0.966 0.195	Zn 0.355 0.845 0.642
O 0.870 0.784 0.195	Zn 0.989 0.657 0.642

Zn 0.355 0.023 0.531	O 0.990 0.655 0.532
Zn 0.168 0.657 0.531	O 0.416 0.140 0.445
Zn 0.989 0.845 0.531	O 0.224 0.597 0.445
Zn 0.224 0.138 0.445	O 0.873 0.789 0.445
Zn 0.414 0.789 0.445	O 0.329 0.335 0.412
Zn 0.875 0.599 0.445	O 0.505 0.684 0.412
Zn 0.329 0.507 0.410	O 0.678 0.508 0.411
Zn 0.506 0.336 0.410	O 0.105 0.081 0.357
Zn 0.677 0.684 0.410	O 0.475 0.908 0.357
Zn 0.472 0.078 0.357	O 0.933 0.538 0.357
Zn 0.106 0.541 0.357	O 0.570 0.270 0.316
Zn 0.934 0.907 0.357	O 0.200 0.443 0.316
Zn 0.202 0.272 0.316	O 0.743 0.813 0.315
Zn 0.741 0.443 0.316	O 0.346 0.016 0.261
Zn 0.570 0.811 0.316	O 0.997 0.843 0.261
Zn 0.169 0.015 0.262	O 0.170 0.667 0.261
Zn 0.998 0.667 0.262	O 0.259 0.211 0.227
Zn 0.346 0.844 0.262	O 0.452 0.754 0.227
Zn 0.451 0.213 0.227	O 0.802 0.561 0.227
Zn 0.261 0.561 0.227	O 0.318 0.503 0.141
Zn 0.800 0.751 0.227	O 0.509 0.327 0.141
Zn 0.319 0.327 0.142	O 0.685 0.695 0.141
Zn 0.507 0.693 0.142	O 0.317 0.327 0.032
Zn 0.686 0.505 0.142	O 0.509 0.695 0.032
Zn 0.507 0.327 0.031	O 0.685 0.503 0.032
Zn 0.319 0.505 0.031	
Zn 0.685 0.693 0.031	Str 87 (WZ-ZnO-NP-1)
O 0.451 0.211 0.946	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW}}\text{-fit}): 0.21 \text{ eV}$
O 0.259 0.561 0.945	$E_{\text{rel}}: 0.08 \text{ eV/ZnO}$
O 0.801 0.753 0.945	Pore _{max} : 0.53 nm
O 0.169 0.016 0.912	V _{pore} : 7 %
O 0.346 0.843 0.912	D _{pore} : 1
O 0.996 0.666 0.912	cell parameters
O 0.200 0.269 0.857	19.702 19.702 5.309 90.00 90.00
O 0.743 0.443 0.857	120.00
O 0.569 0.813 0.857	fractional coordinates
O 0.474 0.080 0.816	Zn 0.889 0.111 0.999
O 0.105 0.538 0.816	Zn 0.722 0.945 0.999
O 0.932 0.907 0.816	Zn 0.889 0.444 0.999
O 0.329 0.507 0.761	Zn 0.722 0.444 0.999
O 0.505 0.334 0.761	Zn 0.389 0.945 0.999
O 0.678 0.683 0.761	Zn 0.389 0.111 0.999
O 0.223 0.139 0.727	Zn 0.890 0.278 0.999
O 0.415 0.789 0.727	Zn 0.555 0.943 0.999
O 0.873 0.597 0.727	Zn 0.555 0.278 0.999
O 0.357 0.023 0.641	Zn 0.553 0.775 0.998
O 0.165 0.655 0.641	Zn 0.553 0.444 0.998
O 0.989 0.847 0.641	Zn 0.389 0.775 0.998
O 0.165 0.023 0.532	Zn 0.389 0.281 0.998
O 0.357 0.847 0.532	Zn 0.058 0.444 0.998

Zn 0.058 0.281 0.998	Zn 0.053 0.611 0.001
Zn 0.455 0.743 0.526	Zn 0.053 0.109 0.001
Zn 0.455 0.379 0.526	O 0.778 0.222 0.880
Zn 0.091 0.379 0.526	O 0.611 0.222 0.880
Zn 0.778 0.222 0.501	O 0.611 0.055 0.880
Zn 0.611 0.222 0.501	O 0.945 0.889 0.880
Zn 0.611 0.055 0.501	O 0.945 0.722 0.880
Zn 0.778 0.389 0.501	O 0.111 0.889 0.880
Zn 0.778 0.056 0.501	O 0.778 0.389 0.879
Zn 0.445 0.056 0.501	O 0.778 0.056 0.879
Zn 0.945 0.889 0.501	O 0.445 0.056 0.879
Zn 0.945 0.722 0.501	O 0.777 0.722 0.879
Zn 0.111 0.889 0.501	O 0.111 0.722 0.879
Zn 0.943 0.389 0.501	O 0.111 0.056 0.879
Zn 0.943 0.220 0.501	O 0.945 0.389 0.879
Zn 0.613 0.891 0.501	O 0.945 0.222 0.879
Zn 0.613 0.389 0.501	O 0.611 0.889 0.879
Zn 0.444 0.891 0.501	O 0.611 0.389 0.879
Zn 0.444 0.220 0.501	O 0.444 0.889 0.879
Zn 0.945 0.556 0.499	O 0.444 0.222 0.879
Zn 0.945 0.055 0.499	O 0.944 0.555 0.878
Zn 0.778 0.556 0.499	O 0.944 0.055 0.878
Zn 0.778 0.889 0.499	O 0.778 0.890 0.878
Zn 0.277 0.889 0.499	O 0.778 0.555 0.878
Zn 0.277 0.055 0.499	O 0.278 0.890 0.878
Zn 0.777 0.722 0.499	O 0.278 0.055 0.878
Zn 0.112 0.722 0.499	O 0.445 0.388 0.875
Zn 0.112 0.057 0.499	O 0.445 0.724 0.875
Zn 0.609 0.719 0.498	O 0.109 0.388 0.875
Zn 0.609 0.556 0.498	O 0.612 0.724 0.875
Zn 0.277 0.719 0.498	O 0.612 0.555 0.875
Zn 0.277 0.225 0.498	O 0.278 0.724 0.875
Zn 0.114 0.556 0.498	O 0.278 0.221 0.875
Zn 0.114 0.225 0.498	O 0.110 0.555 0.875
Zn 0.212 0.621 0.026	O 0.110 0.221 0.875
Zn 0.212 0.257 0.026	O 0.889 0.778 0.380
Zn 0.576 0.621 0.026	O 0.056 0.945 0.380
Zn 0.889 0.778 0.001	O 0.056 0.778 0.380
Zn 0.056 0.945 0.001	O 0.722 0.278 0.380
Zn 0.056 0.778 0.001	O 0.722 0.111 0.380
Zn 0.889 0.944 0.001	O 0.556 0.111 0.380
Zn 0.889 0.611 0.001	O 0.889 0.944 0.379
Zn 0.222 0.944 0.001	O 0.889 0.611 0.379
Zn 0.722 0.278 0.001	O 0.222 0.944 0.379
Zn 0.722 0.111 0.001	O 0.889 0.278 0.379
Zn 0.556 0.111 0.001	O 0.555 0.944 0.379
Zn 0.724 0.780 0.001	O 0.555 0.278 0.379
Zn 0.724 0.611 0.001	O 0.722 0.778 0.379
Zn 0.223 0.780 0.001	O 0.722 0.611 0.379
Zn 0.223 0.109 0.001	O 0.223 0.778 0.379

O 0.223 0.111 0.379
 O 0.055 0.611 0.379
 O 0.055 0.111 0.379
 O 0.888 0.445 0.378
 O 0.888 0.110 0.378
 O 0.723 0.945 0.378
 O 0.723 0.445 0.378
 O 0.389 0.945 0.378
 O 0.389 0.110 0.378
 O 0.557 0.612 0.375
 O 0.221 0.612 0.375
 O 0.221 0.276 0.375
 O 0.557 0.779 0.375
 O 0.557 0.445 0.375
 O 0.389 0.779 0.375
 O 0.389 0.276 0.375
 O 0.055 0.445 0.375
 O 0.055 0.276 0.375

Str 88 (WZ-ZnO-NP-2)

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.28 eV

E_{rel} : 0.23 eV/ZnO

Pore_{max}: 0.39 nm

V_{pore} : 10 %

D_{pore} : 1

cell parameters

9.935 9.877 5.348 90.00 90.00 120.19

fractional coordinates

Zn 0.780 0.226 1.000

Zn 0.774 0.555 0.999

Zn 0.114 0.555 0.999

Zn 0.443 0.231 0.998

Zn 0.121 0.231 0.998

Zn 0.578 0.420 0.526

Zn 0.176 0.420 0.526

Zn 0.890 0.446 0.503

Zn 0.220 0.107 0.500

Zn 0.886 0.779 0.499

Zn 0.226 0.779 0.499

Zn 0.879 0.103 0.498

Zn 0.557 0.103 0.498

Zn 0.422 0.913 0.026

Zn 0.824 0.913 0.026

Zn 0.110 0.887 0.003

O 0.890 0.448 0.877

O 0.221 0.109 0.877

O 0.890 0.777 0.874

O 0.220 0.777 0.874

O 0.889 0.114 0.873

O 0.558 0.114 0.873

O 0.563 0.442 0.872

O 0.213 0.442 0.872

O 0.110 0.886 0.377

O 0.779 0.225 0.377

O 0.780 0.556 0.374

O 0.110 0.556 0.374

O 0.111 0.219 0.373

O 0.442 0.219 0.373

O 0.437 0.891 0.372

O 0.787 0.891 0.372

Str 89 (WZ-ZnO-NP-3)

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.32 eV

E_{rel} : 0.20 eV/ZnO

Pore_{max}: 0.36 nm

V_{pore} : 10 %

D_{pore} : 1

cell parameters

21.778 8.781 5.340 90.01 89.98 87.71

fractional coordinates

Zn 0.419 0.605 0.942

Zn 0.919 0.105 0.942

Zn 0.368 0.242 0.941

Zn 0.868 0.742 0.941

Zn 0.821 0.392 0.941

Zn 0.321 0.892 0.941

Zn 0.723 0.680 0.940

Zn 0.572 0.640 0.940

Zn 0.224 0.180 0.940

Zn 0.072 0.140 0.940

Zn 0.773 0.043 0.939

Zn 0.273 0.543 0.939

Zn 0.669 0.334 0.939

Zn 0.169 0.834 0.939

Zn 0.513 0.347 0.920

Zn 0.013 0.846 0.920

Zn 0.641 0.964 0.914

Zn 0.141 0.464 0.914

Zn 0.638 0.769 0.442

Zn 0.138 0.269 0.442

Zn 0.686 0.119 0.442

Zn 0.587 0.406 0.442

Zn 0.186 0.619 0.442

Zn 0.087 0.906 0.442

Zn 0.783 0.832 0.440

Zn 0.283 0.332 0.440

Zn 0.434 0.371 0.440

Zn 0.934 0.871 0.440

Zn 0.734 0.469 0.439

Zn 0.234 0.969 0.439

Zn 0.837 0.177 0.439	16.415 16.415 5.322 90.00 90.00
Zn 0.337 0.677 0.439	120.00
Zn 0.494 0.664 0.421	fractional coordinates
Zn 0.994 0.165 0.421	Zn 0.669 0.933 0.999
Zn 0.365 0.048 0.413	Zn 0.669 0.737 0.999
Zn 0.865 0.548 0.413	Zn 0.263 0.933 0.999
O 0.514 0.313 0.570	Zn 0.263 0.331 0.999
O 0.014 0.813 0.570	Zn 0.067 0.737 0.999
O 0.627 0.976 0.567	Zn 0.067 0.331 0.999
O 0.127 0.476 0.567	Zn 0.467 0.734 0.999
O 0.418 0.595 0.566	Zn 0.266 0.734 0.999
O 0.918 0.095 0.566	Zn 0.266 0.533 0.999
O 0.574 0.630 0.566	Zn 0.466 0.933 0.998
O 0.074 0.130 0.566	Zn 0.466 0.534 0.998
O 0.366 0.248 0.566	Zn 0.067 0.534 0.998
O 0.866 0.748 0.566	Zn 0.709 0.854 0.527
O 0.818 0.390 0.565	Zn 0.146 0.854 0.527
O 0.318 0.890 0.565	Zn 0.146 0.291 0.527
O 0.722 0.683 0.563	Zn 0.531 0.867 0.501
O 0.271 0.545 0.563	Zn 0.531 0.665 0.501
O 0.771 0.045 0.563	Zn 0.335 0.867 0.501
O 0.222 0.183 0.563	Zn 0.335 0.469 0.501
O 0.669 0.333 0.563	Zn 0.133 0.469 0.501
O 0.169 0.833 0.563	Zn 0.133 0.665 0.501
O 0.492 0.697 0.071	Zn 0.333 0.667 0.501
O 0.992 0.197 0.071	Zn 0.933 0.669 0.499
O 0.140 0.263 0.066	Zn 0.933 0.263 0.499
O 0.640 0.764 0.066	Zn 0.737 0.669 0.499
O 0.432 0.380 0.066	Zn 0.737 0.067 0.499
O 0.932 0.880 0.066	Zn 0.331 0.263 0.499
O 0.588 0.416 0.066	Zn 0.331 0.067 0.499
O 0.379 0.035 0.066	Zn 0.734 0.467 0.499
O 0.879 0.535 0.066	Zn 0.734 0.266 0.499
O 0.088 0.916 0.066	Zn 0.533 0.266 0.499
O 0.689 0.122 0.065	Zn 0.933 0.466 0.498
O 0.189 0.622 0.065	Zn 0.534 0.466 0.498
O 0.284 0.328 0.063	Zn 0.534 0.067 0.498
O 0.784 0.828 0.063	Zn 0.854 0.709 0.027
O 0.736 0.467 0.063	Zn 0.854 0.146 0.027
O 0.236 0.967 0.063	Zn 0.291 0.146 0.027
O 0.337 0.678 0.063	Zn 0.867 0.531 0.001
O 0.837 0.178 0.063	Zn 0.867 0.335 0.001
	Zn 0.665 0.531 0.001
Str 90 (WZ-ZnO-NP-4)	Zn 0.665 0.133 0.001
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.30 eV	Zn 0.469 0.335 0.001
E_{rel} : 0.12 eV/ZnO	Zn 0.469 0.133 0.001
Pore _{max} : 0.53 nm	Zn 0.667 0.333 0.001
V _{pore} : 11 %	O 0.333 0.667 0.879
D _{pore} : 1	O 0.733 0.467 0.878
cell parameters	O 0.733 0.267 0.878

O 0.533 0.267 0.878	23.047 23.047 5.318 90.00 90.00
O 0.534 0.867 0.878	120.00
O 0.534 0.666 0.878	fractional coordinates
O 0.334 0.867 0.878	Zn 0.476 0.953 1.000
O 0.334 0.466 0.878	Zn 0.476 0.095 1.000
O 0.133 0.666 0.878	Zn 0.190 0.667 1.000
O 0.133 0.466 0.878	Zn 0.190 0.095 1.000
O 0.731 0.865 0.876	Zn 0.048 0.953 1.000
O 0.135 0.865 0.876	Zn 0.048 0.667 1.000
O 0.135 0.269 0.876	Zn 0.619 0.954 0.999
O 0.934 0.666 0.876	Zn 0.189 0.524 0.999
O 0.934 0.268 0.876	Zn 0.907 0.954 0.999
O 0.732 0.666 0.876	Zn 0.907 0.524 0.999
O 0.732 0.066 0.876	Zn 0.619 0.236 0.999
O 0.334 0.268 0.876	Zn 0.189 0.236 0.999
O 0.334 0.066 0.876	Zn 0.906 0.808 0.997
O 0.934 0.467 0.876	Zn 0.474 0.808 0.997
O 0.533 0.467 0.876	Zn 0.906 0.669 0.997
O 0.533 0.066 0.876	Zn 0.474 0.237 0.997
O 0.667 0.333 0.379	Zn 0.335 0.669 0.997
O 0.467 0.733 0.378	Zn 0.335 0.237 0.997
O 0.267 0.733 0.378	Zn 0.819 0.608 0.524
O 0.267 0.533 0.378	Zn 0.535 0.782 0.524
O 0.867 0.534 0.378	Zn 0.535 0.324 0.524
O 0.867 0.334 0.378	Zn 0.361 0.608 0.524
O 0.666 0.534 0.378	Zn 0.819 0.782 0.524
O 0.666 0.133 0.378	Zn 0.361 0.324 0.524
O 0.466 0.334 0.378	Zn 0.238 0.905 0.502
O 0.466 0.133 0.378	Zn 0.952 0.333 0.502
O 0.865 0.731 0.376	Zn 0.952 0.191 0.502
O 0.865 0.135 0.376	Zn 0.810 0.191 0.502
O 0.269 0.135 0.376	Zn 0.093 0.332 0.501
O 0.666 0.732 0.376	Zn 0.810 0.332 0.501
O 0.666 0.934 0.376	Zn 0.810 0.050 0.501
O 0.268 0.934 0.376	Zn 0.381 0.047 0.501
O 0.268 0.334 0.376	Zn 0.381 0.905 0.501
O 0.066 0.732 0.376	Zn 0.238 0.762 0.501
O 0.066 0.334 0.376	Zn 0.238 0.047 0.501
O 0.467 0.934 0.376	Zn 0.096 0.905 0.501
O 0.467 0.533 0.376	Zn 0.096 0.762 0.501
O 0.066 0.533 0.376	Zn 0.095 0.048 0.501
	Zn 0.524 0.048 0.501
Str 91 (WZ-ZnO-NP-5)	Zn 0.095 0.619 0.501
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.26 eV	Zn 0.380 0.189 0.500
E_{rel} : 0.13 eV/ZnO	Zn 0.954 0.763 0.500
Pore _{max} : 0.78 nm	Zn 0.380 0.763 0.500
V _{pore} : 11 %	Zn 0.953 0.476 0.500
D _{pore} : 1	Zn 0.953 0.048 0.500
cell parameters	Zn 0.095 0.476 0.500
	Zn 0.667 0.190 0.500

Zn 0.667 0.048 0.500	O 0.524 0.048 0.879
Zn 0.095 0.190 0.500	O 0.095 0.619 0.879
Zn 0.954 0.619 0.499	O 0.094 0.333 0.879
Zn 0.954 0.907 0.499	O 0.810 0.333 0.879
Zn 0.524 0.189 0.499	O 0.810 0.049 0.879
Zn 0.524 0.907 0.499	O 0.953 0.049 0.878
Zn 0.236 0.189 0.499	O 0.953 0.476 0.878
Zn 0.236 0.619 0.499	O 0.094 0.476 0.878
Zn 0.808 0.906 0.497	O 0.094 0.190 0.878
Zn 0.808 0.474 0.497	O 0.667 0.190 0.878
Zn 0.669 0.906 0.497	O 0.667 0.049 0.878
Zn 0.237 0.474 0.497	O 0.953 0.906 0.877
Zn 0.669 0.335 0.497	O 0.953 0.619 0.877
Zn 0.237 0.335 0.497	O 0.524 0.190 0.877
Zn 0.324 0.535 0.024	O 0.524 0.906 0.877
Zn 0.782 0.535 0.024	O 0.237 0.619 0.877
Zn 0.608 0.819 0.024	O 0.237 0.190 0.877
Zn 0.608 0.361 0.024	O 0.955 0.763 0.876
Zn 0.782 0.819 0.024	O 0.379 0.763 0.876
Zn 0.324 0.361 0.024	O 0.379 0.187 0.876
Zn 0.905 0.238 0.002	O 0.236 0.475 0.875
Zn 0.333 0.952 0.002	O 0.810 0.475 0.875
Zn 0.191 0.952 0.002	O 0.810 0.907 0.875
Zn 0.191 0.810 0.002	O 0.668 0.907 0.875
Zn 0.332 0.810 0.001	O 0.668 0.332 0.875
Zn 0.332 0.093 0.001	O 0.236 0.332 0.875
Zn 0.050 0.810 0.001	O 0.813 0.765 0.872
Zn 0.905 0.381 0.001	O 0.813 0.620 0.872
Zn 0.905 0.096 0.001	O 0.523 0.765 0.872
Zn 0.762 0.238 0.001	O 0.523 0.329 0.872
Zn 0.047 0.381 0.001	O 0.378 0.620 0.872
Zn 0.047 0.238 0.001	O 0.378 0.329 0.872
Zn 0.762 0.096 0.001	O 0.905 0.238 0.380
Zn 0.048 0.095 0.001	O 0.333 0.952 0.380
Zn 0.619 0.095 0.001	O 0.191 0.952 0.380
Zn 0.048 0.524 0.001	O 0.191 0.810 0.380
Zn 0.763 0.954 0.000	O 0.905 0.381 0.379
Zn 0.189 0.380 0.000	O 0.905 0.096 0.379
Zn 0.763 0.380 0.000	O 0.047 0.381 0.379
O 0.238 0.905 0.880	O 0.047 0.238 0.379
O 0.952 0.333 0.880	O 0.762 0.238 0.379
O 0.952 0.191 0.880	O 0.762 0.096 0.379
O 0.810 0.191 0.880	O 0.048 0.095 0.379
O 0.381 0.047 0.879	O 0.619 0.095 0.379
O 0.381 0.905 0.879	O 0.048 0.524 0.379
O 0.238 0.762 0.879	O 0.333 0.810 0.379
O 0.238 0.047 0.879	O 0.333 0.094 0.379
O 0.096 0.905 0.879	O 0.049 0.810 0.379
O 0.096 0.762 0.879	O 0.476 0.953 0.378
O 0.095 0.048 0.879	O 0.049 0.953 0.378

O 0.476 0.094 0.378	Zn 0.102 0.249 0.527
O 0.190 0.094 0.378	Zn 0.932 0.468 0.502
O 0.190 0.667 0.378	Zn 0.736 0.468 0.502
O 0.049 0.667 0.378	Zn 0.131 0.063 0.502
O 0.906 0.953 0.377	Zn 0.730 0.667 0.502
O 0.619 0.953 0.377	Zn 0.137 0.667 0.502
O 0.190 0.524 0.377	Zn 0.734 0.269 0.501
O 0.906 0.524 0.377	Zn 0.929 0.266 0.500
O 0.190 0.237 0.377	Zn 0.537 0.266 0.500
O 0.619 0.237 0.377	Zn 0.933 0.667 0.500
O 0.763 0.955 0.376	Zn 0.931 0.864 0.498
O 0.763 0.379 0.376	Zn 0.133 0.864 0.498
O 0.187 0.379 0.376	Zn 0.732 0.067 0.497
O 0.907 0.810 0.375	Zn 0.535 0.067 0.497
O 0.475 0.810 0.375	Zn 0.927 0.060 0.496
O 0.907 0.668 0.375	Zn 0.333 0.060 0.496
O 0.475 0.236 0.375	Zn 0.724 0.861 0.496
O 0.332 0.668 0.375	Zn 0.337 0.861 0.496
O 0.332 0.236 0.375	Zn 0.691 0.745 0.031
O 0.765 0.523 0.372	Zn 0.254 0.745 0.031
O 0.620 0.378 0.372	Zn 0.698 0.951 0.027
O 0.329 0.523 0.372	Zn 0.453 0.951 0.027
O 0.765 0.813 0.372	Zn 0.868 0.732 0.002
O 0.620 0.813 0.372	Zn 0.064 0.732 0.002
O 0.329 0.378 0.372	Zn 0.669 0.137 0.002
	Zn 0.663 0.533 0.002
Str 92 (WZ-ZnO-NP-6)	Zn 0.070 0.533 0.002
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.28 eV	Zn 0.066 0.931 0.001
E_{rel} : 0.18 eV/ZnO	O 0.535 0.467 0.878
Pore _{max} : 0.56 nm	O 0.132 0.467 0.878
V _{pore} : 15 %	O 0.131 0.063 0.878
D _{pore} : 1	O 0.735 0.269 0.878
cell parameters	O 0.934 0.469 0.878
16.402 16.483 5.335 90.00 90.00	O 0.734 0.469 0.878
119.84	O 0.734 0.666 0.877
fractional coordinates	O 0.132 0.666 0.877
Zn 0.871 0.934 1.000	O 0.932 0.864 0.876
Zn 0.263 0.934 1.000	O 0.131 0.864 0.876
Zn 0.867 0.533 1.000	O 0.933 0.665 0.876
Zn 0.869 0.336 0.998	O 0.935 0.270 0.874
Zn 0.667 0.336 0.998	O 0.535 0.270 0.874
Zn 0.265 0.133 0.997	O 0.736 0.072 0.874
Zn 0.068 0.133 0.997	O 0.535 0.072 0.874
Zn 0.873 0.140 0.996	O 0.931 0.064 0.874
Zn 0.467 0.140 0.996	O 0.333 0.064 0.874
Zn 0.463 0.339 0.996	O 0.336 0.260 0.874
Zn 0.076 0.339 0.996	O 0.124 0.260 0.874
Zn 0.546 0.455 0.531	O 0.733 0.866 0.872
Zn 0.109 0.455 0.531	O 0.333 0.866 0.872
Zn 0.347 0.249 0.527	O 0.668 0.733 0.378

O 0.265 0.733 0.378	Zn 0.173 0.641 0.379
O 0.669 0.137 0.378	Zn 0.809 0.005 0.379
O 0.065 0.931 0.378	Zn 0.388 0.172 0.378
O 0.866 0.731 0.378	Zn 0.594 0.966 0.377
O 0.066 0.731 0.378	Zn 0.991 0.374 0.375
O 0.668 0.534 0.377	Zn 0.491 0.837 0.355
O 0.066 0.534 0.377	Zn 0.744 0.831 0.352
O 0.868 0.336 0.376	Zn 0.074 0.510 0.352
O 0.669 0.336 0.376	Zn 0.908 0.675 0.352
O 0.867 0.535 0.376	Zn 0.238 0.336 0.352
O 0.865 0.930 0.374	Zn 0.655 0.174 0.351
O 0.265 0.930 0.374	Zn 0.328 0.501 0.351
O 0.265 0.129 0.374	Zn 0.825 0.498 0.349
O 0.064 0.129 0.374	Zn 0.157 0.166 0.349
O 0.869 0.136 0.374	Zn 0.240 0.837 0.349
O 0.467 0.136 0.374	Zn 0.323 1.000 0.349
O 0.676 0.940 0.374	Zn 0.659 0.664 0.349
O 0.464 0.940 0.374	Zn 0.742 0.336 0.349
O 0.467 0.334 0.372	Zn 0.573 0.502 0.348
O 0.067 0.334 0.372	Zn 0.410 0.664 0.348
	O 0.491 0.836 0.730
Str 93 (WZ-ZnO-NP-7)	O 0.744 0.837 0.726
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.44 eV	O 0.239 0.341 0.726
E_{rel} : 0.22 eV/ZnO	O 0.658 0.670 0.726
Pore _{max} : 0.54 nm	O 0.325 0.003 0.726
V _{pore} : 15 %	O 0.244 0.833 0.725
D _{pore} : 1	O 0.906 0.669 0.725
cell parameters	O 0.739 0.338 0.725
22.855 11.416 5.349 90.01 90.01 60.02	O 0.823 0.506 0.725
fractional coordinates	O 0.157 0.669 0.725
Zn 0.806 0.371 0.878	O 0.076 0.499 0.725
Zn 0.176 0.001 0.878	O 0.573 0.506 0.725
Zn 0.594 0.334 0.877	O 0.409 0.670 0.725
Zn 0.389 0.539 0.877	O 0.160 0.170 0.725
Zn 0.991 0.632 0.875	O 0.401 0.173 0.725
Zn 0.491 0.671 0.855	O 0.825 0.002 0.725
Zn 0.235 0.676 0.852	O 0.581 0.993 0.724
Zn 0.748 0.164 0.851	O 0.321 0.507 0.724
Zn 0.327 0.838 0.851	O 0.661 0.168 0.724
Zn 0.075 0.329 0.851	O 0.991 0.346 0.723
Zn 0.907 0.496 0.851	O 0.491 0.672 0.229
Zn 0.656 0.509 0.851	O 0.326 0.834 0.226
Zn 0.658 0.004 0.849	O 0.741 0.671 0.226
Zn 0.324 0.338 0.849	O 0.242 0.170 0.226
Zn 0.827 0.840 0.849	O 0.574 0.835 0.226
Zn 0.243 0.173 0.849	O 0.657 0.504 0.226
Zn 0.739 0.677 0.849	O 0.408 0.001 0.226
Zn 0.573 0.842 0.849	O 0.906 0.506 0.225
Zn 0.156 0.510 0.849	O 0.077 0.335 0.225
Zn 0.409 0.006 0.849	O 0.661 0.001 0.225

O 0.321 0.341 0.225	Zn 0.277 0.054 0.501
O 0.820 0.343 0.225	Zn 0.946 0.891 0.498
O 0.162 0.001 0.225	Zn 0.946 0.555 0.498
O 0.241 0.670 0.225	Zn 0.445 0.891 0.498
O 0.741 0.171 0.224	Zn 0.445 0.054 0.498
O 0.825 0.837 0.224	Zn 0.109 0.555 0.498
O 0.157 0.505 0.224	Zn 0.109 0.054 0.498
O 0.579 0.337 0.223	Zn 0.944 0.389 0.498
O 0.991 0.660 0.223	Zn 0.944 0.056 0.498
O 0.404 0.510 0.223	Zn 0.611 0.056 0.498
	Zn 0.776 0.890 0.498
Str 94 (WZ-ZnO-NP-8)	Zn 0.776 0.386 0.498
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.38 eV	Zn 0.614 0.890 0.498
E_{rel} : 0.18 eV/ZnO	Zn 0.614 0.224 0.498
Pore _{max} : 0.78 nm	Zn 0.110 0.386 0.498
V _{pore} : 16 %	Zn 0.110 0.224 0.498
D _{pore} : 1	Zn 0.746 0.789 0.025
cell parameters	Zn 0.746 0.458 0.025
19.795 19.795 5.331 90.00 90.00	Zn 0.542 0.789 0.025
120.00	Zn 0.542 0.254 0.025
fractional coordinates	Zn 0.211 0.458 0.025
Zn 0.891 0.946 0.998	Zn 0.211 0.254 0.025
Zn 0.891 0.445 0.998	Zn 0.221 0.943 0.002
Zn 0.555 0.946 0.998	Zn 0.221 0.779 0.002
Zn 0.555 0.109 0.998	Zn 0.057 0.779 0.002
Zn 0.054 0.445 0.998	Zn 0.889 0.277 0.001
Zn 0.054 0.109 0.998	Zn 0.889 0.111 0.001
Zn 0.389 0.944 0.998	Zn 0.723 0.111 0.001
Zn 0.056 0.944 0.998	Zn 0.723 0.946 0.001
Zn 0.056 0.611 0.998	Zn 0.723 0.277 0.001
Zn 0.890 0.776 0.998	Zn 0.054 0.277 0.001
Zn 0.890 0.614 0.998	O 0.943 0.222 0.879
Zn 0.386 0.776 0.998	O 0.778 0.222 0.879
Zn 0.386 0.110 0.998	O 0.778 0.057 0.879
Zn 0.224 0.614 0.998	O 0.278 0.889 0.879
Zn 0.224 0.110 0.998	O 0.111 0.889 0.879
Zn 0.789 0.746 0.525	O 0.111 0.722 0.879
Zn 0.789 0.542 0.525	O 0.948 0.724 0.877
Zn 0.458 0.746 0.525	O 0.276 0.724 0.877
Zn 0.458 0.211 0.525	O 0.276 0.052 0.877
Zn 0.254 0.542 0.525	O 0.945 0.890 0.876
Zn 0.254 0.211 0.525	O 0.945 0.556 0.876
Zn 0.943 0.221 0.502	O 0.444 0.890 0.876
Zn 0.779 0.221 0.502	O 0.444 0.055 0.876
Zn 0.779 0.057 0.502	O 0.110 0.556 0.876
Zn 0.277 0.889 0.501	O 0.110 0.055 0.876
Zn 0.111 0.889 0.501	O 0.944 0.388 0.876
Zn 0.111 0.723 0.501	O 0.944 0.056 0.876
Zn 0.946 0.723 0.501	O 0.612 0.056 0.876
Zn 0.277 0.723 0.501	O 0.779 0.892 0.875

O 0.779 0.387 0.875	13.109 13.109 5.345 90.00 90.00
O 0.613 0.892 0.875	120.00
O 0.613 0.221 0.875	fractional coordinates
O 0.108 0.387 0.875	Zn 0.587 0.671 0.998
O 0.108 0.221 0.875	Zn 0.329 0.915 0.998
O 0.783 0.727 0.872	Zn 0.586 0.915 0.998
O 0.783 0.556 0.872	Zn 0.329 0.413 0.998
O 0.444 0.727 0.872	Zn 0.085 0.671 0.998
O 0.444 0.217 0.872	Zn 0.085 0.414 0.998
O 0.273 0.556 0.872	Zn 0.333 0.667 0.996
O 0.273 0.217 0.872	Zn 0.180 0.820 0.528
O 0.222 0.943 0.379	Zn 0.639 0.820 0.528
O 0.222 0.778 0.379	Zn 0.180 0.361 0.528
O 0.057 0.778 0.379	Zn 0.417 0.583 0.501
O 0.889 0.278 0.379	Zn 0.417 0.834 0.501
O 0.889 0.111 0.379	Zn 0.166 0.583 0.501
O 0.722 0.111 0.379	Zn 0.414 0.085 0.498
O 0.724 0.948 0.377	Zn 0.413 0.329 0.498
O 0.724 0.276 0.377	Zn 0.915 0.586 0.498
O 0.052 0.276 0.377	Zn 0.671 0.587 0.498
O 0.890 0.945 0.376	Zn 0.671 0.085 0.498
O 0.890 0.444 0.376	Zn 0.915 0.329 0.498
O 0.556 0.945 0.376	Zn 0.667 0.333 0.496
O 0.556 0.110 0.376	Zn 0.361 0.180 0.028
O 0.055 0.444 0.376	Zn 0.820 0.639 0.028
O 0.055 0.110 0.376	Zn 0.820 0.180 0.028
O 0.388 0.944 0.376	Zn 0.583 0.417 0.001
O 0.056 0.944 0.376	Zn 0.583 0.166 0.001
O 0.056 0.612 0.376	Zn 0.834 0.417 0.001
O 0.892 0.779 0.375	O 0.417 0.583 0.876
O 0.892 0.613 0.375	O 0.165 0.583 0.876
O 0.387 0.779 0.375	O 0.417 0.835 0.876
O 0.387 0.108 0.375	O 0.667 0.333 0.876
O 0.221 0.613 0.375	O 0.167 0.833 0.875
O 0.221 0.108 0.375	O 0.666 0.833 0.875
O 0.727 0.783 0.372	O 0.167 0.334 0.875
O 0.727 0.444 0.372	O 0.917 0.584 0.874
O 0.556 0.783 0.372	O 0.416 0.083 0.874
O 0.556 0.273 0.372	O 0.416 0.334 0.874
O 0.217 0.444 0.372	O 0.666 0.584 0.874
O 0.217 0.273 0.372	O 0.666 0.083 0.874
	O 0.917 0.334 0.874
Str 95 (WZ-ZnO-NP-9)	O 0.835 0.417 0.376
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW}}\text{-fit}): 0.44 \text{ eV}$	O 0.583 0.417 0.376
$E_{\text{rel}}: 0.21 \text{ eV/ZnO}$	O 0.583 0.165 0.376
Pore _{max} : 0.52 nm	O 0.333 0.667 0.376
V _{pore} : 16 %	O 0.334 0.167 0.375
D _{pore} : 1	O 0.833 0.666 0.375
cell parameters	O 0.833 0.167 0.375
	O 0.334 0.917 0.374

O 0.083 0.666 0.374	Zn 0.831 0.712 0.353
O 0.584 0.666 0.374	Zn 0.827 0.339 0.353
O 0.584 0.917 0.374	Zn 0.575 0.086 0.352
O 0.334 0.416 0.374	Zn 0.826 0.213 0.352
O 0.083 0.416 0.374	Zn 0.074 0.338 0.351
	Zn 0.322 0.208 0.351
Str 96 (WZ-ZnO-NP-10)	Zn 0.071 0.209 0.350
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW}}\text{-fit}): 0.48 \text{ eV}$	Zn 0.584 0.842 0.350
$E_{\text{rel}}: 0.25 \text{ eV/ZnO}$	Zn 0.328 0.715 0.349
Pore _{max} : 0.57 nm	Zn 0.324 0.593 0.349
V _{pore} : 20 %	Zn 0.580 0.962 0.349
D _{pore} : 1	Zn 0.323 0.962 0.349
cell parameters	Zn 0.080 0.840 0.347
13.172 26.428 5.356 90.00 90.01	Zn 0.075 0.710 0.347
119.92	Zn 0.064 0.464 0.347
fractional coordinates	Zn 0.329 0.839 0.345
Zn 0.181 0.690 0.882	O 0.581 0.717 0.728
Zn 0.928 0.690 0.881	O 0.579 0.212 0.727
Zn 0.923 0.411 0.879	O 0.580 0.337 0.727
Zn 0.633 0.915 0.879	O 0.072 0.337 0.727
Zn 0.176 0.914 0.878	O 0.825 0.211 0.727
Zn 0.183 0.193 0.869	O 0.575 0.086 0.726
Zn 0.187 0.535 0.866	O 0.826 0.335 0.726
Zn 0.165 0.799 0.853	O 0.831 0.717 0.726
Zn 0.907 0.292 0.852	O 0.584 0.594 0.725
Zn 0.912 0.802 0.852	O 0.824 0.088 0.725
Zn 0.415 0.798 0.852	O 0.333 0.090 0.725
Zn 0.664 0.674 0.851	O 0.332 0.715 0.725
Zn 0.412 0.923 0.851	O 0.330 0.839 0.725
Zn 0.659 0.296 0.851	O 0.580 0.840 0.724
Zn 0.415 0.674 0.851	O 0.078 0.838 0.724
Zn 0.159 0.298 0.851	O 0.828 0.839 0.724
Zn 0.668 0.800 0.851	O 0.328 0.964 0.724
Zn 0.908 0.167 0.849	O 0.079 0.714 0.724
Zn 0.164 0.419 0.849	O 0.577 0.963 0.724
Zn 0.664 0.046 0.849	O 0.073 0.213 0.724
Zn 0.407 0.047 0.849	O 0.317 0.330 0.723
Zn 0.422 0.304 0.848	O 0.333 0.214 0.721
Zn 0.658 0.169 0.847	O 0.334 0.592 0.720
Zn 0.410 0.170 0.847	O 0.072 0.462 0.719
Zn 0.426 0.547 0.847	O 0.317 0.471 0.717
Zn 0.563 0.321 0.382	O 0.908 0.295 0.228
Zn 0.566 0.600 0.380	O 0.168 0.677 0.227
Zn 0.810 0.095 0.379	O 0.665 0.676 0.227
Zn 0.359 0.096 0.378	O 0.415 0.799 0.226
Zn 0.815 0.824 0.378	O 0.661 0.294 0.226
Zn 0.304 0.316 0.375	O 0.162 0.797 0.226
Zn 0.302 0.476 0.367	O 0.414 0.674 0.226
Zn 0.578 0.717 0.354	O 0.659 0.169 0.226
Zn 0.582 0.212 0.353	O 0.412 0.922 0.226

O 0.915 0.675 0.226	Zn 0.333 0.921 0.851
O 0.660 0.922 0.225	Zn 0.708 0.048 0.851
O 0.162 0.920 0.225	Zn 0.578 0.921 0.851
O 0.663 0.799 0.225	Zn 0.583 0.049 0.850
O 0.913 0.797 0.225	Zn 0.456 0.049 0.850
O 0.154 0.295 0.225	Zn 0.330 0.548 0.850
O 0.906 0.418 0.225	Zn 0.207 0.548 0.850
O 0.907 0.170 0.224	Zn 0.706 0.422 0.850
O 0.409 0.045 0.224	Zn 0.581 0.297 0.850
O 0.414 0.172 0.224	Zn 0.706 0.297 0.850
O 0.659 0.045 0.224	Zn 0.581 0.422 0.850
O 0.413 0.297 0.221	Zn 0.581 0.172 0.849
O 0.155 0.419 0.221	Zn 0.830 0.422 0.849
O 0.417 0.550 0.219	Zn 0.456 0.422 0.849
O 0.167 0.178 0.217	Zn 0.955 0.422 0.849
O 0.172 0.540 0.215	Zn 0.955 0.546 0.849
	Zn 0.581 0.546 0.849
Str 97 (WZ-ZnO-NP-11)	Zn 0.326 0.170 0.849
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW}}\text{-fit}): 0.37 \text{ eV}$	Zn 0.833 0.677 0.849
$E_{\text{rel}}: 0.16 \text{ eV/ZnO}$	Zn 0.834 0.170 0.848
Pore _{max} : 1.12 nm	Zn 0.831 0.548 0.848
V _{pore} : 22 %	Zn 0.706 0.548 0.848
D _{pore} : 1	Zn 0.831 0.296 0.848
cell parameters	Zn 0.455 0.172 0.848
26.269 26.317 5.335 90.01 90.00	Zn 0.455 0.296 0.848
119.94	Zn 0.707 0.172 0.848
fractional coordinates	Zn 0.305 0.097 0.383
Zn 0.088 0.313 0.882	Zn 0.781 0.097 0.383
Zn 0.215 0.313 0.882	Zn 0.305 0.223 0.383
Zn 0.087 0.788 0.881	Zn 0.907 0.223 0.383
Zn 0.691 0.788 0.881	Zn 0.907 0.697 0.382
Zn 0.464 0.938 0.880	Zn 0.780 0.697 0.382
Zn 0.464 0.663 0.879	Zn 0.280 0.571 0.377
Zn 0.189 0.663 0.879	Zn 0.560 0.848 0.372
Zn 0.215 0.914 0.877	Zn 0.278 0.848 0.372
Zn 0.688 0.914 0.877	Zn 0.788 0.586 0.352
Zn 0.078 0.670 0.853	Zn 0.288 0.966 0.352
Zn 0.581 0.670 0.852	Zn 0.668 0.966 0.352
Zn 0.955 0.673 0.852	Zn 0.288 0.337 0.352
Zn 0.707 0.673 0.852	Zn 0.039 0.337 0.352
Zn 0.330 0.296 0.852	Zn 0.417 0.215 0.352
Zn 0.955 0.296 0.852	Zn 0.788 0.215 0.352
Zn 0.208 0.795 0.852	Zn 0.416 0.341 0.352
Zn 0.576 0.795 0.852	Zn 0.914 0.586 0.352
Zn 0.079 0.545 0.851	Zn 0.914 0.341 0.352
Zn 0.455 0.545 0.851	Zn 0.662 0.586 0.352
Zn 0.333 0.423 0.851	Zn 0.416 0.089 0.351
Zn 0.207 0.425 0.851	Zn 0.662 0.089 0.351
Zn 0.080 0.423 0.851	Zn 0.039 0.715 0.351
Zn 0.329 0.048 0.851	Zn 0.665 0.715 0.351

Zn 0.789 0.463 0.351	O 0.414 0.089 0.727
Zn 0.664 0.463 0.351	O 0.291 0.965 0.726
Zn 0.664 0.339 0.350	O 0.665 0.089 0.726
Zn 0.789 0.339 0.350	O 0.539 0.463 0.726
Zn 0.540 0.339 0.350	O 0.664 0.965 0.726
Zn 0.539 0.214 0.350	O 0.913 0.463 0.726
Zn 0.664 0.214 0.350	O 0.038 0.712 0.726
Zn 0.539 0.463 0.350	O 0.664 0.712 0.726
Zn 0.913 0.464 0.350	O 0.039 0.588 0.726
Zn 0.414 0.590 0.350	O 0.538 0.588 0.726
Zn 0.165 0.590 0.349	O 0.414 0.587 0.726
Zn 0.537 0.962 0.349	O 0.163 0.587 0.726
Zn 0.414 0.962 0.349	O 0.540 0.713 0.725
Zn 0.539 0.088 0.349	O 0.162 0.713 0.725
Zn 0.289 0.460 0.349	O 0.287 0.585 0.725
Zn 0.161 0.460 0.349	O 0.415 0.463 0.725
Zn 0.158 0.841 0.348	O 0.164 0.339 0.725
Zn 0.162 0.334 0.348	O 0.038 0.463 0.725
Zn 0.673 0.841 0.348	O 0.540 0.965 0.725
Zn 0.415 0.464 0.348	O 0.415 0.965 0.725
Zn 0.039 0.464 0.348	O 0.162 0.838 0.723
Zn 0.040 0.589 0.348	O 0.665 0.838 0.723
Zn 0.538 0.589 0.348	O 0.286 0.842 0.720
Zn 0.538 0.713 0.348	O 0.545 0.842 0.720
Zn 0.165 0.713 0.348	O 0.081 0.299 0.229
O 0.291 0.216 0.729	O 0.208 0.299 0.229
O 0.291 0.090 0.729	O 0.706 0.422 0.228
O 0.788 0.090 0.729	O 0.706 0.297 0.228
O 0.914 0.216 0.729	O 0.581 0.297 0.228
O 0.914 0.712 0.729	O 0.079 0.671 0.228
O 0.787 0.712 0.729	O 0.581 0.671 0.227
O 0.664 0.339 0.728	O 0.581 0.172 0.227
O 0.789 0.464 0.728	O 0.206 0.422 0.227
O 0.789 0.339 0.728	O 0.457 0.671 0.227
O 0.664 0.464 0.728	O 0.203 0.671 0.227
O 0.664 0.214 0.728	O 0.581 0.422 0.227
O 0.539 0.339 0.728	O 0.956 0.299 0.227
O 0.539 0.214 0.728	O 0.078 0.795 0.227
O 0.914 0.588 0.727	O 0.332 0.299 0.227
O 0.789 0.589 0.727	O 0.830 0.422 0.227
O 0.663 0.588 0.727	O 0.706 0.795 0.227
O 0.914 0.339 0.727	O 0.831 0.547 0.227
O 0.414 0.339 0.727	O 0.705 0.547 0.227
O 0.290 0.340 0.727	O 0.079 0.421 0.227
O 0.039 0.340 0.727	O 0.704 0.670 0.227
O 0.414 0.214 0.727	O 0.332 0.421 0.227
O 0.790 0.214 0.727	O 0.955 0.670 0.227
O 0.539 0.089 0.727	O 0.081 0.546 0.227
O 0.163 0.463 0.727	O 0.455 0.546 0.227
O 0.290 0.463 0.727	O 0.456 0.924 0.226

O 0.831 0.298 0.226	Zn 0.675 0.324 0.530
O 0.456 0.172 0.226	Zn 0.221 0.468 0.530
O 0.705 0.172 0.226	Zn 0.221 0.324 0.530
O 0.456 0.047 0.226	Zn 0.811 0.332 0.501
O 0.332 0.048 0.226	Zn 0.811 0.050 0.501
O 0.706 0.048 0.226	Zn 0.093 0.332 0.501
O 0.456 0.298 0.226	Zn 0.954 0.476 0.501
O 0.580 0.047 0.226	Zn 0.954 0.049 0.501
O 0.956 0.546 0.226	Zn 0.666 0.189 0.501
O 0.331 0.545 0.226	Zn 0.666 0.049 0.501
O 0.204 0.545 0.226	Zn 0.094 0.476 0.501
O 0.580 0.546 0.226	Zn 0.094 0.189 0.501
O 0.457 0.423 0.226	Zn 0.951 0.903 0.500
O 0.955 0.423 0.225	Zn 0.951 0.620 0.500
O 0.208 0.921 0.225	Zn 0.523 0.903 0.500
O 0.702 0.920 0.225	Zn 0.523 0.192 0.500
O 0.830 0.671 0.225	Zn 0.240 0.620 0.500
O 0.331 0.924 0.225	Zn 0.240 0.192 0.500
O 0.582 0.924 0.225	Zn 0.952 0.333 0.500
O 0.331 0.173 0.225	Zn 0.952 0.191 0.500
O 0.831 0.173 0.225	Zn 0.810 0.191 0.500
O 0.583 0.796 0.224	Zn 0.238 0.905 0.498
O 0.202 0.796 0.224	Zn 0.523 0.047 0.497
	Zn 0.096 0.620 0.497
Str 98 (WZ-ZnO-NP-12)	Zn 0.096 0.047 0.497
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.33 eV	Zn 0.381 0.904 0.497
E_{rel} : 0.15 eV/ZnO	Zn 0.381 0.049 0.497
Pore _{max} : 1.12 nm	Zn 0.239 0.762 0.497
V_{pore} : 23 %	Zn 0.239 0.049 0.497
D_{pore} : 1	Zn 0.094 0.904 0.497
cell parameters	Zn 0.094 0.762 0.497
22.980 22.980 5.327 90.00 90.00	Zn 0.946 0.759 0.496
120.00	Zn 0.384 0.759 0.496
fractional coordinates	Zn 0.384 0.197 0.496
Zn 0.905 0.238 0.998	Zn 0.922 0.819 0.030
Zn 0.620 0.096 0.997	Zn 0.922 0.675 0.030
Zn 0.047 0.523 0.997	Zn 0.468 0.819 0.030
Zn 0.047 0.096 0.997	Zn 0.468 0.221 0.030
Zn 0.904 0.381 0.997	Zn 0.324 0.675 0.030
Zn 0.904 0.094 0.997	Zn 0.324 0.221 0.030
Zn 0.762 0.239 0.997	Zn 0.332 0.811 0.001
Zn 0.762 0.094 0.997	Zn 0.332 0.093 0.001
Zn 0.049 0.381 0.997	Zn 0.050 0.811 0.001
Zn 0.049 0.239 0.997	Zn 0.476 0.954 0.001
Zn 0.759 0.946 0.996	Zn 0.476 0.094 0.001
Zn 0.759 0.384 0.996	Zn 0.189 0.666 0.001
Zn 0.197 0.384 0.996	Zn 0.189 0.094 0.001
Zn 0.819 0.922 0.530	Zn 0.049 0.954 0.001
Zn 0.819 0.468 0.530	Zn 0.049 0.666 0.001
Zn 0.675 0.922 0.530	Zn 0.903 0.951 0.000

Zn 0.903 0.523 0.000	O 0.476 0.811 0.378
Zn 0.620 0.951 0.000	O 0.476 0.237 0.378
Zn 0.620 0.240 0.000	O 0.332 0.666 0.378
Zn 0.192 0.523 0.000	O 0.332 0.237 0.378
Zn 0.192 0.240 0.000	O 0.905 0.238 0.377
Zn 0.333 0.952 0.000	O 0.476 0.953 0.377
Zn 0.191 0.952 0.000	O 0.476 0.095 0.377
Zn 0.191 0.810 0.000	O 0.190 0.666 0.377
O 0.953 0.334 0.878	O 0.190 0.095 0.377
O 0.953 0.190 0.878	O 0.048 0.953 0.377
O 0.809 0.190 0.878	O 0.048 0.666 0.377
O 0.811 0.906 0.878	O 0.334 0.809 0.376
O 0.811 0.476 0.878	O 0.334 0.096 0.376
O 0.666 0.906 0.878	O 0.046 0.809 0.376
O 0.666 0.332 0.878	O 0.905 0.381 0.376
O 0.237 0.476 0.878	O 0.905 0.095 0.376
O 0.237 0.332 0.878	O 0.762 0.238 0.376
O 0.238 0.905 0.877	O 0.762 0.095 0.376
O 0.953 0.476 0.876	O 0.048 0.381 0.376
O 0.953 0.048 0.876	O 0.048 0.238 0.376
O 0.666 0.190 0.876	O 0.906 0.953 0.376
O 0.666 0.048 0.876	O 0.906 0.524 0.376
O 0.095 0.476 0.876	O 0.619 0.953 0.376
O 0.095 0.190 0.876	O 0.619 0.237 0.376
O 0.809 0.334 0.876	O 0.189 0.524 0.376
O 0.809 0.046 0.876	O 0.189 0.237 0.376
O 0.096 0.334 0.876	O 0.618 0.095 0.374
O 0.381 0.905 0.876	O 0.048 0.525 0.374
O 0.381 0.048 0.876	O 0.048 0.095 0.374
O 0.238 0.762 0.876	O 0.762 0.952 0.374
O 0.238 0.048 0.876	O 0.762 0.381 0.374
O 0.095 0.905 0.876	O 0.191 0.381 0.374
O 0.095 0.762 0.876	
O 0.953 0.906 0.876	Str 99 (WZ-ZnO-NP-13)
O 0.953 0.619 0.876	$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW}}\text{-fit}): 0.36 \text{ eV}$
O 0.524 0.906 0.876	$E_{\text{rel}}: 0.21 \text{ eV/ZnO}$
O 0.524 0.189 0.876	Pore _{max} : 0.94 nm
O 0.237 0.619 0.876	V _{pore} : 24 %
O 0.237 0.189 0.876	D _{pore} : 1
O 0.525 0.048 0.874	cell parameters
O 0.095 0.618 0.874	19.810 19.810 5.342 90.00 90.00
O 0.095 0.048 0.874	120.51
O 0.952 0.762 0.874	fractional coordinates
O 0.381 0.762 0.874	Zn 0.386 0.109 1.000
O 0.381 0.191 0.874	Zn 0.058 0.781 1.000
O 0.334 0.953 0.378	Zn 0.056 0.111 0.999
O 0.190 0.953 0.378	Zn 0.386 0.944 0.998
O 0.190 0.809 0.378	Zn 0.223 0.780 0.998
O 0.906 0.811 0.378	Zn 0.718 0.935 0.998
O 0.906 0.666 0.378	Zn 0.232 0.448 0.998

Zn 0.058 0.277 0.997	O 0.113 0.221 0.877
Zn 0.889 0.109 0.997	O 0.612 0.893 0.877
Zn 0.552 0.104 0.997	O 0.274 0.555 0.877
Zn 0.063 0.615 0.997	O 0.275 0.891 0.877
Zn 0.552 0.939 0.996	O 0.944 0.889 0.877
Zn 0.228 0.614 0.996	O 0.277 0.222 0.877
Zn 0.723 0.105 0.995	O 0.946 0.221 0.877
Zn 0.062 0.444 0.995	O 0.110 0.056 0.875
Zn 0.788 0.909 0.532	O 0.276 0.057 0.875
Zn 0.258 0.379 0.532	O 0.110 0.891 0.875
Zn 0.621 0.912 0.531	O 0.779 0.052 0.874
Zn 0.255 0.545 0.531	O 0.114 0.388 0.874
Zn 0.456 0.917 0.527	O 0.947 0.386 0.874
Zn 0.250 0.711 0.527	O 0.780 0.219 0.874
Zn 0.947 0.056 0.502	O 0.943 0.722 0.874
Zn 0.111 0.220 0.502	O 0.445 0.224 0.874
Zn 0.941 0.886 0.502	O 0.447 0.899 0.873
Zn 0.281 0.225 0.502	O 0.268 0.720 0.873
Zn 0.275 0.891 0.502	O 0.442 0.058 0.873
Zn 0.946 0.221 0.500	O 0.109 0.724 0.873
Zn 0.781 0.058 0.500	O 0.110 0.554 0.872
Zn 0.109 0.386 0.500	O 0.613 0.057 0.872
Zn 0.111 0.056 0.499	O 0.947 0.556 0.872
Zn 0.944 0.386 0.498	O 0.611 0.220 0.872
Zn 0.780 0.223 0.498	O 0.889 0.779 0.378
Zn 0.935 0.718 0.498	O 0.388 0.277 0.378
Zn 0.448 0.232 0.498	O 0.221 0.112 0.377
Zn 0.277 0.058 0.497	O 0.054 0.945 0.377
Zn 0.109 0.889 0.497	O 0.893 0.612 0.377
Zn 0.104 0.552 0.497	O 0.555 0.274 0.377
Zn 0.615 0.063 0.497	O 0.891 0.275 0.377
Zn 0.939 0.552 0.496	O 0.889 0.944 0.377
Zn 0.614 0.228 0.496	O 0.222 0.277 0.377
Zn 0.105 0.723 0.495	O 0.221 0.946 0.377
Zn 0.444 0.062 0.495	O 0.056 0.110 0.375
Zn 0.909 0.788 0.032	O 0.057 0.276 0.375
Zn 0.379 0.258 0.032	O 0.891 0.110 0.375
Zn 0.912 0.621 0.032	O 0.388 0.114 0.374
Zn 0.545 0.255 0.032	O 0.052 0.779 0.374
Zn 0.917 0.456 0.027	O 0.386 0.947 0.374
Zn 0.711 0.250 0.027	O 0.219 0.780 0.374
Zn 0.220 0.111 0.002	O 0.722 0.943 0.374
Zn 0.056 0.947 0.002	O 0.224 0.445 0.374
Zn 0.886 0.941 0.002	O 0.899 0.447 0.373
Zn 0.225 0.281 0.002	O 0.720 0.268 0.373
Zn 0.891 0.275 0.002	O 0.058 0.442 0.373
Zn 0.221 0.946 0.000	O 0.724 0.109 0.373
O 0.779 0.889 0.878	O 0.554 0.110 0.372
O 0.277 0.388 0.878	O 0.057 0.613 0.372
O 0.945 0.054 0.877	O 0.556 0.947 0.372

O 0.220 0.611 0.372

Str 100 (WZ-ZnO-NP-14)

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.58 eV

E_{rel} : 0.29 eV/ZnO

Pore_{max}: 0.57 nm

V_{pore}: 24 %

D_{pore}: 1

cell parameters

13.242 13.242 5.374 90.00 90.00

119.71

fractional coordinates

Zn 0.827 0.409 1.000

Zn 0.591 0.173 1.000

Zn 0.336 0.664 0.999

Zn 0.598 0.919 0.997

Zn 0.081 0.402 0.997

Zn 0.184 0.364 0.530

Zn 0.636 0.816 0.530

Zn 0.939 0.382 0.518

Zn 0.618 0.061 0.518

Zn 0.419 0.581 0.505

Zn 0.669 0.586 0.502

Zn 0.414 0.331 0.502

Zn 0.409 0.827 0.500

Zn 0.173 0.591 0.500

Zn 0.664 0.336 0.499

Zn 0.402 0.081 0.497

Zn 0.919 0.598 0.497

Zn 0.364 0.184 0.030

Zn 0.816 0.636 0.030

Zn 0.382 0.939 0.018

Zn 0.061 0.618 0.018

Zn 0.581 0.419 0.005

Zn 0.586 0.669 0.002

Zn 0.331 0.414 0.002

O 0.419 0.581 0.878

O 0.665 0.582 0.876

O 0.418 0.335 0.876

O 0.664 0.336 0.875

O 0.172 0.336 0.875

O 0.664 0.828 0.875

O 0.418 0.828 0.870

O 0.172 0.582 0.870

O 0.415 0.086 0.869

O 0.914 0.585 0.869

O 0.928 0.357 0.866

O 0.643 0.072 0.866

O 0.581 0.419 0.378

O 0.335 0.418 0.376

O 0.582 0.665 0.376

O 0.336 0.664 0.375

O 0.828 0.664 0.375

O 0.336 0.172 0.375

O 0.828 0.418 0.370

O 0.582 0.172 0.370

O 0.086 0.415 0.369

O 0.585 0.914 0.369

O 0.357 0.928 0.366

O 0.072 0.643 0.366

Str 101 (WZ-ZnO-NP-15)

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.72 eV

E_{rel} : 0.28 eV/ZnO

Pore_{max}: 0.56 nm

V_{pore}: 25 %

D_{pore}: 1

cell parameters

11.516 11.520 5.365 89.99 90.03

119.99

fractional coordinates

Zn 0.312 0.000 0.565

Zn 0.937 0.376 0.564

Zn 0.561 0.625 0.564

Zn 0.430 0.326 0.540

Zn 0.611 0.168 0.540

Zn 0.104 0.674 0.540

Zn 0.263 0.494 0.540

Zn 0.769 0.506 0.540

Zn 0.443 0.833 0.540

Zn 0.561 1.000 0.064

Zn 0.312 0.375 0.064

Zn 0.936 0.625 0.064

Zn 0.430 0.167 0.041

Zn 0.263 0.833 0.040

Zn 0.610 0.506 0.040

Zn 0.104 0.494 0.040

Zn 0.769 0.326 0.040

Zn 0.443 0.674 0.040

O 0.440 0.334 0.914

O 0.106 0.666 0.914

O 0.602 0.169 0.914

O 0.270 0.504 0.913

O 0.767 0.496 0.913

O 0.433 0.831 0.913

O 0.284 0.000 0.912

O 0.936 0.348 0.912

O 0.588 0.652 0.912

O 0.440 0.169 0.414

O 0.271 0.831 0.414

O 0.602 0.496 0.413	Zn 0.521 0.197 0.847
O 0.106 0.504 0.413	Zn 0.520 0.339 0.847
O 0.767 0.334 0.413	Zn 0.664 0.483 0.847
O 0.433 0.666 0.413	Zn 0.806 0.483 0.847
O 0.589 0.000 0.412	Zn 0.750 0.112 0.383
O 0.284 0.348 0.412	Zn 0.350 0.112 0.383
O 0.936 0.652 0.411	Zn 0.893 0.254 0.382
	Zn 0.349 0.254 0.382
Str 102 (WZ-ZnO-NP-16)	Zn 0.749 0.654 0.382
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW}}\text{-fit}): 0.39 \text{ eV}$	Zn 0.893 0.654 0.381
$E_{\text{rel}}: 0.20 \text{ eV/ZnO}$	Zn 0.315 0.828 0.369
Pore _{max} : 1.12 nm	Zn 0.501 0.828 0.369
V _{pore} : 25 %	Zn 0.476 0.102 0.352
D _{pore} : 1	Zn 0.614 0.102 0.352
cell parameters	Zn 0.757 0.247 0.352
23.039 23.062 5.342 89.99 90.00	Zn 0.477 0.247 0.352
119.97	Zn 0.473 0.958 0.352
fractional coordinates	Zn 0.329 0.962 0.352
Zn 0.100 0.357 0.882	Zn 0.621 0.962 0.352
Zn 0.244 0.357 0.882	Zn 0.757 0.526 0.352
Zn 0.098 0.759 0.881	Zn 0.902 0.389 0.351
Zn 0.648 0.758 0.881	Zn 0.902 0.528 0.351
Zn 0.390 0.614 0.877	Zn 0.475 0.389 0.351
Zn 0.212 0.614 0.877	Zn 0.614 0.528 0.351
Zn 0.246 0.901 0.874	Zn 0.043 0.674 0.351
Zn 0.643 0.901 0.874	Zn 0.619 0.674 0.351
Zn 0.236 0.485 0.855	Zn 0.616 0.245 0.350
Zn 0.087 0.623 0.853	Zn 0.328 0.385 0.350
Zn 0.523 0.622 0.853	Zn 0.045 0.385 0.350
Zn 0.089 0.481 0.852	Zn 0.616 0.387 0.350
Zn 0.380 0.481 0.852	Zn 0.759 0.387 0.350
Zn 0.948 0.337 0.852	Zn 0.184 0.381 0.348
Zn 0.947 0.626 0.852	Zn 0.179 0.819 0.348
Zn 0.666 0.626 0.851	Zn 0.628 0.819 0.348
Zn 0.377 0.337 0.851	Zn 0.045 0.530 0.347
Zn 0.235 0.766 0.851	Zn 0.186 0.672 0.347
Zn 0.518 0.766 0.851	Zn 0.474 0.672 0.347
Zn 0.666 0.055 0.851	Zn 0.472 0.530 0.347
Zn 0.377 0.055 0.851	Zn 0.188 0.530 0.345
Zn 0.521 0.055 0.850	Zn 0.330 0.530 0.345
Zn 0.380 0.910 0.849	O 0.758 0.103 0.729
Zn 0.518 0.910 0.849	O 0.333 0.103 0.729
Zn 0.948 0.482 0.849	O 0.901 0.246 0.728
Zn 0.521 0.482 0.849	O 0.333 0.246 0.728
Zn 0.809 0.195 0.848	O 0.616 0.102 0.727
Zn 0.664 0.340 0.848	O 0.474 0.102 0.727
Zn 0.373 0.195 0.848	O 0.757 0.670 0.727
Zn 0.809 0.630 0.848	O 0.901 0.670 0.727
Zn 0.664 0.197 0.847	O 0.616 0.245 0.727
Zn 0.807 0.339 0.847	O 0.474 0.960 0.727

O 0.759 0.387 0.727
 O 0.616 0.387 0.727
 O 0.902 0.387 0.727
 O 0.759 0.245 0.727
 O 0.473 0.245 0.727
 O 0.473 0.387 0.727
 O 0.902 0.529 0.727
 O 0.616 0.529 0.727
 O 0.759 0.530 0.726
 O 0.042 0.672 0.726
 O 0.331 0.386 0.726
 O 0.617 0.671 0.726
 O 0.044 0.386 0.726
 O 0.617 0.961 0.726
 O 0.332 0.961 0.726
 O 0.044 0.529 0.725
 O 0.187 0.387 0.725
 O 0.473 0.529 0.725
 O 0.186 0.528 0.724
 O 0.183 0.672 0.724
 O 0.476 0.672 0.724
 O 0.330 0.528 0.724
 O 0.184 0.816 0.722
 O 0.620 0.815 0.721
 O 0.324 0.821 0.718
 O 0.484 0.821 0.718
 O 0.236 0.341 0.228
 O 0.092 0.341 0.228
 O 0.234 0.481 0.228
 O 0.089 0.624 0.227
 O 0.523 0.624 0.227
 O 0.088 0.766 0.227
 O 0.521 0.053 0.227
 O 0.665 0.766 0.227
 O 0.091 0.481 0.227
 O 0.664 0.340 0.227
 O 0.378 0.481 0.227
 O 0.663 0.197 0.226
 O 0.663 0.056 0.226
 O 0.521 0.197 0.226
 O 0.380 0.056 0.226
 O 0.949 0.341 0.226
 O 0.807 0.340 0.226
 O 0.379 0.341 0.226
 O 0.521 0.340 0.226
 O 0.663 0.482 0.226
 O 0.948 0.623 0.226
 O 0.663 0.623 0.226
 O 0.807 0.482 0.226
 O 0.950 0.482 0.225

O 0.521 0.482 0.225
 O 0.382 0.622 0.225
 O 0.227 0.622 0.225
 O 0.807 0.198 0.224
 O 0.379 0.198 0.224
 O 0.522 0.913 0.224
 O 0.379 0.913 0.224
 O 0.806 0.624 0.224
 O 0.239 0.909 0.223
 O 0.658 0.909 0.223
 O 0.229 0.767 0.223
 O 0.525 0.767 0.222

Str 103 (WZ-ZnO-NP-17)

$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.53 eV

E_{rel} : 0.27 eV/ZnO

Pore_{max}: 0.83 nm

V_{pore}: 29 %

D_{pore}: 1

cell parameters

16.447 16.447 5.358 90.00 90.00

120.78

fractional coordinates

Zn 0.862 0.929 0.999

Zn 0.070 0.138 0.999

Zn 0.867 0.331 0.996

Zn 0.669 0.133 0.996

Zn 0.661 0.922 0.995

Zn 0.078 0.339 0.995

Zn 0.868 0.132 0.992

Zn 0.743 0.887 0.530

Zn 0.113 0.257 0.530

Zn 0.542 0.890 0.528

Zn 0.110 0.458 0.528

Zn 0.747 0.253 0.527

Zn 0.935 0.065 0.501

Zn 0.935 0.265 0.501

Zn 0.735 0.065 0.501

Zn 0.928 0.467 0.500

Zn 0.533 0.072 0.500

Zn 0.929 0.862 0.499

Zn 0.138 0.070 0.499

Zn 0.331 0.867 0.496

Zn 0.133 0.669 0.496

Zn 0.922 0.661 0.495

Zn 0.339 0.078 0.495

Zn 0.132 0.868 0.492

Zn 0.887 0.743 0.030

Zn 0.257 0.113 0.030

Zn 0.890 0.542 0.028

Zn 0.458 0.110 0.028	19.707 19.707 5.351 90.00 90.00
Zn 0.253 0.747 0.027	120.00
Zn 0.065 0.935 0.001	fractional coordinates
Zn 0.265 0.935 0.001	Zn 0.557 0.943 0.999
Zn 0.065 0.735 0.001	Zn 0.557 0.614 0.999
Zn 0.467 0.928 0.000	Zn 0.386 0.943 0.999
Zn 0.072 0.533 0.000	Zn 0.386 0.443 0.999
O 0.733 0.865 0.876	Zn 0.057 0.614 0.999
O 0.135 0.267 0.876	Zn 0.057 0.443 0.999
O 0.935 0.065 0.875	Zn 0.721 0.442 0.999
O 0.938 0.267 0.874	Zn 0.721 0.279 0.999
O 0.733 0.062 0.874	Zn 0.558 0.279 0.999
O 0.737 0.263 0.874	Zn 0.562 0.781 0.996
O 0.931 0.866 0.873	Zn 0.219 0.781 0.996
O 0.134 0.069 0.873	Zn 0.219 0.438 0.996
O 0.531 0.866 0.873	Zn 0.389 0.778 0.991
O 0.134 0.469 0.873	Zn 0.389 0.611 0.991
O 0.935 0.466 0.873	Zn 0.222 0.611 0.991
O 0.534 0.065 0.873	Zn 0.591 0.879 0.531
O 0.132 0.868 0.872	Zn 0.591 0.712 0.531
O 0.333 0.871 0.872	Zn 0.288 0.879 0.531
O 0.129 0.667 0.872	Zn 0.288 0.409 0.531
O 0.928 0.664 0.871	Zn 0.121 0.712 0.531
O 0.336 0.072 0.871	Zn 0.121 0.409 0.531
O 0.865 0.733 0.376	Zn 0.445 0.890 0.501
O 0.267 0.135 0.376	Zn 0.445 0.555 0.501
O 0.065 0.935 0.375	Zn 0.110 0.555 0.501
O 0.267 0.938 0.374	Zn 0.943 0.557 0.499
O 0.062 0.733 0.374	Zn 0.943 0.386 0.499
O 0.263 0.737 0.374	Zn 0.614 0.557 0.499
O 0.866 0.931 0.373	Zn 0.614 0.057 0.499
O 0.069 0.134 0.373	Zn 0.443 0.386 0.499
O 0.866 0.531 0.373	Zn 0.443 0.057 0.499
O 0.469 0.134 0.373	Zn 0.442 0.721 0.499
O 0.466 0.935 0.373	Zn 0.279 0.721 0.499
O 0.065 0.534 0.373	Zn 0.279 0.558 0.499
O 0.868 0.132 0.372	Zn 0.781 0.562 0.496
O 0.871 0.333 0.372	Zn 0.781 0.219 0.496
O 0.667 0.129 0.372	Zn 0.438 0.219 0.496
O 0.664 0.928 0.371	Zn 0.778 0.389 0.491
O 0.072 0.336 0.371	Zn 0.611 0.389 0.491
	Zn 0.611 0.222 0.491
Str 104 (WZ-ZnO-NP-18)	Zn 0.879 0.591 0.031
$\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.46 eV	Zn 0.879 0.288 0.031
E_{rel} : 0.23 eV/ZnO	Zn 0.712 0.591 0.031
Pore _{max} : 1.12 nm	Zn 0.712 0.121 0.031
V _{pore} : 31 %	Zn 0.409 0.288 0.031
D _{pore} : 1	Zn 0.409 0.121 0.031
cell parameters	Zn 0.890 0.445 0.001
	Zn 0.555 0.445 0.001

Zn 0.555 0.110 0.001
 O 0.609 0.888 0.877
 O 0.609 0.721 0.877
 O 0.279 0.888 0.877
 O 0.279 0.391 0.877
 O 0.112 0.721 0.877
 O 0.112 0.391 0.877
 O 0.445 0.890 0.875
 O 0.445 0.555 0.875
 O 0.110 0.555 0.875
 O 0.945 0.556 0.874
 O 0.945 0.389 0.874
 O 0.611 0.556 0.874
 O 0.611 0.055 0.874
 O 0.444 0.389 0.874
 O 0.444 0.055 0.874
 O 0.445 0.723 0.873
 O 0.277 0.723 0.873
 O 0.277 0.555 0.873
 O 0.778 0.556 0.872
 O 0.778 0.222 0.872
 O 0.444 0.222 0.872
 O 0.779 0.389 0.872
 O 0.611 0.389 0.872
 O 0.611 0.221 0.872
 O 0.888 0.609 0.377
 O 0.888 0.279 0.377
 O 0.721 0.609 0.377
 O 0.721 0.112 0.377
 O 0.391 0.279 0.377
 O 0.391 0.112 0.377
 O 0.890 0.445 0.375
 O 0.555 0.445 0.375
 O 0.555 0.110 0.375
 O 0.556 0.945 0.374
 O 0.556 0.611 0.374
 O 0.389 0.945 0.374
 O 0.389 0.444 0.374
 O 0.055 0.611 0.374
 O 0.055 0.444 0.374
 O 0.723 0.445 0.373
 O 0.723 0.277 0.373
 O 0.555 0.277 0.373
 O 0.556 0.778 0.372
 O 0.222 0.778 0.372
 O 0.222 0.444 0.372
 O 0.389 0.779 0.372
 O 0.389 0.611 0.372
 O 0.221 0.611 0.372

Str 105 (WZ-ZnO-NP-19)
 $\Delta E_{\text{gap}}(\text{PBE}_{\text{GW-fit}})$: 0.81 eV
 E_{rel} : 0.32 eV/ZnO
 Pore_{max} : 0.75 nm
 V_{pore} : 33 %
 D_{pore} : 1
 cell parameters
 16.419 16.419 5.373 90.00 90.00
 120.00
 fractional coordinates
 Zn 0.667 0.935 0.998
 Zn 0.068 0.333 0.998
 Zn 0.065 0.932 0.998
 Zn 0.868 0.931 0.996
 Zn 0.863 0.132 0.996
 Zn 0.069 0.137 0.996
 Zn 0.951 0.895 0.526
 Zn 0.744 0.049 0.526
 Zn 0.105 0.256 0.526
 Zn 0.940 0.452 0.524
 Zn 0.548 0.688 0.524
 Zn 0.312 0.060 0.524
 Zn 0.933 0.067 0.502
 Zn 0.923 0.264 0.501
 Zn 0.736 0.859 0.501
 Zn 0.141 0.077 0.501
 Zn 0.533 0.868 0.498
 Zn 0.135 0.467 0.498
 Zn 0.132 0.865 0.498
 Zn 0.337 0.869 0.496
 Zn 0.332 0.663 0.496
 Zn 0.131 0.668 0.496
 Zn 0.456 0.905 0.026
 Zn 0.249 0.544 0.026
 Zn 0.095 0.751 0.026
 Zn 0.888 0.348 0.024
 Zn 0.652 0.740 0.024
 Zn 0.260 0.112 0.024
 Zn 0.267 0.733 0.003
 Zn 0.464 0.723 0.001
 Zn 0.277 0.941 0.001
 Zn 0.059 0.536 0.001
 O 0.933 0.067 0.875
 O 0.930 0.266 0.873
 O 0.734 0.864 0.873
 O 0.136 0.070 0.873
 O 0.534 0.861 0.872
 O 0.139 0.872 0.872
 O 0.128 0.466 0.872
 O 0.334 0.866 0.872

O 0.332 0.666 0.872
O 0.134 0.668 0.872
O 0.938 0.872 0.871
O 0.734 0.062 0.871
O 0.128 0.266 0.871
O 0.931 0.467 0.869
O 0.533 0.664 0.869
O 0.336 0.069 0.869
O 0.267 0.733 0.375
O 0.466 0.730 0.373
O 0.270 0.936 0.373
O 0.064 0.534 0.373

O 0.666 0.928 0.372
O 0.072 0.939 0.372
O 0.061 0.334 0.372
O 0.868 0.934 0.372
O 0.866 0.132 0.372
O 0.066 0.134 0.372
O 0.466 0.928 0.371
O 0.262 0.534 0.371
O 0.072 0.738 0.371
O 0.864 0.333 0.369
O 0.667 0.731 0.369
O 0.269 0.136 0.369



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