

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**DESIGN, DEVELOPMENT AND APPLICATION OF
NANOSTRUCTURE BASED SENSOR PLATFORMS FOR
CHEMICAL AND BIOLOGICAL SENSING**

ONUR ALEV
**A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF PHYSICS**

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**THESIS SUPERVISOR
PROF. DR. ZAFER ZİYA ÖZTÜRK**

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T.C.
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FEN BİLİMLERİ ENSTİTÜSÜ

KİMYASAL VE BİYOLOJİK
ALGILAMALAR İÇİN
NANOYAPI TEMELLİ SENSOR
PLATFORMLARININ TASARIMI,
GELİŞTİRİLMESİ VE UYGULANMASI

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TEZ DANIŞMANI
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SUMMARY

Chemical sensors and biosensors are of the highest importance in the field of medical diagnostics, food industries, agriculture, national security, and environmental monitoring. Recently, there have been emerging demands for a new approach in sensing technology with high accuracy, mobile, low cost, and easier to use, among which biosensors are a possible application. To this end, new sensor platforms for the development of sensing technology have been required to apply desired fields. Especially, demand grows for point-of-care devices for health diagnostics and monitoring. To meet this demand, sensor platforms should be improved.

The creation of new materials of different dimensionality and functionality is one of the most important goals of designing the sensor platform. In this case, the properties of nanostructured materials can be different and, in many ways, far superior to those of the bulk counterpart because of enlarged surface area without increasing the device dimensions. Transition metal dichalcogenides (MoS_2 , WS_2 , etc.) and transition metal oxides (TiO_2 , ZnO , etc.) have been successfully fabricated as Nanorods, nanowires, nanotubes, monolayers, and few-layer crystals for sensing technology.

In this thesis, nanostructure-based sensor platforms were fabricated with different techniques such as hydrothermal, magnetron sputter, and atomic layer deposition for sensor applications.

Keywords: Chemical Sensors, Biosensors, Nanostructured Materials, Mass Sensitive Devices, Atomic Layer Deposition, Electrochemical Deposition, RF Magnetron Sputtering, Hydrothermal.

ÖZET

Sensörler tıbbi teşhis, gıda endüstrisi, ziraat, ulusal güvenlik ve hava kalitesi görüntüleme gibi birçok alandaki uygulamalarda kullanılmaktadır. Son yıllarda, doğru, taşınabilir, düşük maliyetli ve kolay kullanılabilir biyosensörlere karşı artan bir talep bulunmaktadır. Belirli alanlara yönelik bu talebi karşılamak için sensör teknolojilerinde bazı ilerlemeler yapılması gerekmektedir. Özellikle hasta başı tanısı için biyosensör geliştirmeye yönelik büyük bir ihtiyaç mevcuttur. Bu ihtiyacı karşılamak için sensör platformlarının geliştirilmesi gerekmektedir.

Sensör platformunun tasarımı için en önemli hedef yeni malzemelerin farklı boyutlarda üretim fonksiyonel hale getirilmeleridir. Özellikle nanoyapılı malzemelerin özellikleri cihaz boyutunu arttırmadan yüzey alanı arttığı için çok daha iyi olmaktadır. Geçiş metali dikalginitler (MoS_2 , WS_2 vb.) veya oksitler (TiO_2 , ZnO vb.) nanoçubuklar, nanoteller, nanotüpler, tek katman veya birkaç katmandan oluşan kristal yapılar şeklinde sensör teknolojilerinde kullanılmak amacı ile sentezlenebilirler.

Bu tezde, hidrotermal, magnetron saçtırma ve atomik katman kaplama gibi farklı yöntemler ile nanoyapılar kullanılarak sensör platformlar geliştirilecektir.

Anahtar Kelimeler: Kimyasal Sensör, Biyosensör, Nanoyapılı Malzemeler, Kütle Duyarlı Cihazlar, Atomik Katman Büyütme, Elektrokimyasal Depolama, RF Magnetron Saçtırma, Hidrotermal

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LIST of ACRONYMS and ABBREVIATIONS

<u>Acronyms and Abbreviations</u>	<u>Explanation</u>
ALD	: Atomic layer deposition
AlN	: Aluminum nitride
AFM	: Atomic force microscopy
BN	: Boron Nitride
BSA	: Bovine serum albumine
BTEX	: Benzene, toluene, ethylbenzene and xylen
CEES	: 2-Chloroethyl ethyl sulfide
CN	: Carbon nitride
CNT	: Carbon nanotubes
CO	: Carbon monoxide
CO ₂	: Carbon dioxide
CVD	: Chemical vapor deposition
CWA	: Chemical warfare agents
C ₃ H ₈	: Propane
CH ₄	: Methane
DEZ	: Diethyl zinc
DMMP	: Dimethyl methylphosphonate
EDS	: Electron dispersive spectroscopy
FET	: Field effect transistor
FWHM	: Full-width half-maximum
GO	: Graphene oxide
GPIB	: General purpose interface bus
H ₂	: Hydrogen
HCN	: Hydrogen cyanide
H ₂ S	: Hydrogen sulfide
hTF	: Human transferrin
IDE	: Inter digital electrodes
IPA	: Isopropyl alcohol
KCl	: Potassium chloride
LOD	: Limit of detection

MOS ₂	:	Molybdenum sulfide
MOX	:	Metal-oxide
NH ₃	:	Ammonia
NO	:	Nitrogen oxide
NO ₂	:	Nitrogen dioxide
PLD	:	Pulse laser deposition
PVD	:	Physical vapor deposition
rGO	:	Reduced graphene oxide
ppb	:	Particle per billion
ppm	:	Particle per million
RF	:	Radio frequency
R.H.	:	Relative humidity
RT	:	Room temperature
SO ₂	:	Sulfur dioxide
SEM	:	Scanning electron microscopy
SWNT	:	Single wall nanotube
QCM	:	Quartz crystal microbalance
TiO ₂	:	Titanium dioxide
TLV	:	Threshold limit value
TMDC	:	Transition dichalcogenides
VOC	:	Volatile organic compounds
WO ₂	:	Tungsten oxide
WS ₂	:	Tungsten disulfide
XPS	:	X-ray photoelectron spectroscopy
XRD	:	X-ray diffraction
ZnO	:	Zinc oxide

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1. INTRODUCTION

The senses of living organisms provide a powerful way to interact with their surroundings and help for collecting information from the surrounding environment [1]. This flawless mechanism inspires scientists to develop new sensor technologies. Thus, analytic instrumentation which builds upon the principles of molecular recognition can analyze temperature, pressure, and chemical information about a sample. In addition, with the advancement of nanotechnology, nanostructural materials such as one-dimensional (1D) and two-dimensional (2D) materials can be easily integrated into sensor systems and as a result, new generation sensors are emerging [2-4].

A typical sensor comprises two important components: the sensitive layer and the transducer [1, 5]. The sensing material is responsible for interacting with the surrounding environment. Thus, choosing the sensitive layer is the crucible for sensor performance. For this reason, the sensitive layer should have a certain set of properties depending on the application field [6]. First, the sensitive layer must be stable during the interaction and must exhibit a reproducible response to the target analyte for a prolonged period. Second, the sensing material must have chemical, catalytic, and electrophysical properties suitable for the target analyte [7]. For example, in biosensor applications, the selection of the appropriate bio-recognition layer for surface immobilization is important in the detection of antigen-antibody interaction [8, 9]. On the other hand, sensors to be used for disease detection from human breath should use a sensing layer sensitive to volatile organic molecules [10]. Third, to fabricate highly sensitive sensors, 1D and 2D materials offer larger active sites due to higher surface-to-volume ratio [7]. Various materials have been used to meet the above requirements in both gas and biosensor applications [11]. Among these materials, 2D metal-oxides (MOXs) and Transition metal dichalcogenides (TMDCs) are highly attractive due to their superior molecular sensing capability, unique physical and chemical features, biocompatibility, semi-conducting properties, high surface-to-volume ratio, and diversity in fabrication methods [12, 13]. These features make MOXs and TMDCs one of the most important candidates for sensing applications.

Another important component of a sensor is the transducing platform. The transducer produces a measurable change in an electrical or other output which is

proportional to the input stimulus measured [1, 14]. The most studied transducer classes are mass sensitive, chemi-resistive, electrochemical, and optic sensors [15]. Each transducer technology has its advantages and provides different types of information [16]. Thus, a transducer that can detect every analyte with high performance in every environment cannot be mentioned. Instead, choosing the optimum transducer platform which is suitable for the environment to be used may be the best approach [16]. For example, while developing a sensor that will detect proteins such as cholesterol or glucose in the blood, it may be necessary to choose a transducer that can operate in a liquid environment [17, 18]. On the other hand, while developing sensors that will detect industrial gases, it may be more accurate to choose a sensor platform that is resistant to harsh atmospheres [19].

Last decades, small dimensional sensing devices have been studied for practical applications. However, very few of these efforts have met commercial viability. For this reason, fast, reliable, and durable sensing devices are immediately developed to meet the demands of society. Therefore, the combination of two-dimensional materials as the sensing layer and a transducer element selected according to the application area can form the basis of new generation sensor studies.

2. NANOSTRUCTURED MATERIALS FOR BIO/CHEMICAL SENSING APPLICATIONS

In this chapter, types of sensing devices, their sensing mechanism, performance parameters, influence factors, and how to collect information from them will be briefly introduced.

2.1. Types of Nanostructured Materials for Bio/Chemical Applications

The potential of nanotechnology can enable to manipulation of materials at the nanoscale. It is reported that some material features may differ depending on the dimensions [20, 21]. Thus, nanostructured materials offer unique properties which cannot be achieved with bulk structures [22]. One of the most important features of nanostructural materials is the high surface-to-volume ratio [22]. The importance of this feature for sensor applications is that it provides a large number of reactive sites, which can interact with the target analyte [23]. In addition, physical and chemical properties determined by the size also contribute to their major role in the new generation of sensors [7].

The fact that at least one of the dimensions that form material is below 100 nm is sufficient for that material to be called nanostructured. Also, a material can be nanoscale not only in one dimension but also in two or all dimensions. Therefore, a general classification of materials can be identified in four groups namely 0D, 1D, 2D, and 3D [24]. As the dimensions go down to nanoscales, the physical and chemical properties of materials change significantly. For this reason, each group of nanomaterials has its characteristics.

Recently, 0D materials have attracted great interest, especially with the production of quantum dots [25]. Various materials such as graphene, metal, MOX, and TMDC have been synthesized as quantum dots [26-28]. Significant results have been obtained in various applications such as optoelectronics, catalyst, energy, medical, and sensing due to size-dependent unique optical, chemical, and physical properties [29-31].

Among nanostructural materials, 1D materials may be the most interesting structures because of various morphological diversity including nanowires, nanorods,

nanotubes, nanobelts, and nanoflakes [5, 25, 32]. Various materials such as carbon, metal, MOX, and polymer can be synthesized as 1D via chemical and physical processes [25, 33-36]. However, wet-chemical synthesis methods such as solve/hydrothermal, electrochemical deposition, and anodization are one of the most facile and most applied methods for the fabrication of 1D materials [7, 25, 37].

After the fabrication of thin carbon films, 2D materials have become the focus of attention in material sciences [38, 39]. The shape-dependent electronic and surface features make 2D materials highly favorable for surface-active applications such as sensing, catalyst, and energy storage [40]. For this reason, choosing the proper material suitable for the application is vital for optimum performance. Up to now, several hundreds of different 2D materials with extraordinary properties have been studied [39].

2.1.1. Graphene and Graphene Oxide

Due to unique thermal, chemical, optical, and electronic features, carbon-based nanomaterials can be considered an important material for new technologies [41]. The family of carbon-based nanomaterials contains materials such as graphene, graphene oxide, fullerenes, and carbon nanotubes and each has completely different properties from one other [42]. Thereby, it would be useful to examine each one separately.

Among carbon-based materials, perhaps the first to be mentioned is fullerenes. It was the first symmetric carbon nanostructure and led to the discovery of other carbon-based nanomaterials [43]. This growing interest in carbon-based materials has been taken to another level with CNTs [44]. CNTs are formed by the cylindrical arrangement of carbon atoms. Single-walled carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs) are the two most important structures [45]. CNTs exhibited amazing characteristics which make them valuable nanomaterials in several real-world applications such as aeronautics [46], durable materials [47], and cell phone technologies [48].

The popularity of carbon-based materials gained momentum with the discovery of graphene. Since graphene was first reported by Novoselov *et al.*, it has become one of the most published topics due to its extraordinary physical and chemical properties [38]. The intrinsic properties of graphene depend on the number of layers in the stack making it more attractive [49, 50]. These striking features of graphene indicate that

graphene-based materials can be a revolutionary candidate in the fields of sensors, transistors, solar cells, catalysts, and membrane technology [41]. Recently, among graphene-based materials, graphene oxide (GO) has attracted more interest due to its surface oxygen-containing groups which allow surface functionalization [51, 52]. These groups can be reduced or removed via different techniques [53, 54]. The product formed after the reduction of an oxygen-containing species is called reduced graphene oxide (rGO) [53, 55]. The better electrode properties of rGO compared to GO and graphene enable this material to be used frequently in surface-active devices such as batteries, supercapacitors, and sensors [55].

2.1.2. Transition Metal Dichalcogenides

TMDC are generally defined as MX_2 , where M represents a transition metal including Ti, Zr, Hf, Mo, W, etc. and X is a chalcogen such as Se, S, and T [56]. The structure is held together by an interatomic covalent bond and weak interlayer van der Waals forces [56]. In contrast to graphene, each TMDC has a different crystal structure and stacking orders between layers [57]. As a result of this, bulk TMDCs differ from semiconductors (MoS_2 and WS_2), semimetals (WTe_2), and insulators (HfS_2) [58]. As in graphene, layer-dependent properties have aroused great interest in TMDC as well [59]. At least 40 of the 60 TMDC known since their first discovery by Dickinson and Pauling have a layered structure [60, 61].

Some intrinsic properties of TMDC change as the thickness is reduced from bulk to a few monolayers [61]. For example, some semiconductor TMDC, which have an indirect band gap in bulk form, exhibit direct band gap properties in monolayered or a few layered forms [62]. Due to their direct band gap in the visible spectrum and strong photoluminescence, TMDCs are promising candidates to be used in optoelectronic applications including photodetectors, solar cells, and light-emitting diodes [63]. Besides these optical properties, TMDC can be used in a wide range of surface-active applications due to their surface features. Ding et al. reported a study that tungsten disulfide (WS_2) is used in many applications such as catalysis, batteries, gas sensors, and biosensors [64].

TMDC can be fabricated by many more methods compared to carbon-based materials. For example, MoS_2 , which is one of the most studied TMDC, can be synthesized through various techniques such as hydrothermal route [65], sputtering

[66], atomic layer deposition (ALD) [67], and sol-gel technique [68]. Moreover, the exfoliation techniques such as mechanical and liquid phases are frequently used in the production of high-quality layered TMDC [69, 70]. This diversity in synthesis methods of TMDC offers diverse morphological and compositional structures [61]. Though TMDCs have been known for decades, the discovery of their properties and applications are relatively new. Thus, TMDCs can be an important candidate for sensing applications [59].

2.1.3. Metal Oxides

MOXs are composed of oxide ions formed by metal and oxygen, and they are one of the most diverse members of solids [71]. With the development of nanotechnology, improvements in the chemical properties of metal oxide materials were observed due to the enhancement in the characteristics of nanosized nature [72]. Intensive studies have been carried out on the fabrication of MOX nanostructures with different morphologies such as nanotubes, nanorods, nanobelts, nanofibers, and quantum dots [73]. Up to now, nanostructured MOXs have been synthesized using various techniques including top-down and bottom-up approaches [72, 74]. Shen et al. reported a comprehensive study about MOX nanostructures synthesized using different methods [73].

Up to now, MOX materials have been used in many fields, including materials chemistry, condensed matter physics, geology, materials science, and mechanical and electrical engineering [75]. One of the main reasons for this diversity is that the materials in the MOX family display a variety of phenomena such as semiconductivity, superconductivity, piezoelectricity, negative thermal expansion, etc. [75-77]. For example, zinc oxide (ZnO), which is one of the most studied MOXs, is known as piezoelectric property [78]. Thanks to piezoelectricity, ZnO-based devices can be used in energy harvesting, motion sensors, pressure sensors, and wearable biosensors [78]. Some MOXs such as tungsten oxide (WO_3) and titanium dioxide (TiO_2) can be used in optoelectronic applications due to their electron transport and optical absorption properties [79-81]. In addition, their surface features such as defects, grain boundaries, etc. that are sensitive to changes in their environment as well as surface-to-volume ratio make MOX materials important candidates in surface-active applications such as gas sensors, biosensors, and fuel cells [72, 82, 83].

2.1.4. Other Nanostructured Materials

Other nanostructured materials, including Xenes, carbon nitride, boron nitride, Phosphorene, and MXenes, also show great potential in device applications although relatively new and less studied than the materials mentioned above [1, 2, 84-86]. Great achievements with graphene, MOXs, and TMDC boost the interest in these materials.

Xenes family are known as mono-elemental 2D crystals and includes group III, IV, V, and VI elements in the Periodic Table [87]. Borophene, silicene, germanene, and stanene are some of the important members of this family [87]. Tao et al. reported the classification and types of Xenes in a comprehensive review study [88]. They reported that Xenes can be synthesized by several methods including physical vapor deposition (PVD), chemical vapor depositions (CVD), molecular beam epitaxy (MBE), and pulse laser deposition (PLD). Xenes can be applied to various device applications due to their electronic structure ranging from insulators to semiconductors [1]. Thus, Xenes offer a promised potential for new generation nanostructured materials [84].

Boron nitride (BN) is a material found in the natural forming of B and N atoms [89]. BN has three crystalline forms: hexagonal BN (h-BN), cubic BN (c-BN), and wurtzite BN (w-BN) [89]. Among them, h-BN is the most stable phase of BN and shows similarities with graphene in terms of in-plane structural formations [89]. On the other hand, h-BN is an electrical insulator, thermally conductive, and dielectric material [90]. Thereby, h-BNs can be used in applications such as insulating and dielectric layers, protective coatings, thermally conductive adhesives, etc. [89, 91].

Carbon nitrides (CN) have attracted great interest since the report that CNs can be good candidates for extreme hardness [92]. CNs are another carbon-based material with a nitrogen-rich structure [85]. Among various analogs of CN, graphitic carbon nitride (g-C₃N₄) may be one of the most studied CN-based materials due to its metal-free semiconductivity, active surface sites, and light absorption properties [93]. Its van der Waals bonding between layers and flake-like structure are very similar to graphite [94, 95]. As a result of these features, g-C₃N₄ has been applied in applications of photocatalysts, energy conversion and storage, and light-emitting devices [96-98].

Phosphorene, which is a monolayer or few layer form of black phosphorus, has an orthorhombic structure where phosphorus atoms bonded via covalent bonds [99]. Alike graphite, the layers are held together by van der Waals forces [99]. The discovery

of layer-dependent features of phosphorene such as optical, mechanical, thermal, and electronic opens new possibilities for phosphorene in various applications [100, 101].

2.2. Device structures

A chemical sensor is a device that can measure analytical parameters and convert the chemical data into a measurable signal [102, 103]. One of the most important parts which affect the sensing performance of chemical sensors is the transducer. Moreover, choice of transducer element plays a crucial role in the application area [103]. A corresponding definition of a transducer is a device that can transform the chemical information resulting from the interaction between the analyte and the sensor into a useful analytic signal [104, 105]. In the following sections, the most used transducer types in sensing applications are described, and their operation mechanisms are discussed.

2.2.1. Chemiresistors

The chemiresistive type devices are considered one of the most studied groups in the field of sensor systems. Chemiresistors offer important advantages such as low cost, ease of use, low power consumption, ease in fabrication, and miniaturization. The working principle of chemiresistors can be described as the change in sensor resistance as a result of the chemical reaction between the analyte and the sensor surface. Electron accepting analytes extract an electron from the chemiresistive sensor and increase its resistance, whereas electron donating analytes decrease the resistance. Thus, measuring this resistance change is correlated to the target analyte [106-108]. In its simplest form, a chemiresistor consists of a sensing material and electrodes in which the change in resistance is measured as described in Figure 2.1 (adopted from ref. [1]). The change in resistance or current of the chemiresistor sensor is directly related to the concentration or amount of analytes [109].

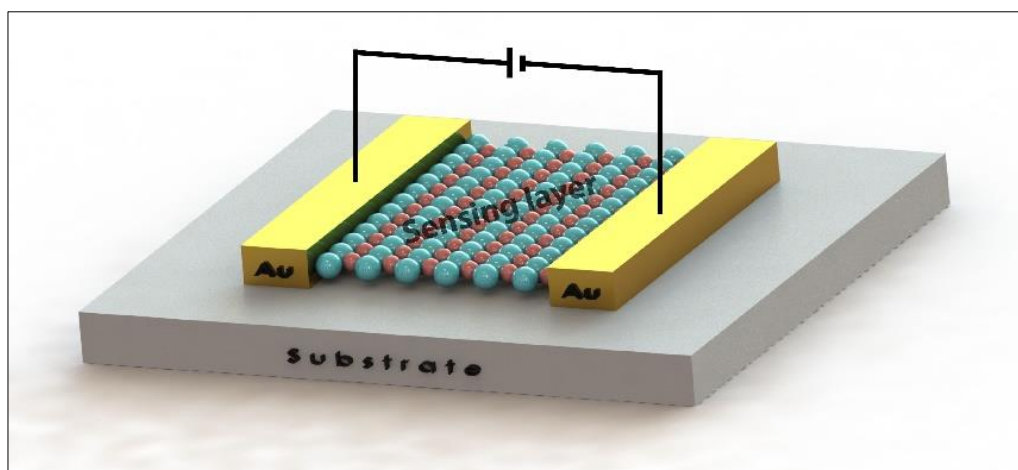


Figure 2.1: A schematic illustration of a chemiresistor sensor.

2.2.2. Field Effect Transistors (FETs)

Another transducer type for chemical sensing is based on the field-effect geometry. FET sensors consist of a semiconductor channel as a sensing layer between the source and drain electrodes at the top and the gate electrode at the bottom [110]. Mainly, the sensor performance of FET-based gas sensors is determined by the electronic properties of the channel material such as band gap, work function, and carrier mobility [111]. The interaction between the target analyte and the semiconductor channel material affects the electronic features of the FET device [110]. Thereby, by measuring the change of the drain current, the sensor response to the target analyte can be observed.

2.2.3. Schottky Diodes

Schottky devices, formed by a semiconductor with metal/metal-like materials, have been used for different applications such as biosensors and gas sensors [112-115]. The interaction between the target analyte and the sensor mainly takes place on the surface of the semiconductor. As a result of this interaction, the current through the device and thus the Fermi level can be modulated [2]. Precisely altering of Schottky barrier height allows the detection of target molecules with high sensitivity and low power. Although 2D materials such as metal-oxide and graphene can be applied to this device structure, wide band gap semiconductors such as GaN and AlN are not suitable [116].

2.2.4. Mass Sensitive Sensors

Mass-sensitive devices can be defined as piezoelectric transducers that are sensitive to the change in mass [103]. Thereby, the working principle of a mass-sensitive device is based on the piezoelectric effect [117]. Quartz crystal microbalance (QCM)-based mass-sensitive devices offer the advantage of high sensitivity, label-free measurements, online monitoring, and shorter analysis time to detect pathogens, toxins, or biologically active molecules [118-120]. Moreover, QCM-based biosensors are often used to determine antigen-antibody, enzyme-substrate, or receptor-ligand interactions [118, 119, 121].

A typical QCM device consists of AT-cut quartz sandwiched between two metal circular electrodes (Au, Ag, etc.) as seen in Figure 2.2(a). An applied alternating voltage between these electrodes induces very stable mechanical oscillations due to the high quality of quartz [122]. A change in the resonance frequency of a QCM device is proportional to the amount of mass absorbed or placed onto the surface. In Figure 2.2(b), a typical sensor response curve of a QCM sensor is given [123]. The mass-frequency relationship is described by the Sauerbrey equation [124]:

$$\Delta f = \frac{-2.3 \times 10^{-6} f^2 \Delta m}{A} \quad (2.1)$$

where f is the fundamental frequency of a QCM, Δf is the frequency change, A is the active surface area and Δm is the absorbed or placed mass on the QCM surface. Selectivity is the most important disadvantage of QCM-based sensors. However, this shortcoming can be eliminated by using different sensitive layers, which make QCM-based sensors more useful.

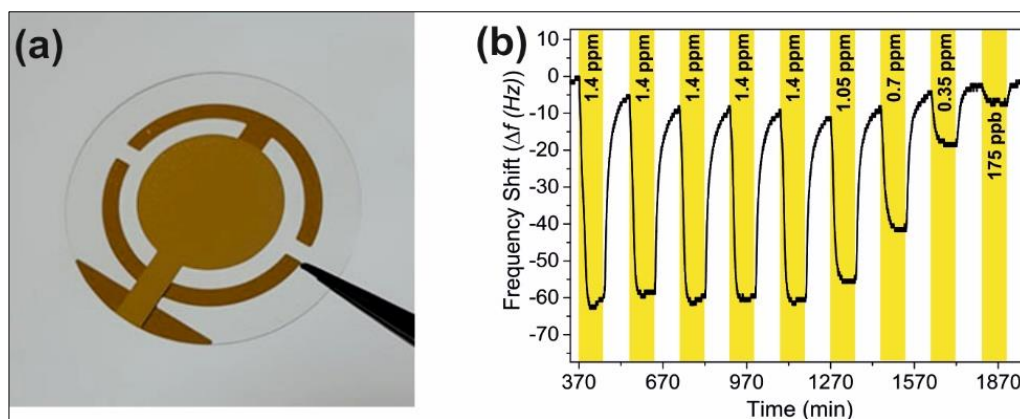


Figure 2.2: (a) a picture of a QCM oscillator and (b) typical sensor response of a QCM sensor.

2.2.5. Electrochemical Sensors

An electrochemical sensor which is a class of chemical sensors is used as a working electrode to detect the target analyte, mostly in a liquid medium [125]. These types of sensors are one of the most studied transducers that are frequently used in the detection of physical, chemical, and biological changes in the surrounding environment [126-131]. The working principle of the electrochemical sensor is based on electrical change depending on the presence analyte. In general, electrochemical sensor measurements are performed by measuring electrical current, potential, or resistance [132]. The conventional electrochemical sensors have three electrodes consisting of a working electrode which has a sensitive layer, the counter electrode which completes the electric circuit, and the reference electrode which maintains and monitors the cell potential [133]. As a result of the electrolyte process between the electrodes in the reaction medium, the polarization of anode and cathode induces an electrochemical reaction. Thus, this reaction can be controlled and monitored by an electrochemical workstation [125, 134].

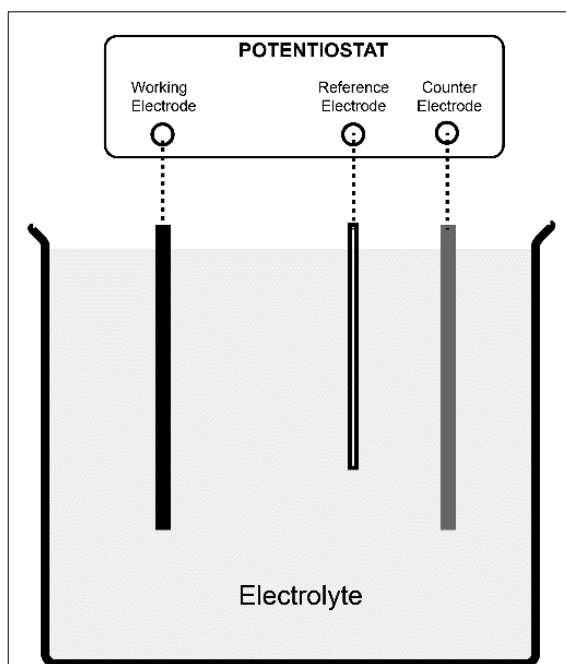


Figure 2.3: Conventional electrochemical cell in a system of three electrodes.

2.2.6. Impedance Sensors

Impedance sensors have a similar electrode design to potential type electrochemical sensors [135]. However, instead of dc measurements, the alternating current (AC) is applied to the electrodes to examine the conduction process against the analyte, and generated current is measured [136]. Thus, impedance sensors offer a transducer to probe electrode reactions and give information about grain boundaries, reaction rates, and quantification of chemical species [137].

2.3. Sensing Applications

Nanostructured materials have been applied in a wide range of sensing applications [1, 22, 40, 41, 138]. In this section, the applications were classified into two categories: chemical sensors and biosensors. Because each category has its own limitations and working principles, they require different approaches to fabricate high-performance sensors.

2.3.1. Chemical Gas Sensors

In our daily life, we interact with many gases such as carbonous (CO and CO₂), sulfurous (H₂S and SO₂), volatile organic compounds (ethanol, acetone, toluene,

xylene), and nitrogenous (NH_3 , NO , and NO_2), even if we do not realize it directly [1]. These gases can be originated from both natural sources and industrial processes. For example, BTEX compounds (benzene, toluene, ethylbenzene, xylenes) spread into all compartments of the earth as a result of the petrochemical industry [139]. It is also reported that BTEX compounds cause carcinogenic, mutagenic, and toxic effects on living species [140]. In addition to BTEX, flammable and explosive gases such as ammonia (NH_3), hydrogen (H_2), propane (C_3H_8), and methane (CH_4) pose a danger to life and property. On the other hand, some gases such as hydrogen sulfide (H_2S), hydrogen cyanide (HCN), NH_3 , and acetone are present in the human exhaled breath [141, 142]. These gases named breath markers can be related to specific diseases such as diabetes, schizophrenia, asthma, and lung cancer [10]. Consequently, the detection and monitoring of gases are vitally important in industrial processing, human health and safety, and air quality management [1].

2.3.2. Biosensors

International Union of Pure and Applied Chemistry (IUPAC) defined the Biosensor as “*a device consisting of a receptor and a transducer element which is able to provide selective quantitative or semi-quantitative analytical information using a biological recognition element*” [143, 144]. Biosensors are commonly used in biology and medicine to detect biological analytes such as biomarkers, pathogens, pesticides, toxins, etc., [145]. Generally, a typical biosensor consists of a specific bio-recognition element and a transducer [146]. Biosensors are expected to show superior performance in terms of sensitivity and selectivity to low concentrations of analytes in complex biological environments such as blood, saliva, urine, food sample, or wastewater [145]. Thus, bio-recognition elements are utilized as a biochemical mechanism for recognition against the target analyte. The most common forms of bio-recognition elements are biomimetic, enzyme, cellular structures, nucleic acid/DNA, and antibody/antigen [145]. Since the first biosensor concept, biosensors have become an important tool in a wide range of applications including disease diagnosis, drug development, forensics, and food quality concerns [138, 146]. However, there is still a need for low-cost, compact, shorter time span between sampling and monitoring, and user-friendly biosensors.

2.4. Outline of the Thesis

In this thesis, nanostructured MOX and TMDC were fabricated by different techniques such as electrochemical deposition, RF magnetron sputter, hydrothermal, and ALD. Structural and morphological characterizations were performed in different spectroscopic techniques. Finally, devices using these nanostructures were produced and sensor tests were carried out.

In the fourth chapter, ZnO thin films were fabricated by the ALD method. The thin films were characterized by AFM, XPS, SEM, EDS, and Uv-Vis. Then, the thin films were grown on QCM oscillators to perform biosensor measurements. In this respect, the sensor surface was modified with the anti-transferrin (specific MAM TRC2) to show selectivity against the transferrin molecules. The fabricated sensors were tested against different concentrations of human transferrin (hTF).

In the fifth chapter, tungsten disulfide thin films were grown on QCM oscillators via the RF magnetron sputtering technique. Structural and morphological properties of the fabricated thin films were investigated by SEM and XPS. The sensors were tested at RT against various gases including acetone, toluene, xylene, isopropyl-alcohol (IPA), hydrogen cyanide (HCN), hydrogen sulfide (H_2S), NH_3 , DMMP, and 2-Chloroethyl ethyl sulfide (CEES).

In the sixth chapter, Cu-doped ZnO nanorods (NRs) were fabricated by the electrochemical deposition method. the effect of Cu doping into ZnO NRs was systematically studied, and the mechanism behind the improvement in sensor properties was explained. The pristine and Cu-doped ZnO NRs coated QCM sensors were tested at room temperature against various gases including toluene, xylene, isopropyl, ethyl acetate, dichlorobenzene, NO_2 , HCN and H_2S , and the effect of Cu doping on the sensing performance was discussed.

In the seventh chapter, Cu doped ZnO NRs were synthesized by hydrothermal route for chemiresistive gas sensor tests. Fabricated nanostructures were investigated by XRD, XPS, SEM, and EDS. The sensors were exposed to various gases and the Cu doping effect on gas sensing properties was investigated.

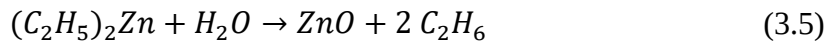
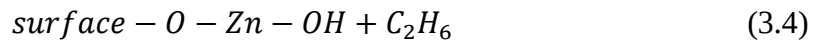
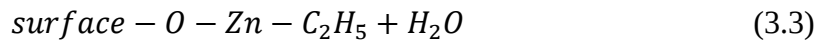
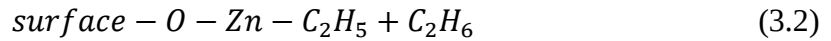
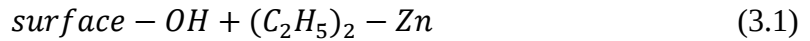
3. EXPERIMENTAL METHODS

In this dissertation, nanostructured materials such as MOX and TDMS were fabricated on different transducers for sensor applications. This chapter describes methods and instrumentations for fabrication, characterization, and sensor tests.

3.1. Fabrication Methods

3.1.1. Atomic Layer Deposition

ALD is a CVD technique for the preparation of thin films with precise thickness control in nm scale [147, 148]. Within this thesis, the ALD system (OKYAYTECH P100) was used to fabricate the ZnO and Al₂O₃ thin films. The precursors for the Zn and Al were diethyl zinc ((C₂H₅)₂Zn, DEZ) and triethylaluminium (Al(CH₃)₃, TMA), respectively. Ar gas was used as the purging gas between precursors with a flow rate of 20 sccm. The base pressure in the chamber was 8×10⁻² Torr. ALD is a cycle-based process and each ALD cycle consists of four steps [149]. First, the functional groups of DEZ react with the surface OH⁻ groups of the substrates as given in equation 3.1. The second step involves purging the by-products and the unreacted DEZ (see equation 3.2). In the third step, the second precursor (H₂O) is introduced to react with the adsorbed species on the surface (see equation 3.3). The final step consists of purging the by-products and the unreacted DEZ. Consequently, a monolayer of ZnO is formed on the substrate surface as seen in Equation 3.5. The film thickness can be increased with the increasing number of cycles.



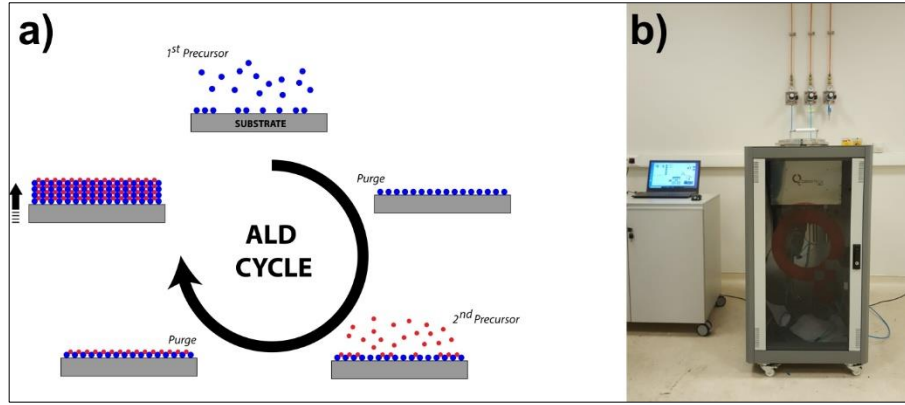


Figure 3.1: (a) A schematics of an ALD growth process and (b) a photograph of the ALD system.

3.1.2. RF Magnetron Sputtering

Magnetron sputtering is one of the most used PVD techniques to fabricate thin films with high adherence and surface uniformity [150]. Moreover, magnetron sputtering offers relatively low substrate temperatures and high growth rates [150]. In a typical growth process of magnetron sputtering, the target, which is desired material to be deposited, is bombarded with energetic Ar^+ ions. These energetic ions collide with the target and eject atoms/molecules which form thin films on a substrate [151]. The film stoichiometry and morphology depend on the deposition pressure, substrate temperature, and deposition power [150]. Within this thesis, WS_2 thin films were fabricated by NANOVAK-400 magnetron sputtering and VAKSIS MIDAS magnetron sputtering systems.

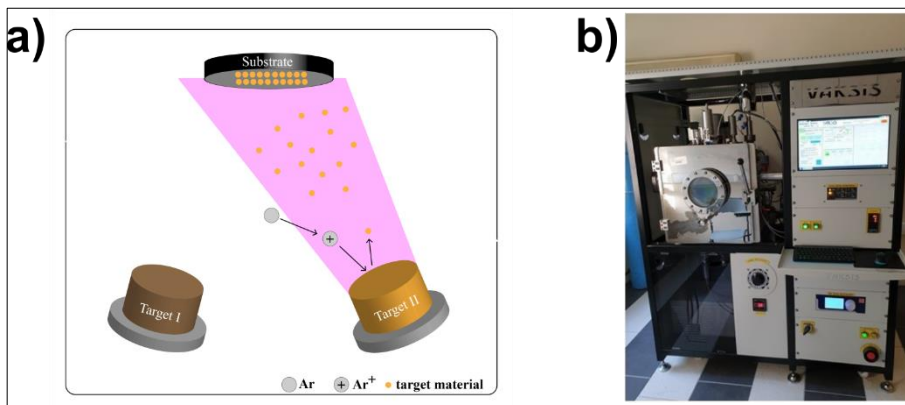


Figure 3.2: RF magnetron sputtering and a photograph of the VAKSIS MIDAS RF magnetron sputtering system.

3.1.3. Electrochemical Deposition

The electrochemical deposition technique is used to synthesize solid materials onto conductive surfaces [152]. In a typical electrochemical deposition system, there are two or three electrodes immersed in the analyte that contains the precursor materials (metal salts) as seen in Figure 3.3(a) (adopted from ref. [153]). The electrolyte can also contain several additives for various purposes such as increasing electrolyte conductivity, surface activation, and stability of the electrolyte. The electrodes are called the working electrode (cathode) the surface on which the material is grown, the counter electrode (anode) used to complete the electrical circuit, and the reference electrode for the reference point and potential control over the chemical process. When a potential difference is applied to the electrodes, positively charged ions in the electrolyte travel towards the cathode and negatively charged ions travel towards the anode. Thus, the electrical circuit was completed [152, 153].

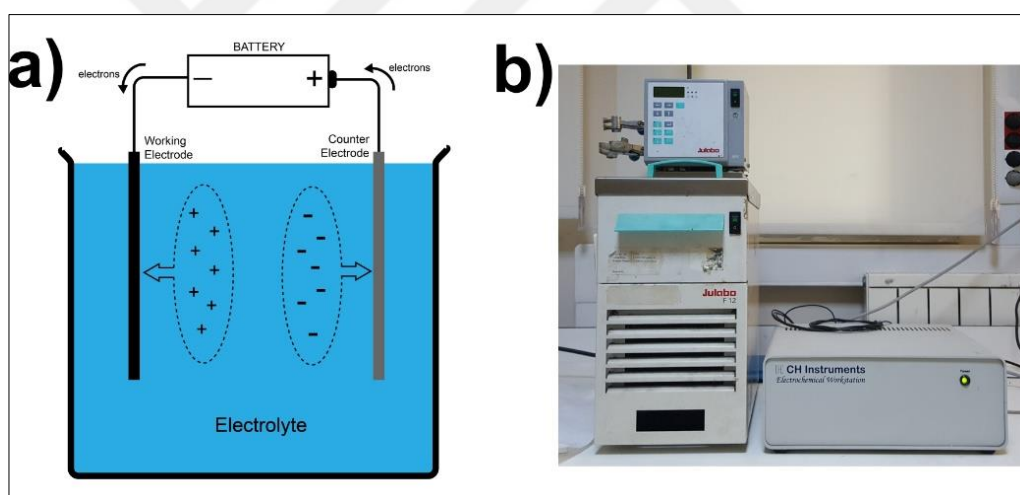


Figure 3.3: (a) A schematic illustration of electrochemical cell and (b) a photograph of CH Instruments 670C electrochemical workstation.

3.1.4. Hydrothermal Method

The hydrothermal route is one of the most studied methods for synthesizing inorganic nanostructural materials. A variety of materials such as MOX, TMDC, nitrides, tellurides, phosphates, etc. have been fabricated by the hydrothermal method in various nanostructured forms like nanowires, nanorods, nanobricks, and nanoflakes. This technique also is an effective tool for processing nano-hybrid and nanocomposite materials [154]. Byrappa and Adschiri [155] defined hydrothermal synthesis as

“heterogeneous reaction in the presence of aqueous solvents or mineralizers under high-pressure-high-temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions”. Therefore, the reaction chamber where the hydrothermal treatment will take place must be resistant to temperature, high pressure, and corrosive solvents. Generally, the hydrothermal chamber consists of a Teflon chamber placed inside a stainless-steel autoclave.

3.2. Characterizations of Fabricated Structures

3.2.1. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most important tools to examine and analyze the morphology of a structure [156]. The image obtained with SEM is based on the physical interactions between the electron beam and the specimen. The electrons are generated by an electron gun (mostly tungsten filament) and focused by condenser lenses into a beam called the primary electrons. When the primary electrons interact with the specimen, loosely bound electrons can escape from a region in a few nanometers on the material surface. These electrons are called secondary electrons have relatively low energies (3-5 eV) and give information about the topography, surface texture, and roughness. After the interaction between the electron beam and the specimen, electrons emitted from the surface with energies higher than 50 eV are called backscattered electrons which give information about composition and topography. Another information-containing signal in SEM is characteristic X-rays provide chemical information. When a collision occurs between the primary electrons and inner-shell electrons, the inner-shell electron can be displaced. Thus, this empty electron position can be occupied by an electron from an outer shell, and X-rays are emitted because of this movement of the electron. In addition to the backscattering electron, secondary electron, and characteristic X-rays, there are some other phenomena used for structure analysis such as Auger electrons, cathodoluminescence, and transmitted electrons [157].

3.2.2. X-Ray Diffraction

X-ray diffraction spectroscopy is one of the most versatile instruments to investigate the crystal structure of a solid. XRD also provides information about lattice

constants, phases, grain size, crystallinity, and defects. XRD is based on the scattering of monochromatic X-Rays from the material. The interaction of the X-rays with the material produces constructive interference when satisfying Bragg's law:

$$n\lambda = 2d\sin\theta \quad (3.6)$$

where n is an integer, λ is the wavelength of the incident X-rays, d is the interplanar spacing, and θ is the diffraction angle. This law indicates that the wavelength of the electromagnetic radiation depends on the diffraction angle and the interplanar spacing [158]. When the diffraction criteria are required, the scattering occurs in a coherent manner [159]. The diffracted X-rays are counted by the X-Ray detector and converted to d-spacings. Obtained d-spacings are compared with the standard reference patterns for identification of the compound.

3.2.3. X-Ray Photoelectron Spectroscopy

XPS is a surface analyzing technique for identifying the elemental composition at the surface of a material. In addition, XPS is an ultra-high vacuum technique and can collect information from the surface to a depth of 10 nm. When incident photons impinge on the sample, the energy is transferred due to photon-electron interaction. If this energy is enough to eject the electron from the atom, the electron is emitted. The kinetic energy (K.E.) of the emitted electron provides binding energies (B.E.) which are unique for each material. Then, the energy spectrum is constructed using B.E. [160].

3.2.4. Atomic Force Microscopy

Atomic force microscopy is a technique that allows the investigation of the surface structure with high resolution and accuracy. AFM offers the advantage of taking measurements in an ambient atmosphere without the need for sample preparation. Unlike other surface inspection techniques that use electrons or light, the AFM probe physically interacts with the specimen and scans over its surface. Thus, AFM builds up a topographic image of the surface. A typical AFM consists of three key components. The first one is the probe, which is a piezoelectric transducer. The dimensional change over the surface generates an electrical potential due to the reverse

piezoelectric effect. Another important part of the AFM is the force sensor. A force sensor consists of a cantilever in which the probe is integrated and an optical lever that regulates the force between the probe and the surface of the specimen. Lastly, the feedback control unit is responsible for maintaining the probe-sample distance [161].

3.3. Sensor Measurements

3.3.1. Gas Sensor

In this thesis, gas sensor measurements were performed via a homemade automated gas sensor measurement system. The target gases were obtained via gas cylinders, bubblers, and permeation tube gas generator. In the case of gas generation through bubbles, gas washing glass containing VOC is immersed in a thermostated bath to obtain a saturated gas stream with VOC (see Figure 3.4(a)). Gas concentrations can be calculated by using Antoine's equation [162, 163]. The permeation gas generator (Owlstone inc., V-OVG) is used to obtain VOCs at lower concentrations. As seen in Figure 3.4(b), a permeation tube is a sealed cylinder containing an analyte of interest inside. When the tube is placed into the gas generator, the analyte permeates through the walls of the tube. The gas concentration of the generated gas depends on the temperature and flow rate of the carrier gas flow. Gas cylinders were used to obtain dry air as a carrier and reference gas, NO₂, H₂, and CO. Finally, all gas flows and gas concentrations are adjusted and controlled via mass flow controllers and a multi-gas controller device (MKS 647C).

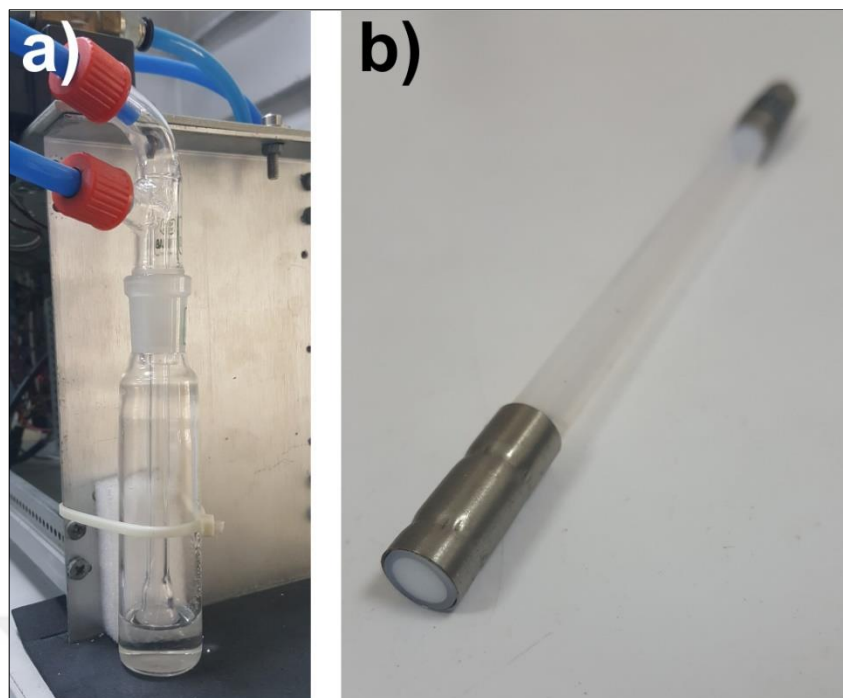


Figure 3.4: (a) A picture of a gas washing bottle and (b) a picture of a permeation tube (Owlstone inc.).

A homemade sensor cell with a volume of 50 ml that can measure 8 samples simultaneously was used for QCM measurements (see Figure 3.5(b)). Thanks to the electronic card integrated into the measuring cell, the frequency values of the QCMs are measured and transferred to the computer. The frequency of the QCM oscillators was recorded as a function of time via the Labview program. In the case of chemiresistive sensor measurements, Au inter-digital electrodes (IDEs) were thermally evaporated on the surface of samples with a shadow mask. As seen in Figure 3.5(a) chemiresistive sensor measurements were performed in a homemade stainless-steel chamber (volume of 1 L) which is connected to gas lines and electronic devices. In addition, sensor temperatures can be controlled and monitored with the help of the hot plate integrated into the chamber. The temperature of the hot plate was controlled with a Lakeshore 340 temperature controller. A constant bias voltage was applied to samples for time-dependent current measurements under the gas flow. Keithley 6517A electrometers and 6482 picoammeter are used to apply a constant bias voltage and measure the direct current. All communications in the measurement system are carried out with GPIB and rs-485 connections and are automatically operated with the Labview program.

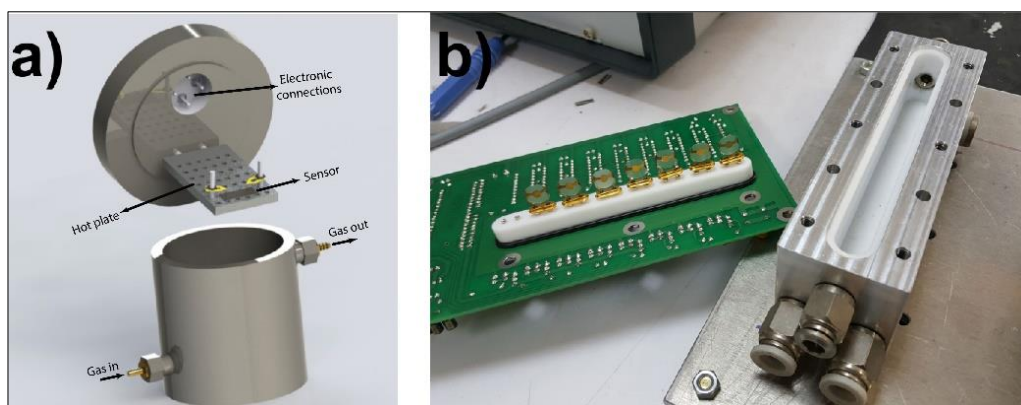


Figure 3.5: (a) Schematic illustration of the chemi-resistive sensor chamber and (b) a photo of the QCM measurement cell.

3.3.2. Biosensor

QCM-based biosensor tests were carried out on the homemade biosensor cell as seen in Figure 3.6. The frequency of the QCM oscillators was measured by the frequency drive circuit (designed and fabricated by Prof. Dr. Mehmet Ali Ebeoğlu and Asst. Prof. Firat Aydemir from Dumlupınar University) and Agilent 53131A frequency counter. The time-dependent frequency curve was monitored by the Labview program. The target analyte was sent to the cell via a peristaltic pump (Watson-Marlow 120s).

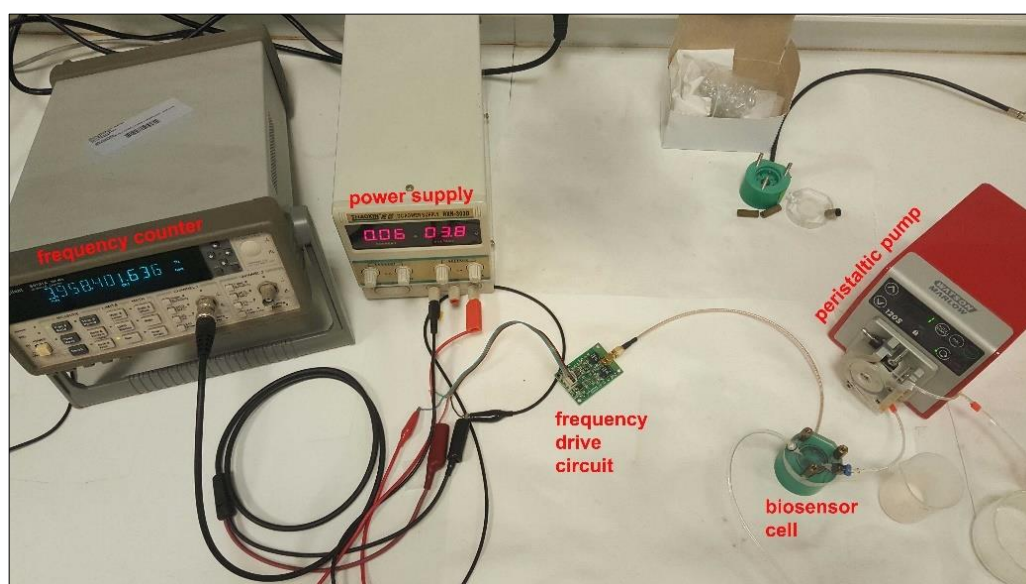


Figure 3.6: Biosensor test set-up.

4. ZnO THIN FILM COATED QCM BIOSENSOR SENSOR FOR DETECTION OF TRANSFERRIN

4.1. Introduction

Transferrin is an important transporter of iron ions synthesized in the liver [164]. An increase in the amount of transferrin in the blood may be correlated with some diseases such as rheumatism, cirrhosis, leukemia, and tumor [165]. On the other hand, acute hepatitis, anemia, and pregnancy are related to increased levels of transferrin in the blood [165, 166]. Though transferrin can be detected via conventional techniques such as ELISA and RIA, these methods require expensive and complex instruments. Thus, fast, compact, cheap and sensitive devices must be developed to be used in the detection of transferrin molecules [167]. In this respect, biosensors can be a good candidate to be used in point-of-care diagnostics due to their ease of use, compact, and portable features [168-170].

One of the most important parts that determine the performance of a biosensor is the transducer element. Among various transducers, QCM is a mass-sensitive device that offers an affinity-based and label-free biosensor platform as explained in Section 2.1.4 [120, 171]. These features make QCM-based biosensors an important platform for immunoassays [171]. In general, it provides a selective and highly sensitive platform to antigen by binding the antibody (receptor) to the sensor surface [172]. Atay et al. developed a QCM based immunosensor to detect human breast cancer [166]. Piriñci et al. fabricated QCM-based immunosensor to detect ochratoxin A [173]. Ngo et al. reported that the QCM biosensor immobilized with the antibodies exhibits superior performance to *Escherichia coli* bacteria [119]. Consequently, QCM-based immunoassays gained great importance in the application of biosensors.

Another important parameter that affects the immunoassay performance is antibody immobilization and its stabilization [174]. Though conventional techniques such as self-assemble monolayer (SAM) and Langmuir-Blodgett are used for receptor immobilization, the biocompatible nanomaterials showed promising results to develop new generation biosensors [4, 145, 172]. Among various nanomaterials, ZnO nanostructures have attracted great interest in biosensing applications due to their low cost, biocompatibility, and relative chemical stability [8]. In addition, the high

isoelectric point of ZnO provides a suitable platform to bind biomolecules [9]. Various deposition methods such as hydrothermal, electrochemical deposition, and CVD can be used in the fabrication of ZnO nanostructures [175]. ALD is a CVD technique that offers uniform film growth with angstrom precision [176]. Moreover, thin films fabricated by ALD have optimized surface properties and compatibility with semiconductor technologies [147]. Thus, ALD growth ZnO thin films can be used for biosensor applications.

In this study, ZnO thin film coated QCM biosensors were fabricated to detect transferrin molecules. ZnO thin films were grown on QCM oscillators by the ALD technique. Structural and morphological characterizations of ZnO thin films were performed by scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Ultraviolet-visible spectroscopy (UV-Vis). The sensor surface was modified with the antibodies (specific MAM TRC2) of the transferrin to show selectivity against the target analyte. The fabricated sensors were tested against different concentrations of human transferrin (hTF).

4.2. Experimental Details

ZnO thin films were grown on Au-coated 5 MHz AT-cut QCM oscillators (Quartz Pro) and soda lime glass substrates via the ALD system (OkyayTech ALD T200). Diethyl zinc (DEZ) and H₂O were used as precursors, and N₂ (purity of 99.999%) was used as the purging gas. The chamber pressure during the film growth was kept at 0.8 mTorr. The film properties were investigated by changing the temperature of the reaction chamber, pulse times, and the number of cycles. These parameters were given in Table 4.1.

Table 4.1: The parameters of ALD grown ZnO thin films.

Sample	Cycle	Chamber temp. (°C)	Puls time (ms)	Purging time (ms)
1	710	200	15	30
2	355	200	15	30
3	177	200	15	30
4	355	200	10	30
5	355	200	20	30
6	710	200	10	30
7	355	100	15	30

Morphological and structural characterizations were performed on ZnO thin film coated soda lime glass substrates. Morphological characterizations and elemental analyses of the fabricated thin films were carried out by SEM and EDS. The surface porosities were investigated via AFM. The samples were analyzed with XPS using an Al K α x-ray ($h\nu = 1486.6$ eV) source and a hemispherical electron analyzer. The base pressure of the analysis chamber was 1.33×10^{-8} Pa during the measurements. The spectra were fitted using the CasaXPS using mixed Gaussian-Lorentzian peaks after subtracting the Shirley-type background to extract the chemical bonding energies. Transmittance measurements were performed by UV-Vis spectrophotometer.

ZnO thin films were coated on Au-coated 5 MHz AT-cut QCM oscillators for biosensing measurements. The picture and dimensions of The QCM transducers used in this study are given in Figure 4.1. Thanks to the Sauerbrey equation, ZnO thickness on the QCM were calculated.

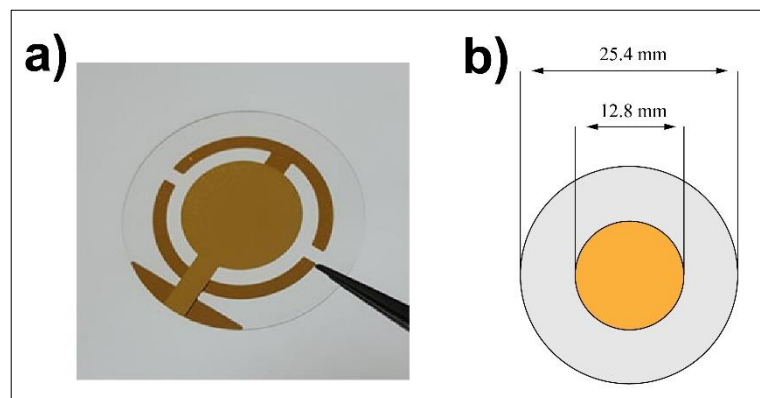


Figure 4.1: The picture and the dimensions of QCM oscillators.

The surface of ZnO/QCM sensor was functionalized with hTF-specific monoclonal “MAM TRC2”, which was purchased from TUBITAK MAM Genetic Engineering and Biotechnology Institute, to make the sensors selective towards hTF. The desired amount of TRC2 was added to 200 µl Phosphate buffer saline (BSA, pH: 7.4) and dripped onto the sensor surface with the help of a micropipette. After one hour incubation at room temperature and atmospheric conditions, the sensors were cleaned with PBS and deionized water, respectively. Then, the sensors were dried with N₂. Three different concentrations of TRC2 (0.5, 1 and 1.5 µg) were immobilized to find the optimum amount. Then, the blocking was performed to prevent non-specific hTF binding to non-antibody-binding surfaces. For this purpose, 200 µl PBS including 200 µg bovine serum albumin (BSA) was dripped on the sensor surface and incubated for one hour. Then, the sensor surface was cleaned with PBS and deionized water. Then, the sensors were dried with N₂. TRC2 immobilized ZnO/QCM sensors were tested against hTF with two different biosensor measurement techniques: static and dynamic. In case of static measurement, hTF containing PBS drips onto the sensor surface. After one hour incubation, sensors were cleaned with PBS and deionized water. Then the sensors were dried with N₂. In dynamic biosensor measurement, hTF is sent to the TRC2/ZnO sensor platforms under a continuous liquid flow with the help of a peristaltic pump. The process flow was given in Figure 4.2. After each step, QCM frequency was measured by Agilent 53131A frequency meter and QCM drive circuit.

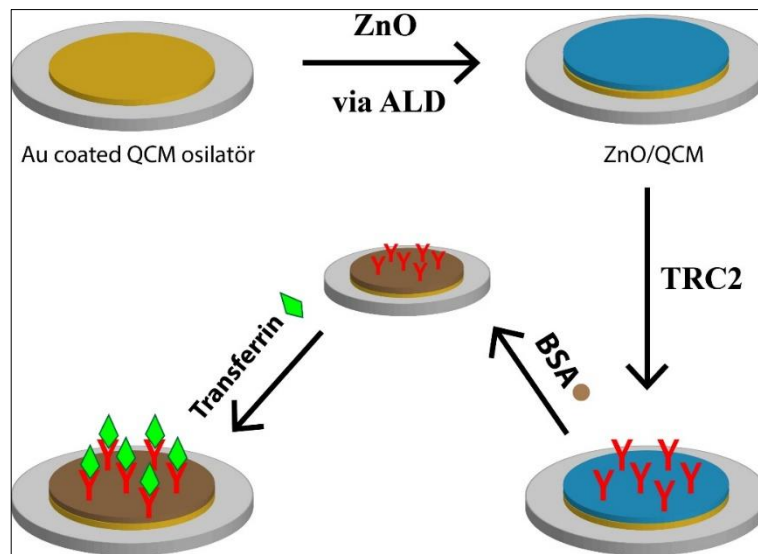


Figure 4.2: Schematic illustration of surface modifications.

4.3. Results and Discussion

4.3.1. Structural Characterizations

The surface morphology to which the receptor will bind is of great importance for sensor performance. Thus, the surface morphologies of ZnO thin films depending on ALD parameters were investigated by SEM. SEM images of ZnO thin films grown with different ALD cycles on Si substrates are given in Figure 4.3. During these processes, pulse times are fixed at 15 ms for both precursors, and the temperature of ALD reaction chamber is kept constant at 200°C. According to the Figure 4.3, It was observed that the surface morphology did not change with the film thickness. However, surface properties were investigated in more detail by AFM studies.

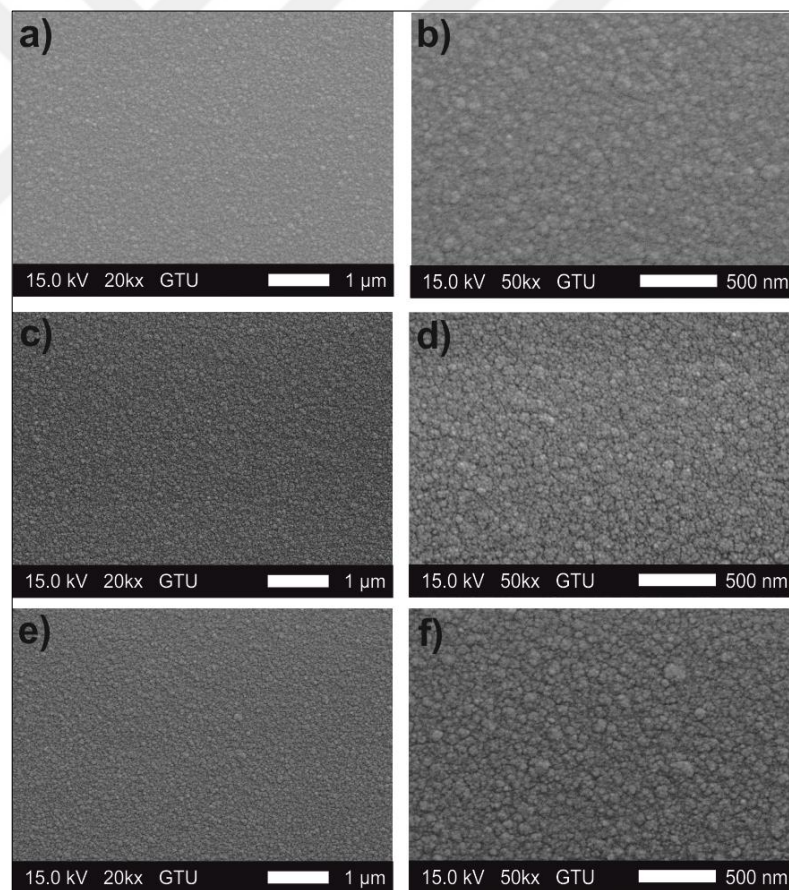


Figure 4.3: SEM images of ZnO thin films: (a)-(b) 710, (c)-(d) 355, and (e)-(f) 177 ALD cycles.

In the film growth processes with ALD, the precursor pulse times are one of the important parameters that determine the film properties. [148]. The pulse time means the quantity of reactant (DEZ and H₂O) per ALD cycle. More than sufficient reactant results in the accumulation of chemicals in the chamber that are not bonded to the surface, which can influence the next cycle. On the other hand, the shorter pulse time causes poor quality of film due to incomplete reactions between the substrate surface and precursor chemical [177]. SEM images of ZnO thin films grown with 10, 15, and 20 ms pulse times are given in Figure 4.4. During these processes, the number of cycles, purge times, and chamber temperatures were kept constant at 355, 30 s, and 200°C, respectively. ZnO thin films homogenously covered the entire substrate surface. In addition, no significant change in morphology was observed with pulse time.

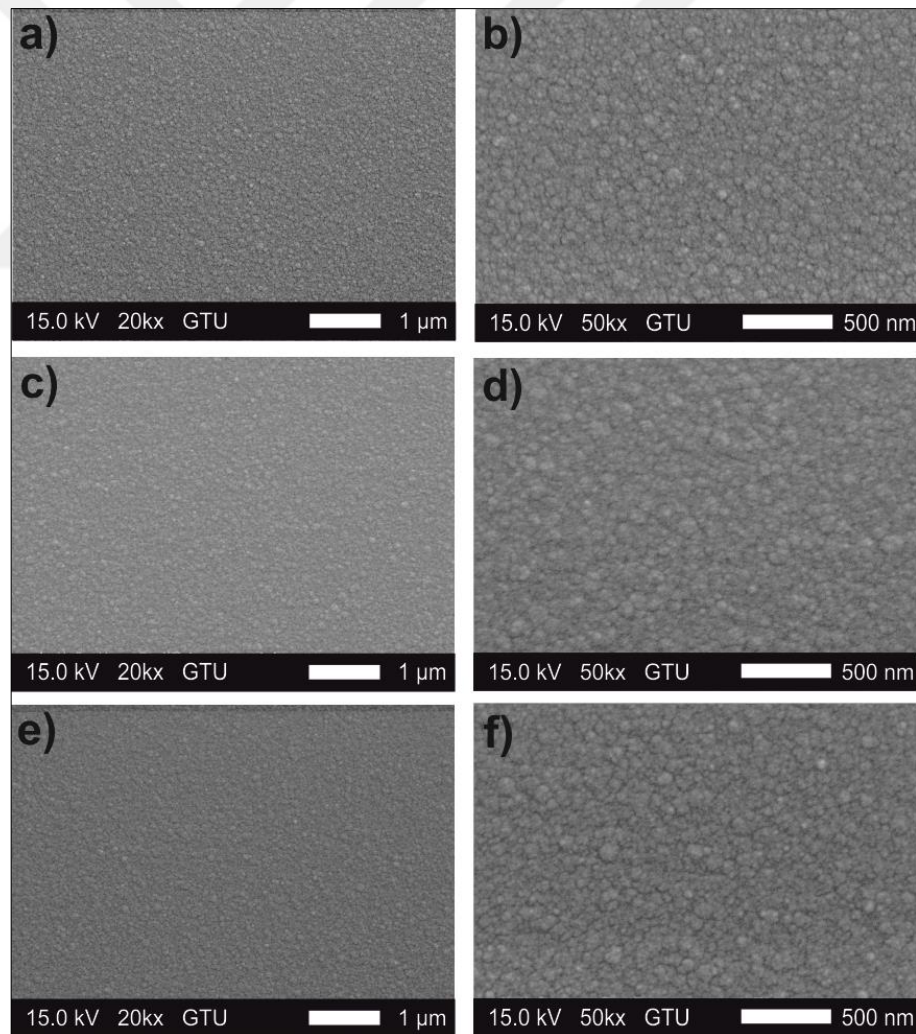


Figure 4.4: Pulse times of DEZ and H₂O; (a)-(b) 10 ms, (c)-(d) 15 ms, and (e)-(f) 20 ms.

Another ALD parameter that directly affects the film properties is chamber temperature. The temperature optimizations were performed between 100 and 200°C due to a significant decrease in growth rate at low temperatures ($< 100^{\circ}\text{C}$) and temperature limitations of the ALD system (max. 250°C). During the temperature optimizations, the number of cycles, pulse, and purge times were kept constant at 355, 15 ms, and 30 s, respectively. It was observed that the granular structure on the surface grows with increasing chamber temperatures (see Figure 4.5).

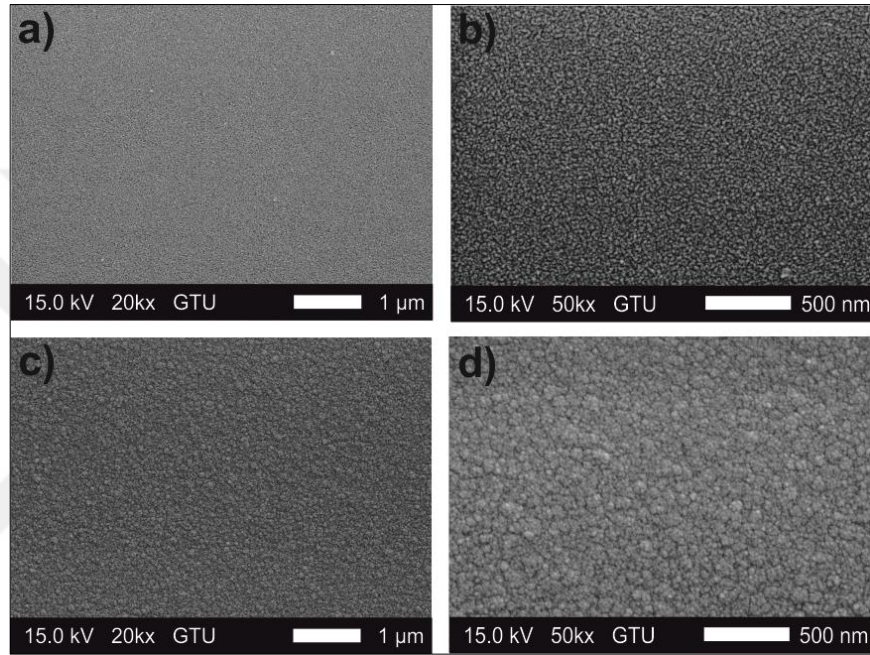


Figure 4.5: SEM images of ZnO thin films grown at (a) 100°C and (b) 200°C .

Elemental analyses of the ZnO thin films were performed by EDS. The spectra depending on the number of ALD cycles are given in Fig 4.6(a). Chamber temperature, pulse times, and purging times were 200°C , 15 ms, and 30 s, respectively. It is seen that the Zn amount increased with increasing cycles. Fig. 4.6(b) shows EDS spectra depending on the DEZ pulse times (chamber temperature at 200°C , 355 cycles, and purging times of 30 s). Though the intensity of Zn increases with the increasing pulse times, the intensities are quite lower than O intensities. Temperature-dependent EDS spectra (100 and 200°C) is given in Figure 4.6(c). During temperature optimizations, the number of ALD cycles, pulse times, and purging times were kept constant at 355, 15 ms, and 30 s, respectively. According to the spectra, O peak intensity decreases with the decreasing temperature. On the other hand, there is an inverse relationship between the temperature and the intensity of the Zn peak.

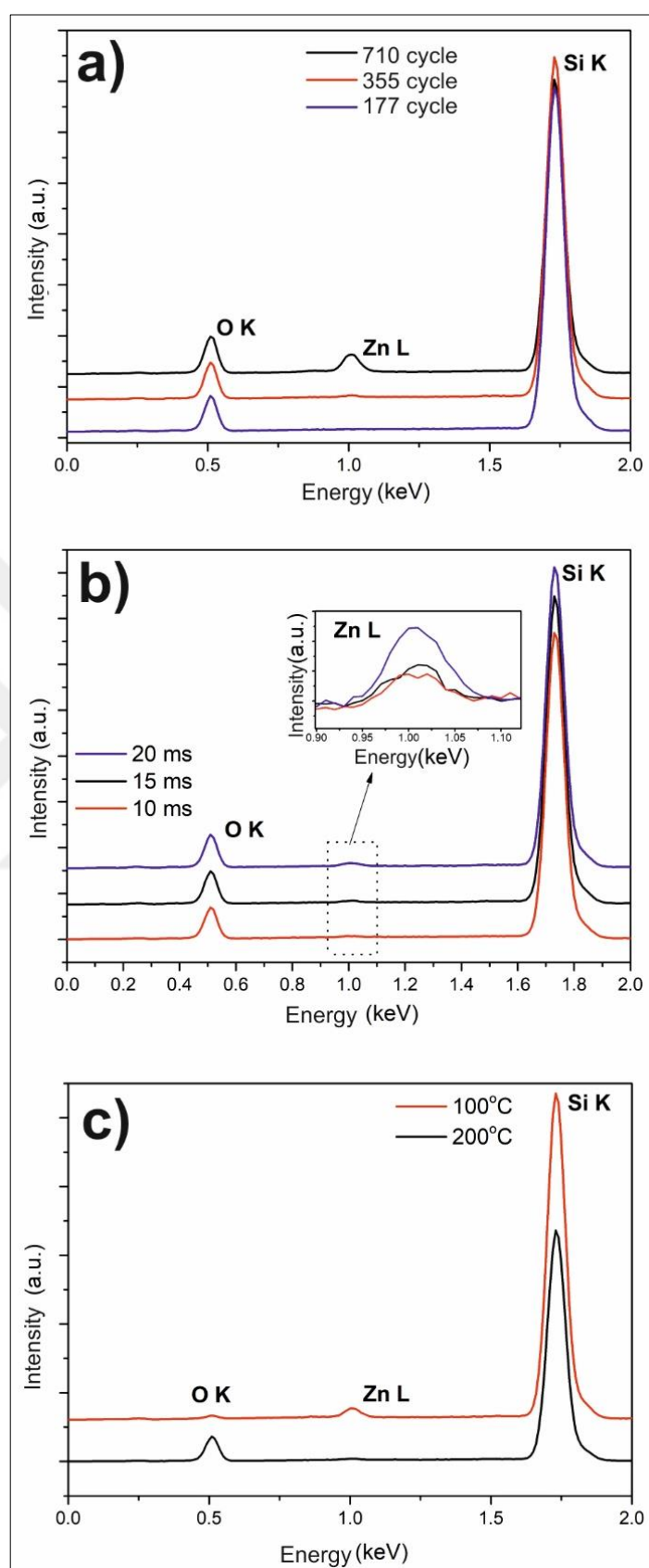


Figure 4.6: EDS spectra depending on (a) ALD cycles, (b) pulse time, and (c) chamber temperature.

The porosity of the ZnO thin films was performed by AFM. Figure 4.7 shows AFM images of the fabricated samples. It is observed that there is an inverse proportion between the number of cycles (film thickness) and surface porosity as seen in Figure 4.7(a-c). The surface porosities were measured 3.880, 1.928, and 1.697 nm for 710, 355, and 177 cycles, respectively. Moreover, there is no relationship between precursor pulse time (DEZ) and the surface porosity as seen in Figure 4.7(b, d-e). 10, 15, and 20 ms of pulse times have 1.959, 1.928, and 1.597 nm porosities, respectively.

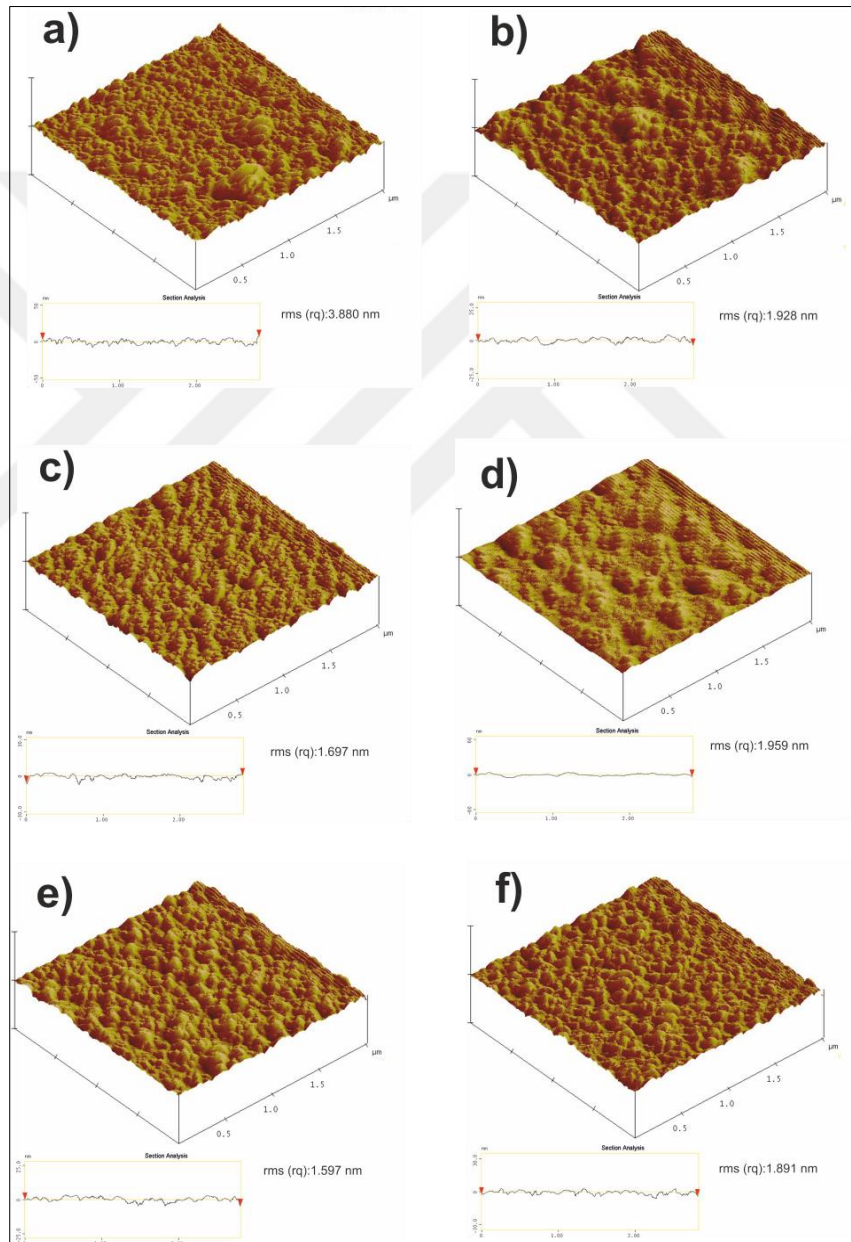


Figure 4.7: The surface porosities of ZnO thin films: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6.

O 1s and Zn 2p regions of ZnO thin films fabricated on glass substrates were carried out by XPS to investigate the chemical bonding and the surface properties. The base pressure of the XPS chamber was 1.33×10^{-8} Pa during the measurements. The binding energies of the spectra were calibrated by the carbon C 1s peak (284.8 eV) reference. As shown in Figure 4.8, the O 1s spectra consist of the main peak at 530 eV associated with the lattice bonding and the shoulder peak at 531.64-532.56 eV related to defect-oxide (oxygen vacancies) [5]. Although a change in the area ratio of the main peaks (lattice oxide/oxygen vacancy) is observed with the change in pulse times, these changes do not follow a clear trend. Moreover, surface defects increase with the increasing film thickness as seen in Figure 4.8(a-c).

Zn 2p spectra of the fabricated ZnO thin films are given in Figure 4.9. The binding energies of 1044.55 eV and 1021.45 eV are related to Zn 2p_{1/2} and Zn 2p_{3/2} lines, respectively. The separation between Zn 2p_{1/2} and Zn 2p_{3/2} peaks is 23 eV consistent with the oxidation state of Zn⁺² in ZnO [5]. With the increase of the film thickness, the binding energy of the lattice oxide peak shifted to lower energies (see Figure 4.9(a)). This shift indicates the strong Zn-O bond in the ZnO thin films [178]. As seen in Figure 4.9(b), with the increase of DEZ pulse time, the binding energy shifted to lower energies. Increasing the pulse time in the ALD method means that more precursor material is sent to the reaction chamber. Thus, more Zn-O bonds will be formed.

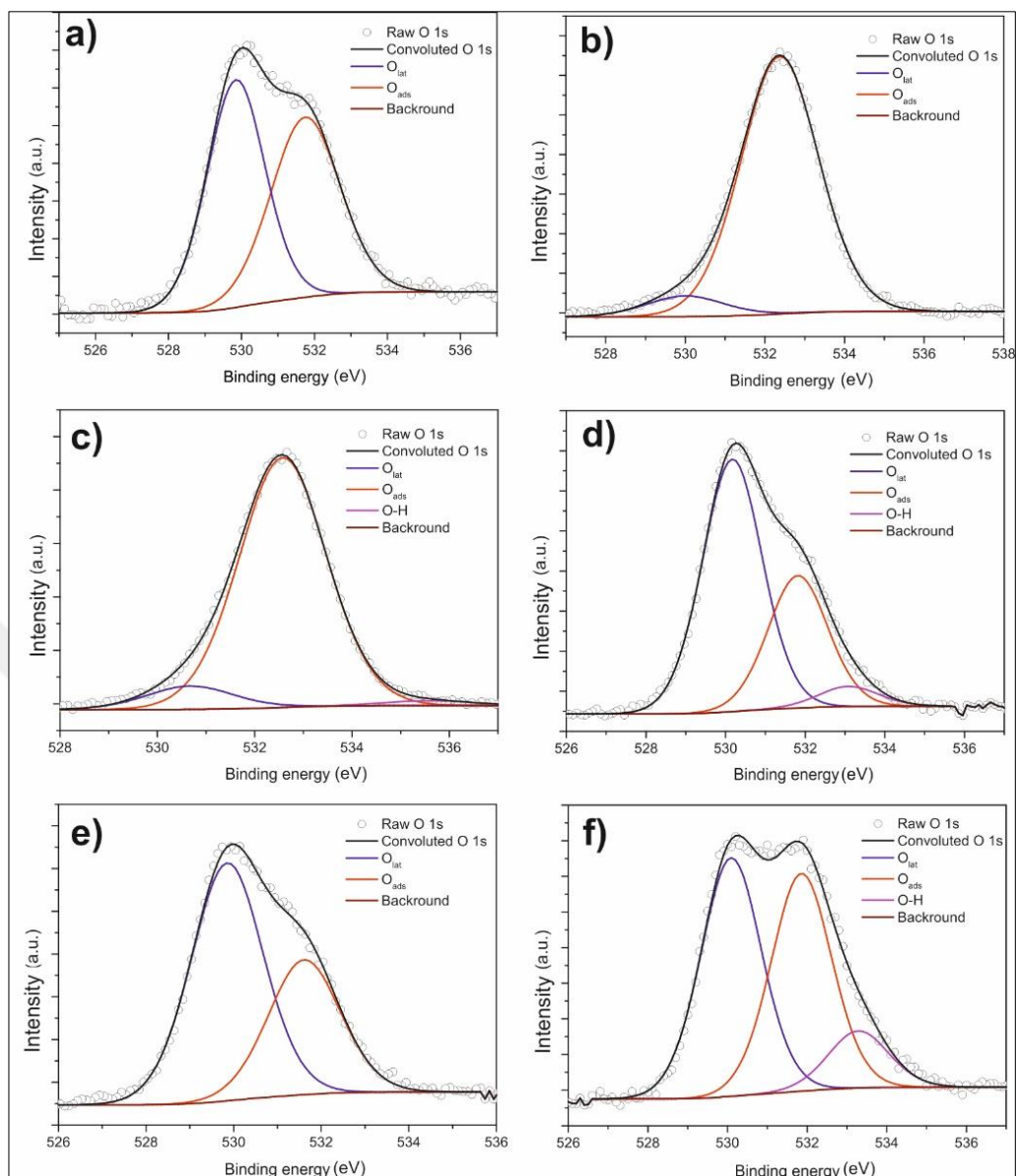


Figure 4.8: O 1s spectra of ZnO Thin films: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6.

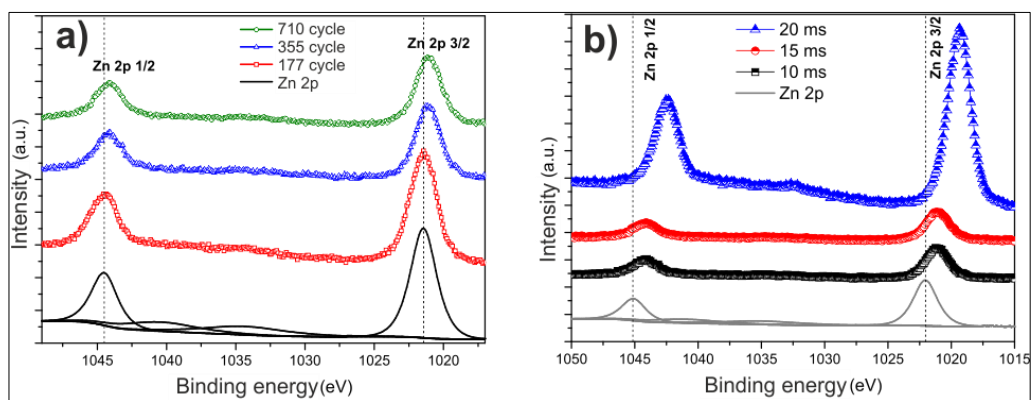


Figure 4.9: (a) Number of cycle and (b) pulse time dependent Zn 2p spectra of ZnO thin films.

The results of the reflectance measurements are given in Figure 4.10. As seen in Figure 4.10(a), the reflectance decreases with the increasing film thickness. According to Figure 4.10(b), the reflectance decreases especially at pulse time of 20 ms compared to 10 ms and 15 ms due to forming of more Zn-O bonds.

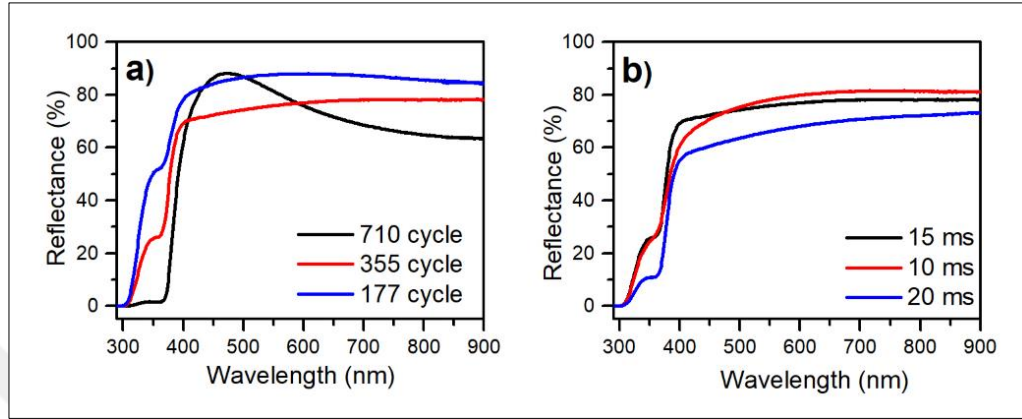


Figure 4.10: (a) number of cycle and (b) pulse time dependent UV-Vis spectra of ZnO thin films.

4.3.2. Biosensor Tests

According to the structural characterizations, sample 2 was chosen for biosensor measurements. To determine the average thickness and readability of ZnO thin films grown by the ALD method, the frequencies were measured before (f_0) and after the coating. For better adhesion of ZnO thin films to the QCM surface, Al_2O_3 (number of cycles: 40, chamber temperature: 200°C , pulse time: 15 ms, and purge time: 30 s) is coated between ZnO and QCM by the ALD method. In Figure 4.11(a), frequency shifts of thirteen QCMs coated with ZnO thin film are given. The frequencies of the ZnO/QCM oscillators are shifted approx. 3 kHz. Thanks to the Sauerbrey equation (given in Section 2.1.4), the film thicknesses were calculated. As seen in Figure 4.11, ZnO film thicknesses are between 82.6 and 94.2 nm.

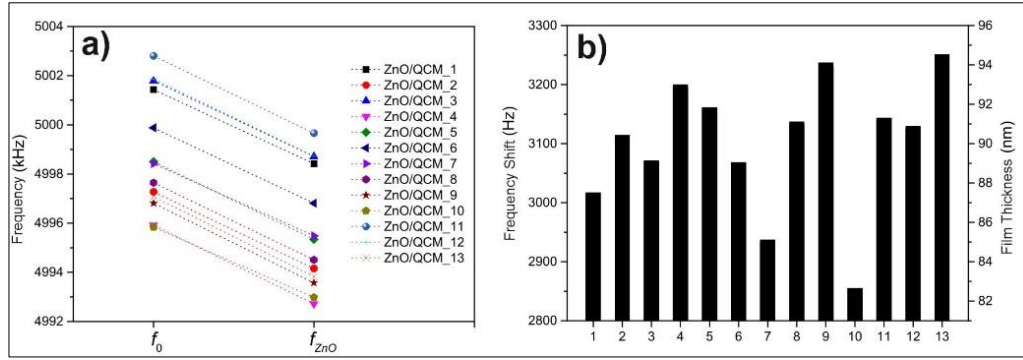


Figure 4.11: (a) the frequency shifts and (b) the film thicknesses dependent frequency shifts.

TRC2 immobilization was performed with three different concentrations (0.5, 1 and, 1.5 μg) on ZnO/QCM oscillators. After the anti-hTF immobilizations, blocking was performed with BSA. Finally, ZnO/QCM functionalized with TRC2 sensor platforms were tested to 100 ng hTF. Figure 4.12 show the results of static measurements against 100 ng hTF. To examine the repeatability in the sensor results, two samples of each immobilization amount were fabricated. Frequency decreases were observed due to the anti-hTF adsorbed onto the surface. When the sensor results against 100 ng of transferrin molecule were examined, the sensors with 1 μg TRC2 immobilized showed the highest sensor response. This means the optimum amount for anti-hTF immobilization to the surface is 1 μg .

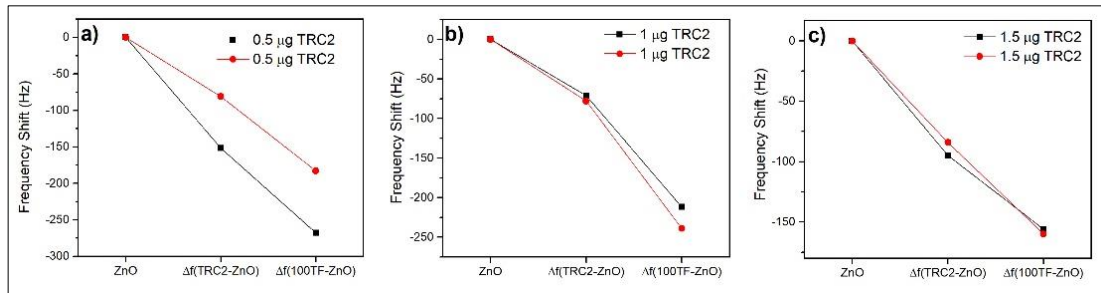


Figure 4.12: hTF sensing results based on TRC2 immobilization.

After determining the optimum amount of TRC2 immobilization for the ZnO surface, the biosensor platforms were tested against different amounts of hTF. TRC2 immobilized ZnO/QCM biosensors were repeatedly exposed to the increasing TF amount (see Figure 4.13). The fabricated sensor exhibited 91, 196, 303, and 375 Hz sensor responses (frequency shift) against 100 ng, 150 ng, 250 ng, and 500 ng hTF,

respectively. According to the results, TRC2/ZnO biosensor platform gives consistent results in the range of 100-1000 ng hTF.

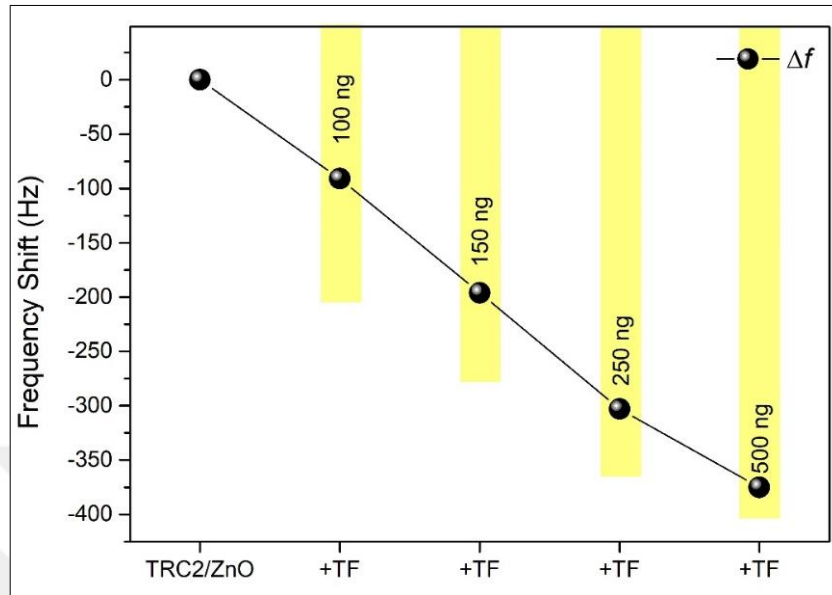


Figure 4.13: Biosensing performance against hTF.

Another important biosensor parameter is the repeatability. In this respect, TRC2 (1 μ g) immobilized ZnO/QCM platforms fabricated under the same conditions were tested against 100 ng hTF. Figure 4.14(a) shows the frequency shifts of ten sensors for ZnO coating, TRC2 immobilizations, and 100 ng hTF. It has been observed that the frequencies decrease as the mass is adsorbed to the surface of the QCM sensors. Moreover, the sensor responses of these identical sensors to the hTF molecule are given in Figure 4.14(b).

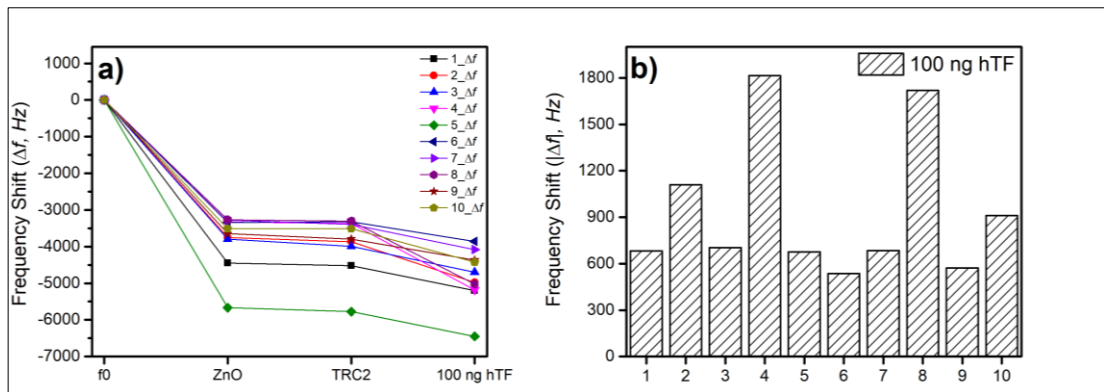


Figure 4.14: (a) frequency shifts for all steps and (b) frequency shifts against 100 ng hTF.

TRC2 immobilized ZnO/QCM sensors were tested under a dynamic fluid flow against hTF protein to examine the effect of biosensor measurement techniques on sensor performance. In this technique, TRC2 immobilization was performed by incubation as in the static measurements. Then, the QCM sensors were placed in the same measurement cell as in the static measurements. The volume of the measurement cell was 0.5 ml. The frequency of the QCMs was recorded as a function of time. PBS was used as reference and carrier liquid. PBS containing hTF is passed through the sensor surface with the help of a peristaltic pump and the changes in the resonance frequency of the QCMs were evaluated as sensor responses. The frequency-time curve is given in Figure 4.15. Firstly, PBS flow into the QCM chamber is started. When a steady state was obtained, the blocking process was carried out with 200 μ l PBS containing 200 μ g BSA. After blocking, the sensor was exposed to 100 ng hTF. The sensor did not exhibit sensor response to 100 ng hTF. Then, when the sensor was tested against 500 ng hTF, a frequency shift of 5 Hz was observed.

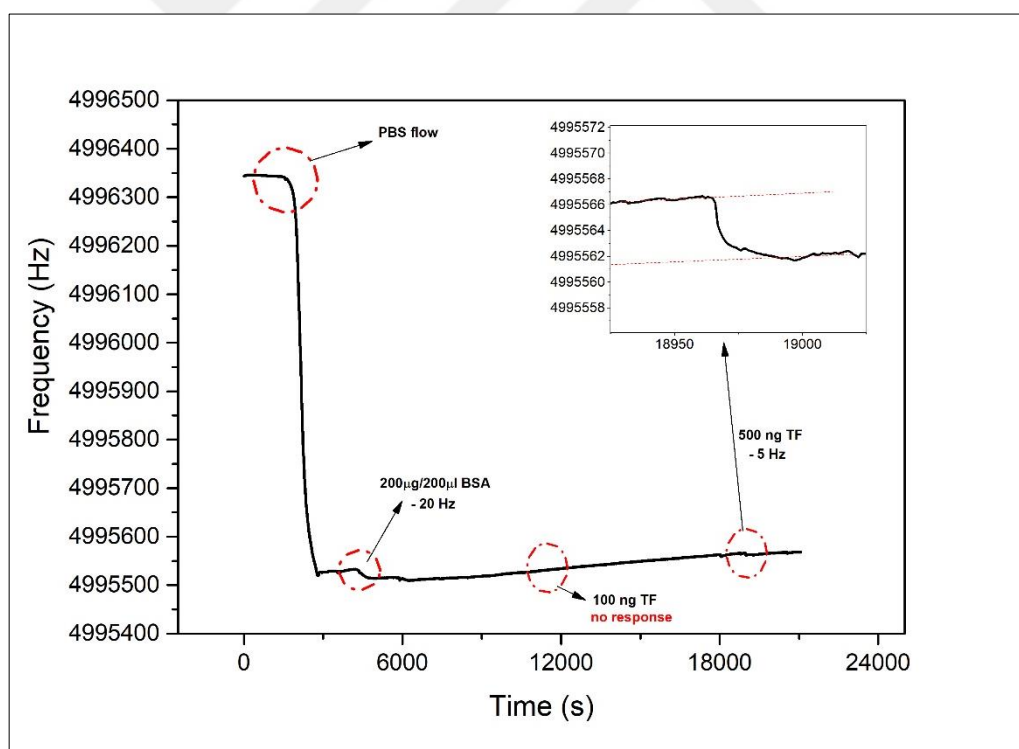


Figure 4.15: Frequency dependent time curve.

4.4. Conclusion

In biosensing studies, receptor immobilization on the platform surface has vital importance. In this study, ZnO thin films were fabricated on a QCM oscillator to detect transferrin, which is one of the important molecules found in human blood. ZnO thin films were fabricated with different ALD parameters such as chamber temperature, precursor pulse time, and the number of ALD cycles. Then, structural and morphological characterizations were performed by SEM, EDS, XPS, AFM, and UV-Vis. The sensor surface was modified with the anti-hTF (specific MAM TRC2) to show selectivity against the target analyte. The fabricated sensors were tested against different concentrations of human transferrin (hTF). The results are summarized below.

ZnO thin films were grown by the ALD method and homogeneously covered the entire substrate surface. While the number of cycles and pulse times do not affect the morphology, the increasing temperature of the reaction chamber increases the size of granular structures. There is a direct ratio between the number of cycles and the surface porosity. However, no relation was observed between precursor pulse time and the film porosity. According to the XPS results, it was observed that the surface defects increase significantly with the decrease of the film thickness.

The anti-hTF (TRC2) immobilizations on the ZnO surfaces were successfully performed. In static biosensor measurements, TRC2 immobilized ZnO/QCM platform exhibited sensor response to hTF in the range of 100-1000 ng. TRC2 immobilized ZnO/QCM sensor showed lower sensor response to hTF in the dynamic measurements than that of static measurements. Also, since QCM frequency is highly affected by environmental factors, it has been observed that there are differences between measurements performed at different times.

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5. WS₂ THIN FILM BASED QCM GAS SENSOR

WS₂ thin films were deposited on quartz crystal microbalance (QCM) oscillators via radio frequency magnetron sputtering to detect hazardous gases at room temperature (RT). WS₂ coated QCM sensors were tested against various hazardous gases including acetone, toluene, xylene, isopropyl-alcohol, hydrogen cyanide, hydrogen sulfide, ammonia, dimethyl methylphosphonate (DMMP, nerve agent simulant) and 2-Chloroethyl ethyl sulfide (mustard simulant). It was observed that fabricated sensors exhibit superior sensor performance to DMMP gas at RT. Additionally, one of the sensors showed reliable stability, high sensitivity, and a low theoretical limit of detection of 5 ppb. As a result, WS₂ coated QCM sensor has a great potential for the monitoring of nerve agent.

5.1. Introduction

Chemical warfare agents (CWAs) are extremely poisonous synthetic chemicals and have large-scale fatal effects on living organisms. CWAs can be classified as H-series (mustard and lewisite), G-series (nerve agents such as tabun, sarin and soman) and V-series. Among them, G-series nerve agents have been recognized as one of the most dangerous CWA due to their rapid and irreversible effects on the central nervous system. Thereby, there is a need to develop a sensing system that can detect these CWAs for security and environmental monitoring.

Sensing experiments are often carried out with simulant compounds because of high danger of nerve agents. The dimethyl methylphosphonate (DMMP) has been studied as a simulant of sarin due to its similar structure and functional groups. Up to now, several techniques have been developed for DMMP detection and monitoring such as mass spectrometry, optic sensors, Raman scattering method, chemi-resistive sensors, and mass sensitive sensors. Among these techniques, quartz crystal microbalance (QCM), one of the mass sensitive sensor types, is a reliable and promising method because of its simplicity, low power requirement, high sensitivity, and ease of use.

*This chapter has been submitted as a O. Alev, O. Özdemir, E. Goldenber, L. Ç. Arslan, S. Büyükköse, Z. Z. Öztürk “WS₂ thin film based quartz crystal microbalance gas sensor for dimethyl methylphosphonate detection at room temperature”, Thin Solid Films, (2022).

The sensing performance of QCM based sensors depends on the chemical and physical properties of the sensing layer. Therefore, the development of the sensing layer is of great importance. In the last decades, scientists have worked on different materials such as graphene, metal alloys, polymers, metal oxides, and transition metal dichalcogenides (TMDCs). TMDCs have been considered as good candidates for sensing applications due to their unique physical and chemical properties. Among various TMDCs materials, WS₂ offers great potential for the detection of hazardous gases at room temperature (RT) due to high specific surface area and large crystal spacing. Li et al. reported that WS₂ based sensor exhibited excellent sensor performance against ammonia (NH₃). Xu et al. observed that WS₂ based sensor is able to detect CO gas at RT. Liu et al. fabricated a WS₂ based gas sensor, which exhibited excellent selectivity to NO₂ gas at 160°C. Consequently, WS₂ can lead to advance the detection of DMMP in terms of sensitivity and selectivity as a result of hydrogen bonding between Lewis and Brønsted acid sites, providing hydroxyl groups, and strong polarity oxygen atoms in DMMP.

In this chapter, we report sensing properties of WS₂ coated QCM sensor towards hazardous gases and propose a sensing mechanism. WS₂ thin films were fabricated on QCM oscillators by the radio frequency (RF) magnetron sputtering method. The sensors were tested at RT against various hazardous gases including acetone, toluene, xylene, isopropyl-alcohol (IPA), hydrogen cyanide (HCN), hydrogen sulfide (H₂S), NH₃, DMMP, and 2-Chloroethyl ethyl sulfide (CEES). For a better understanding of sensor performance, sensor tests were also performed in a humid atmosphere and the limit of detection values for each gas were determined. The gas sensing mechanism of WS₂ coated QCM sensor was discussed in correlation with detailed X-ray photoelectron spectroscopy (XPS) studies.

5.2. Experimental Details

WS₂ thin films were deposited on AT-cut QCM (resonance frequency: 10 MHz) transducers at RT by using NANOVAK-400 magnetron sputtering system. The depositions were performed using WS₂ target (purity of 99.9% and a diameter of 50 mm) with a constant target-to-substrate distance of 120 mm. The base pressure in the chamber was 0.9 mPa. WS₂ films were deposited using an RF power of 130 W (13.56 Hz) at 0.93 Pa and 1.99 Pa under Ar atmosphere. The deposition rate was between

1.30 to 1.50 Å/s. Fabricated samples were named as WS2_1 and WS2_2 for 0.93 and 1.99 Pa, respectively. Morphological and structural characterizations were performed on WS₂ films grown on Au coated glass substrates.

A morphological study of the samples was carried out using a scanning electron microscope (SEM, Philips XL 30S) with an operating voltage of 30 kV. Energy dispersive X-ray spectroscopy (EDS) system coupled with the SEM (Philips XL 30 SFEG) was used for EDS analysis and EDS patterns were recorded with an acceleration voltage of 15 keV. The thin films were grown ex-situ and subsequently placed into a vacuum chamber. XPS data were recorded after in-situ etching of the surface with 1 keV Ar⁺ ions bombardment (10 min). The samples were analyzed with XPS using an Al K α x-ray ($h\nu$ = 1486.6 eV) source and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The base pressure of the analysis chamber was 1.33×10^{-8} Pa during the measurements. All spectra were recorded with pass energy of 30 eV. The energy analyzer was operated in Fixed Analyzer Transmission mode. The W 4f and S 2p spectra were fitted by the CasaXPS (version 2.3) using mixed Gaussian–Lorentzian peaks after subtracting Shirley-type background in order to extract the chemical bonding energies.

All the samples were located in the same measurement cell with a volume of 50 ml connected to an automated gas sensing setup for investigating the sensing properties as reported in our previous work. All gas sensing measurements were performed at RT (23°C) and the total flow rate was kept constant at 100 standard cubic centimeters per minute. Typical experiments of sensor test consisted of repeated exposure to analyte gas and subsequent purging with dry air to reset the baseline. The frequencies of the QCMs were recorded as a function of time. The changes in the resonance frequencies of the QCMs were evaluated as sensor responses. For all the measurements, high purity dry air (purity of 99.99%) obtained from gas cylinder was used as the reference and carrier gas. For the production of the toluene, xylene, and IPA vapors, the carrier gas was purged through a vaporizer filled with the chemical compound (in liquid phase) under investigation in order to be saturated with the vapor of the analyte. The vaporizers for the analytes were immersed in a thermostated bath to maintain a constant temperature of –10°C. Owlstone Vapor Generator (V-OVG (Owlstone, UK)) using permeation tubes (traceable to standard NIST) was used to generate and control the concentration of trace level vapor of the acetone, HCN, H₂S, NH₃, DMMP, and CEES. The pre-calibrated permeation tubes (from Owlstone company) were used to

produce desired vapor concentrations. When the tubes are heated in a permeation oven, the high purity dry air diffuses through the tube wall into the chamber. Thus, a pre-calibrated gas concentration was achieved. Furthermore, gas sensing measurements were repeated at humidity background (40% R.H. at 23°C) to examine the effects of the humidity on the sensing performance. Desired concentrations of gases were controlled via mass flow controllers and a multi-gas controller device (MKS 647C). Sensors were exposed to various concentrations of gases as given in Table 5.1. Details about the gas generating system were given in the previous works.

Table 5.1: Test analytes and tested concentration values.

Analyte	Concentrations (ppm) lowest to highest				
Acetone	0.95	1.9	3.8	5.7	7.6
H ₂ S	0.875	1.75	3.5	5.25	7
HCN	1.06	2.12	4.25	6.37	8.5
NH ₃	1.45	2.9	5.8	8.7	11.6
DMMP	0.175	0.35	0.7	1.05	1.4
CEES	1.25	2.5	5	7.5	10
Toluene	240	480	720	960	1200
Xylene	80	160	240	320	400
IPA	260	520	780	1040	1300

5.3. Results and Discussion

5.3.1. Structural Characterization

The surface and cross-sectional morphologies of the WS₂ thin films were evaluated by SEM (Figure 5.1(a)). The film thicknesses were found between 180-200 nm. It is apparent that the sputtering pressure affects the morphology. While there was no texture on the surface at the pressure of 0.93 Pa (see Figure 5.1(a)), flake like structures were observed on the WS₂ thin films when the sputtering pressure was 1.99 Pa as seen in Figure 5.1(b). These results can be explained by the relationship between the sputtering pressure and Ar pressure which effects the deposition rate. At high deposition pressures Ar partial pressure increased, resulting higher surface roughness and formation of flake-like structures on the surface. Formation of porous nanostructures on a film surface can be explained by Thornton model (Zone I) at high pressures.

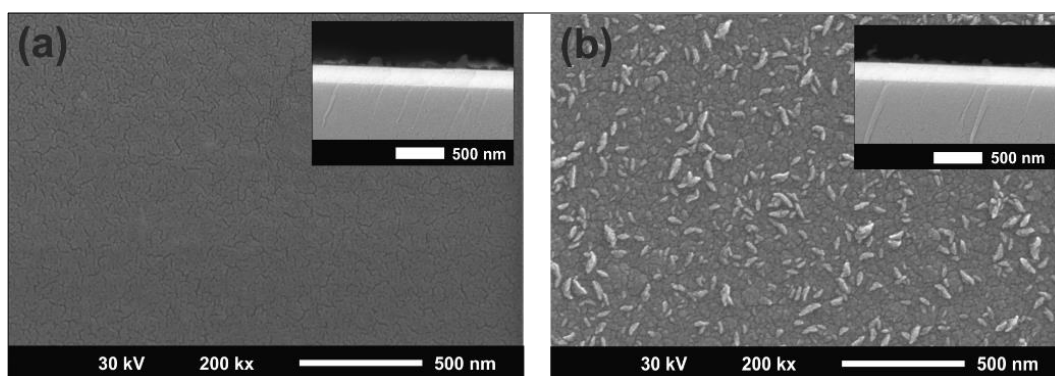


Figure 5.1: SEM images of (a) WS₂_1 and (b) WS₂_2 thin films. The insets show cross section images.

The W 4f-5p and S 2p XPS spectra of the samples grown under different ambient pressures are reported in Figure 5.2(a). The peaks of the WS₂ samples are fitted by a Voigt function under the constraint of identical full width at half maximum for all components prior to subtraction of the Shirley background to account for the inelastic photoelectrons. The W 4f level is fitted to two doublet, with each doublet spaced 2.1 eV apart due to the spin-orbit splitting. The fitting of the W 4f-5p spectra suggests that W on the surface is in the form of W(IV) and W(VI) bound both with S and O, the proportions of which depends on the deposition pressure. The doublet peaks at 33.1 and 35.2 eV correspond to the WS₂, while the second doublet components at 36.1 and 38.2 eV are ascribed to the WO₃ that are due to the oxygen contaminants introduced during the growth and transfer process. The weak component at 39.5 eV is associated with the W 5p peak. It is important to stress that no metallic tungsten component is observed which implies a full sulfurization and oxidation of W species during the growth process. Meanwhile, in Figure 5.2(b) the peaks located at 162.3 eV and 163.5 eV can be associated with the characteristic signal of S 2p_{3/2} and 2p_{1/2}, respectively. The energy positions of S 2p and W 4f components confirm the formation of WS₂ contained in the sample.

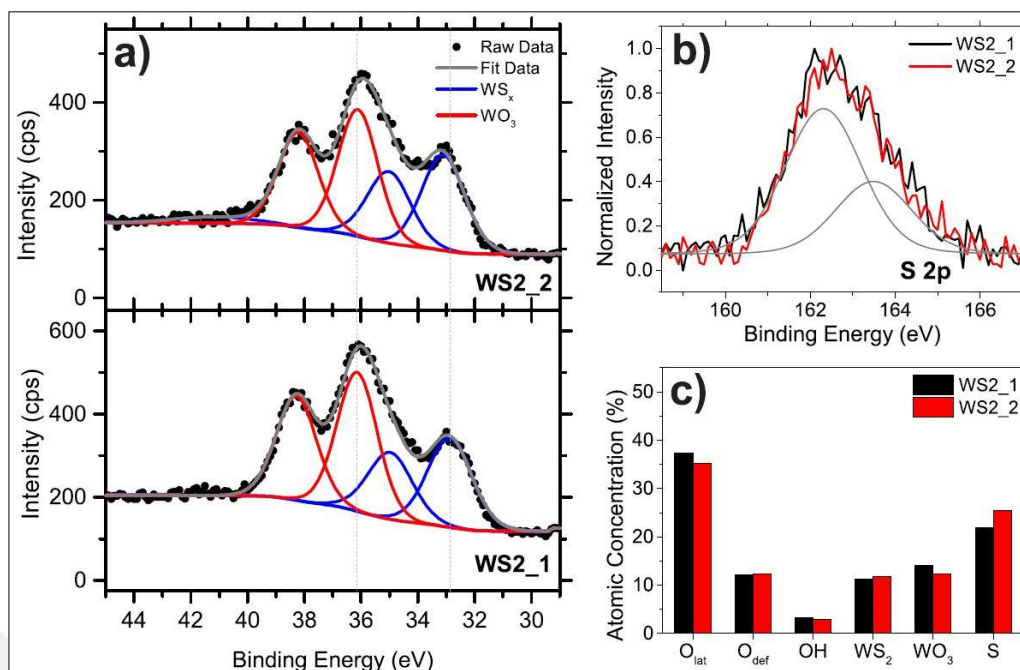


Figure 5.2: (a) XPS spectra for W4f-5p region with curve-fitting, (b) XPS spectra for S 2p region with curve-fitting, and (c) the comparison of the concentrations (in atomic %) of O, W, and S components.

Concentrations of surface components in WS₂ samples are displayed in Figure 5.2(c). For this quantification, we ignore the carbon content. After an in-situ etching of the surface with 1 keV Ar⁺ ions, the C 1s signal decreased below the detection limit and the oxygen content in the samples decreased to 30%. Moreover, a clear narrowing of the W 4f and S 2p regions was observed as a consequence of the removal of carbon and oxygen residuals. However, sputter etching leads to a change in the chemical bonding and formation of metallic states on the surface, therefore the spectra from the surface of unetched samples was presented. Overall, the oxygen content decreased slightly with increasing deposition pressure, however, sulfur concentration increased with increasing pressure. Correspondingly, the atomic ratio S/W(IV), deduced from the area under S 2p and W 4f peaks associated with WS₂, is equal to 1.71 and 1.81 for WS2_1 and WS2_2, respectively. Similarly, EDS analysis revealed also sulfur deficiency. The reason for the slight departure from stoichiometry is associated with the uncontrollable growth process of thin films deposited by high-rate reactive and metallic magnetron sputtering systems. In addition, the missing sulfur with respect to the ideal formula of the WS₂ can also be associated with the oxygen incorporation in the films.

5.3.2. Gas Sensor Measurements

The gas sensing performance of WS₂ thin film coated QCM sensors were tested for the detection of various hazardous gases including simulants of CWAs such as DMMP and CEES. Time-dependent frequency shifts (Δf , sensor response) of fabricated sensors against 7.6 ppm acetone, 1200 ppm toluene, 400 ppm xylene, 10 ppm CEES, 1.4 ppm DMMP and 11.6 ppm NH₃ are given in Figure 5.3. The sensors showed clear responses and stable baselines. Moreover, the noise level of the WS₂/QCM sensors was about 2 Hz. Uncoated QCM sensor did not show any response to analyte gases, while the WS₂/QCM sensors exhibit a very high sensor response to DMMP at a low concentration of 1.4 ppm, which is considered quite low concentration.

For better interpretation of sensing measurement data, the mean sensitivity values (S_m) were calculated by using the following equation;

$$S_m = \frac{1}{n} \sum_{i=1}^n \frac{\Delta f_i}{c_i} (\text{Hz/ppm}) \quad (5.1)$$

where Δf is the frequency shift when the sensor is exposed to analyte concentration c_i , i is an index for desired gas concentration and n is the number of gas exposures for each analyte. A comparison of the mean sensitivities for all tested gases is given in Figure 5.4(a). It is clear from the radar chart that both WS₂ sensors show the highest sensitivity to DMMP among the tested gases. Besides, WS2_1 had three times higher sensitivity towards DMMP than that of WS2_2. The calibration curves fitted by the linear regression model of the WS2_1 sensor against all analyte gases are given in Figure 5.4(b). A linear relationship between the gas concentration and the sensor response was found for all the analyte gases.

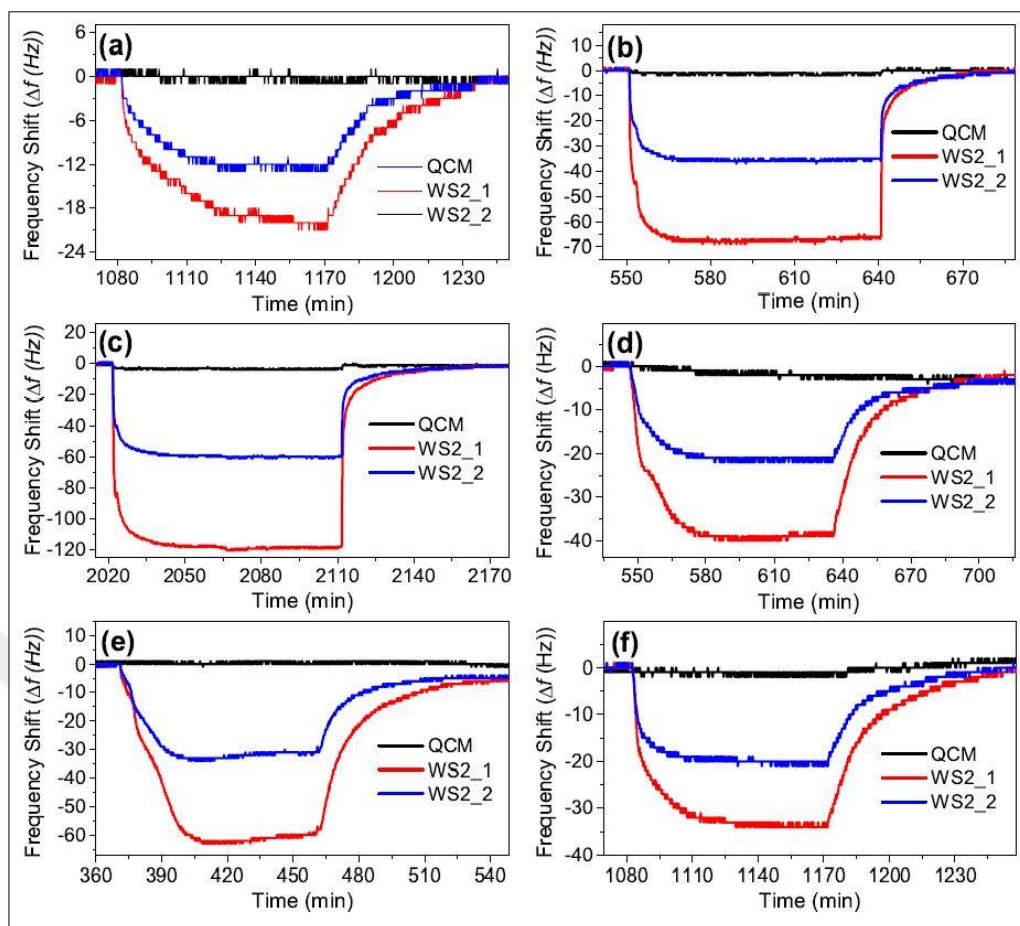


Figure 5.3: Frequency shifts under exposure of (a) 7.6 ppm acetone, (b) 1200 ppm toluene, (c) 400 ppm xylene, (d) 10 ppm CEES, (e) 1.4 ppm DMMP and (f) 11.6 ppm NH_3 .

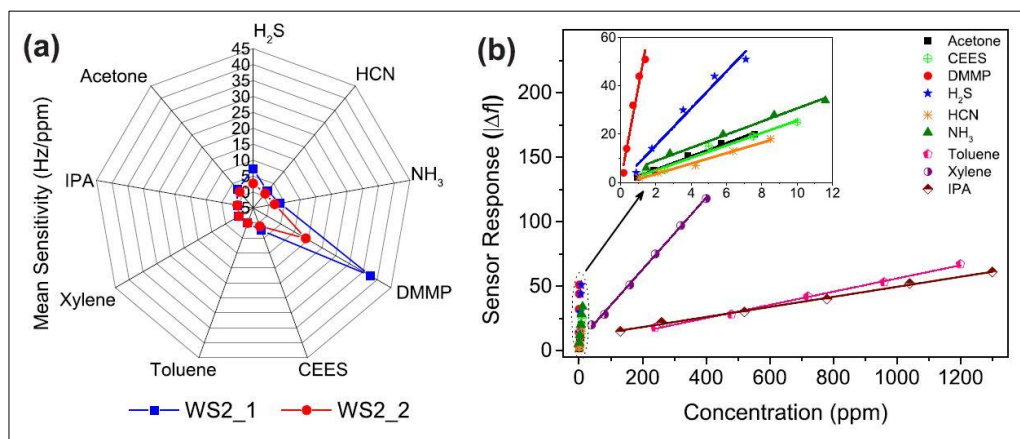


Figure 5.4: (a) Mean sensitivities of WS2_1 and WS2_2 and (b) calibration curves of WS2_1.

Figure 5.5 illustrates the typical real-time response curves of WS2_1 against DMMP gas at RT. Firstly, the sensor was continuously exposed to 1.4 ppm DMMP for five cycles under the same conditions. When DMMP was sent to the measurement

cell, the frequency of the sensor shifted rapidly, and reached a steady state value. When the target gas was turned off, the frequency turned back to the baseline value. The WS₂/QCM sensor exhibited repeatable and stable responses which indicate that the sensor has reproducible and consistent behavior. Then, the sensor was exposed to various concentrations of DMMP down to 0.175 ppm. As shown in Figure 5.5, frequency shifts were 60, 55, 41, 18 and 7 Hz to 1.4, 1.05, 0.7, 0.35 and 0.175 ppm, respectively. The sensor responses decreased with decreasing DMMP concentrations. The semi-empirical limit of detection (LOD) for DMMP gas was derived as described in our previous report. LOD was calculated using the following equation;

$$DL(ppm) = 3(rmds/sensitivity) \quad (5.2)$$

where rmsd value is the root-mean-square deviation which is calculated using the curve-fitting equation. The sensitivity was calculated by linear fitting of sensor response (Δf) vs. gas concentration. Among the measured gases, the lowest LOD value was obtained for DMMP gas with a concentration of 5 ppb. Calculated LOD values of WS₂_1 sensor and threshold limit values (TLV) were given in Table 5.1. It can be clearly seen that WS₂_1 sensor can detect all tested analytes below TLV.

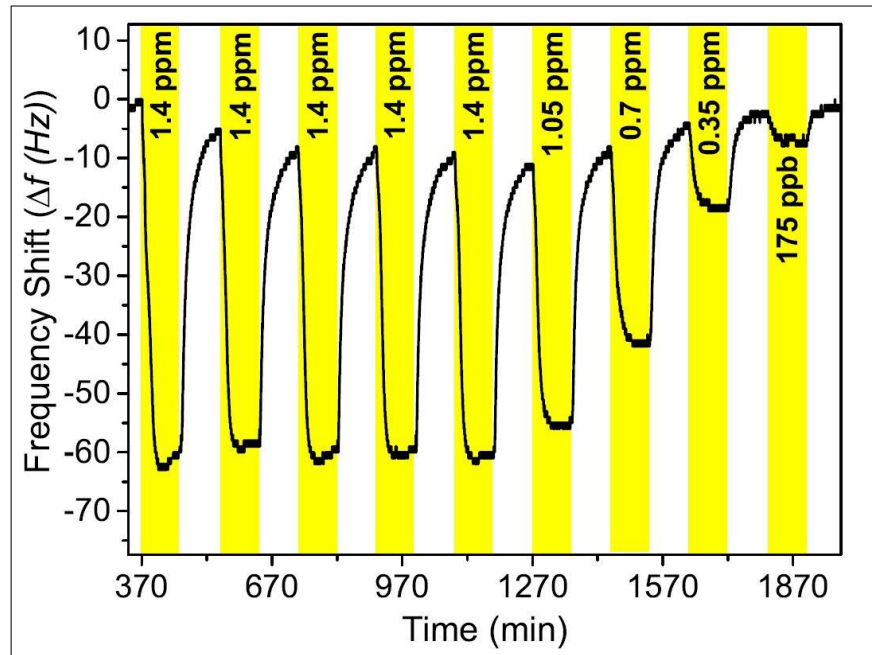


Figure 5.5: Dynamic sensor response of WS₂_1 sensor against DMMP at RT.

Table 5.2: Mean Sensitivity, measured lowest concentration (in ppm), LOD values (in ppm) of WS2_1 sensor and TLV (in ppm) of the test analytes.

Analyte gas	S_m	Measured lowest concentration	LOD	TLV
Acetone	2.61	0.95	0.8	250
H ₂ S	7.25	0.8875	0.26	1
HCN	1.91	0.55	0.033	10
NH ₃	3.57	1.45	0.96	250
DMMP	37.38	0.175	0.005	0.1
CEES	2.48	1.25	0.76	392
Toluene	0.06	240	27	50
Xylene	0.35	80	7	100
IPA	0.7	260	35	200

The presence of humidity is one of the main challenges in real-time sensor applications. To better understand the sensing performance of WS₂ coated QCM sensor, the gas sensing measurements were also carried out at 40% R.H. atmosphere. Sensor responses of WS2_1 sensor in dry air and at 40% R.H. are comparatively given in Figure 5.6(a). Sensor responses were higher in humidity environment than that of the dry air environment. The sensor responses to 1.4 ppm DMMP were 41 and 113 in dry air and 40% R.H. atmosphere, respectively. This means the WS₂ based sensor can be affected by humidity due to adsorbed water molecules onto the surface of WS₂. This behavior can be explained by the enhanced acidity of the surface of WS₂ due to the hydroxylation reaction of the co-adsorbed water. However, the effect of humidity on DMMP sensitivity was relatively low compared to the other gases. Another important property for a sensor is long-term stability. Figure 5.6(b) presents sensor responses of WS2_1 to 1.4 ppm DMMP within 60 days. There was almost no change in sensor response within that period. This indicates that the sensing characteristic of WS₂ based QCM gas sensor is stable in the given time interval.

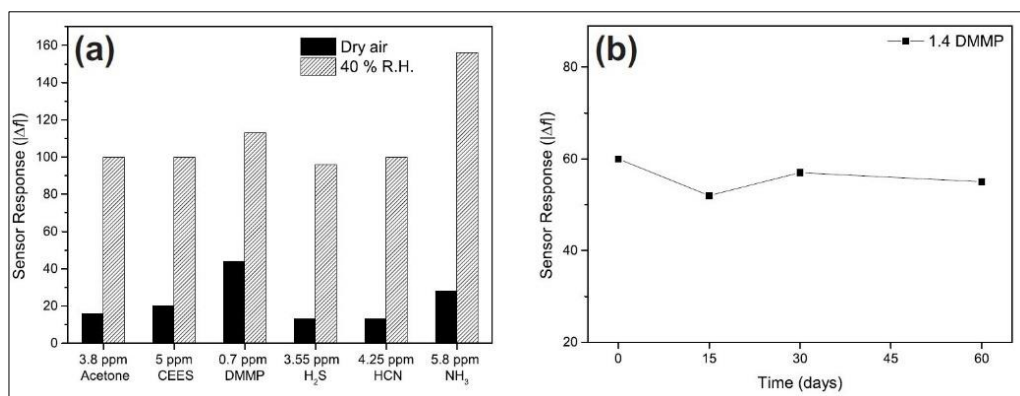


Figure 5.6: (a) Sensor responses of WS2_1 to various gases in dry air and 40% R.H. atmosphere and (b) the long-term stability of WS2_1 sensor to 1.4 ppm DMMP.

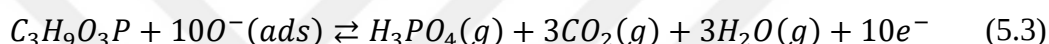
Table 5.3 shows the DMMP sensing performance of WS₂/QCM sensor compared with recently reported DMMP sensors. It can be seen that WS₂ coated QCM sensor has exhibited relatively high sensing performance to DMMP gas for such concentration levels.

Table 5.3: Comparison of the DMMP sensing performance of WS₂/QCM sensor with the recent studies.

Material	Transducer	Temperature (°C)	Concentration (ppm)	Response	Ref.
rGO	Chemiresistive	RT	1	0.02	[179]
WSe _s	Chemiresistive	RT	10	0.08	[180]
SnO ₂ /MnO ₂	Chemiresistive	250	5	9	[181]
PMFOS	SAW	30	10	6.4	[182]
WO ₃ /rGO	Chemiresistive	150	10	17.6	[183]
In ₂ O ₃ -Au	QCM	RT	30	60	[184]
WO ₃	QCM	10	4	70	[185]
AgNW/graphene	FET	RT	5	0.05	[186]
V ₂ O ₅	QCM	RT	3	30	[187]
WS ₂ thin film	QCM	RT	0.175	7	This study

5.3.3. Sensing Mechanism

The sensing mechanism can be explained by the adsorption and desorption of DMMP molecules via hydrogen bonding on the defects and vacancies on WS₂ surface. It has been reported that active sites such as Brønsted and Lewis acids are responsible for molecular adsorption on WS₂ surface. However, DMMP adsorption at RT takes place mainly at the Brønsted sides. To better understand the sensing mechanism of WS₂ thin films, Figure 5.7 illustrates the reaction between DMMP gas and the surface. At first, oxygen molecules, mostly O²⁻ and O⁻, are adsorbed on the surface of WS₂ thin film in air. When the sensor is exposed to DMMP at RT, hydrogen bonding formed between H atoms of the gas and the surface adsorbed oxygen species of the WS₂ with the following reaction:



This process results in a decrease in the resonant frequency due to increasing mass on the WS₂/QCM sensor. Much higher DMMP response compared to the other gases can be related to P=O and –OCH₃ groups of DMMP gas. Oxygen atoms in these groups have strong polarity and can be adsorbed on the surface-active sides of WS₂ thin film, causing a higher sensitivity and selectivity. The higher sensitivity of WS₂_1 is associated with the higher degree of oxidation of the surface as obtained from XPS.

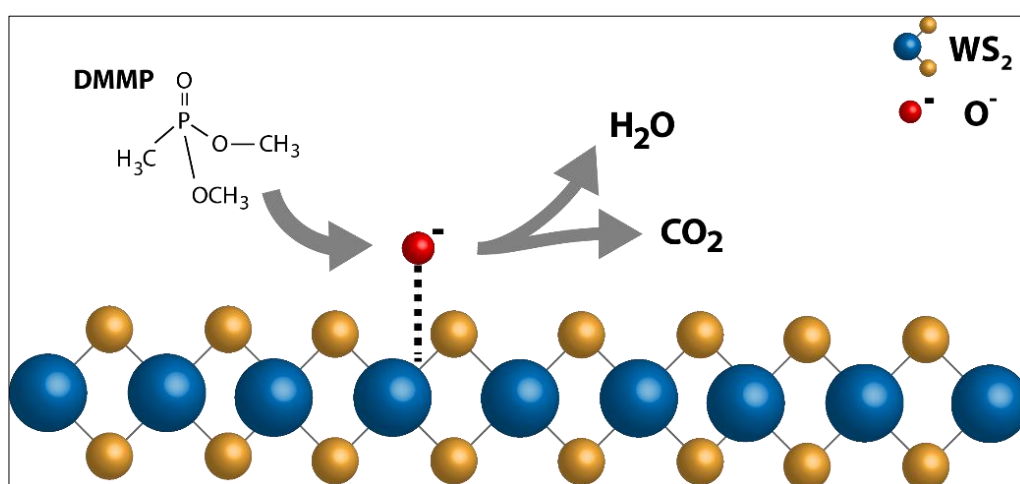


Figure 5.7: Schematic diagram of the sensing mechanism of WS₂.

5.4. Conclusion

WS₂ thin films were synthesized on the QCM oscillators by using magnetron sputtering method. WS₂ coated QCM sensors were tested toward nine different hazardous gases including DMMP, which is known as a simulant of sarin nerve agent, in a dry and humid atmosphere at RT. The sensors showed the highest sensitivity to DMMP gas. Moreover, WS₂ based sensor was able to detect DMMP gas at a concentration as low as 175 ppb. The detection limit of the sensor for DMMP gas was calculated as 5 ppb which is quite below the threshold limit value. WS₂/QCM sensor exhibited superior sensor performance in terms of sensitivity, selectivity among measured gases, repeatability, and durability at RT. The sensing mechanism of WS₂ thin films is associated with the physical adsorption of DMMP through the oxygen defects located on the surface. As a conclusion, our results indicate that WS₂ based QCM sensor have the potential for the detection of nerve agents in real-time applications.

6. Cu-DOPED ZnO NANORODS BASED QCM SENSOR FOR HAZARDOUS GASES

Cu doped ZnO nanorods (NRs) were deposited on quartz crystal microbalance (QCM) oscillators to detect hazardous gases at room temperature. Cu doped and pristine ZnO NRs have been successfully synthesized by a two-step electrochemical deposition technique. Electrodeposition conditions were optimized to get highly ordered ZnO NRs. The NRs have about the diameter of 100 nm and length of 400 nm. Fabricated sensors were tested against isopropyl alcohol, dichlorobenzene, ethyl acetate, toluene, xylene, H₂S, HCN and NO₂. The results indicated that Cu doping advances sensor response of ZnO NRs especially for H₂S and HCN. 1% Cu doped ZnO NRs sensor showed the highest sensor response. Doping concentration dependent increment in sensor response was explained with the enhancement of physisorption properties of the NRs surface. Among the tested gases, the response values for H₂S and HCN at room temperature were measured as ~ 68 at 6.6 ppm and ~ 57 at 8.8 ppm, respectively. The limit of detection values of 1% Cu doped ZnO NRs sensor were calculated as 79 and 169 ppb for H₂S and HCN, respectively.

6.1. Introduction

Effective and inexpensive systems for detection of environmentally hazardous gases are of vital importance for preventing increased indoor and atmospheric pollution [188-190]. For the last few decades, scientists have been investigating to develop highly sensitive, cheap and rapid sensing systems [191-194]. However, sensor performances including accuracy, selectivity and durability must be improved to meet the requirements of real-time environmental monitoring.

Transduction platform and sensing material are the most important parts of a sensor which affect its performance. Up to now, different transduction units such as chemiresistive, surface acoustic wave (SAW), quartz crystal microbalance (QCM) and optic systems have been adopted to the gas sensor systems [195-198]. Mass sensitive based gas sensors such as QCM can directly measure the change in mass

*This chapter has been submitted as a O. Alev, N. Sarıca, O. Özdemir, L. Ç. Arslan, S. Büyükköse, Z. Z. Öztürk “Cu-doped ZnO nanorods based QCM sensor for hazardous gases”, J. Alloys Compd, (2020).

when gas molecules are adsorbed on the sensing layer [199, 200]. Therefore, QCM based sensors do not need the charge carriers and heat treatment even if metal-oxide semiconductors (MOXs) materials are used as sensing element [201]. Those are the most important advantages of QCM based sensors over other transduction platforms.

MOXs, conducting polymers and metal alloys are the most studied gas-sensing materials [2, 202-204]. MOXs are environment friendly and efficient sources for sensing several different kind of gases [190]. ZnO is one of the most studied MOX material due to its easy fabrication and unique surface properties [195, 205, 206]. Moreover, 1D morphologic forms of ZnO can be synthesized via different methods including hydrothermal process, chemical vapor deposition (CVD) or electrochemical deposition [207-209]. Electrochemical deposition technique has the merit of producing ZnO nanostructures, by controlling the size and morphology at low temperatures [201]. Despite various studies performed on QCM based gas sensors, there are limited works on MOX/QCM based sensors for the detection of hazardous gases. ZnO can be a useful material for the detection of hazardous gases such as hydrogen cyanide (HCN), hydrogen sulfide (H₂S) or dichlorobenzene [210, 211]. Georgieva et al. reported that ZnO nanostructured films formed on QCM resonators by electrochemical deposition can be used in NO₂ sensing applications [212]. Horzum et al. used electrospinning method to fabricate MOXs nanofibers on QCM oscillators [213]. They showed that MOX nanofibers coated QCM sensors have promising results against VOCs. Xie et al. used ZnO nanostructures coated QCM resonator sensors to detect alcohols [214]. Recently we have showed that Pd doping enhanced sensor properties of ZnO/QCM gas sensor [201].

The sensing process of QCM sensors is based on the adsorption of target molecules [200, 215]. Thus, the modification of the surface of ZnO layer may affect the sensing characteristics. The doping is one of the most effective methods for altering the physical properties. Up to now, different transition metals such as Ag, Cr, Co, Pd and Cu have been used as dopant elements for effective doping of ZnO [216-218]. Among these, Cu can substitute Zn atoms in ZnO lattice because of similar atomic radii of Cu and Zn [219]. Additionally, Cu is important due to creating localized impurity levels in ZnO host lattice [210, 220]. Salem et al. have reported that doping ZnO nanostructures with Cu can decrease the band gap and the electrical resistivity [221]. Similar reports have shown that substitution of Cu in ZnO improves gas

sensitivity [210, 222, 223]. It is also reported that Cu doping can significantly reduce the operation temperature of ZnO for H₂S sensing [224].

Even though there is a broad range of literature on QCM based gas sensors and ZnO doping with transition metals, there is a very limited number of works on metal doped ZnO/QCM gas sensors. In this chapter, the effect of Cu doping in ZnO NRs were systematically studied, and mechanism behind the improvement in sensor properties was explained. ZnO NRs and Cu-doped ZnO NRs were fabricated by facile electrochemical deposition method. Literature shows that the substitution limit of Cu into ZnO is low (around 5%) [225]. So, the doping content was chosen between 0 – 5% molar ratios to understand the effect of doping on the sensor properties of ZnO. The pristine and Cu doped ZnO NRs coated QCM sensors were tested at room temperature against various hazardous gases including toluene, xylene, isopropyl, ethyl acetate, dichlorobenzene, NO₂, HCN and H₂S and the effect of Cu doping on the sensing performance was discussed.

6.2. Experimental Details

Vertically oriented ZnO NRs were synthesized via two step electrochemical deposition method on Au electrodes of AT-cut QCM (resonance frequency: 10 MHz) transducers using CHI instruments workstation. All chemicals used in this study including potassium chloride (KCl), zinc chloride (ZnCl₂) and copper (II) chloride dihydrate (Cl₂Cu•2H₂O) are commercially available. In three electrode system, Au electrodes of QCM, Ag/AgCl, and Pt electrodes were used as a working electrode, reference electrode and counter electrode, respectively. Firstly, a thin zinc oxide layer called a seed layer was grown on QCM using 5 mM ZnCl₂ and 0.1 M KCl aqueous solution. Constant cathodic current ($J = 0.012 \text{ mA/cm}^2$) was applied for 2000 s to form seed layer onto Au electrode at room temperature as explained in the literature [201]. This seed layer helps the NRs to grow more uniformly on the QCM surface. Then, ZnO NRs were synthesized on the seed layer by changing the concentration of ZnCl₂ and KCl in order to obtain uniform NRs. Optimization parameters of the synthesized samples are shown in Table 6.1. ZnO NRs formation was carried out using CHI workstation with a three-electrode system similar to the seed layer formation. The reaction temperature was kept constant at 80°C and constant cathodic potential of - 0.9 V was applied for 3000 s.

Table 6.1: Growth parameters of ZnO seed layer.

Sample	KCl molar concentration (mM)	ZnCl ₂ molar concentration (mM)
S1	12	5
S2	6	1.25
S3	6	2.5
S4	6	5
S5	6	10
S6	3	5
S7	1.5	5

Cu doped ZnO NRs were grown on QCM by two-step electrochemical deposition method. Initially, the ZnO seed layer was grown on QCM electrodes as explained earlier. Cu doped ZnO NRs were grown on the seed layer using 1.5 mM KCl and 5 mM ZnCl₂ aqueous solution. Copper (II) chloride dehydrate was used as the copper source in this solution and the molar concentration ratio of Cu to Zn was changed between 0 to 5% in steps of 1% mol.

To investigate the crystal structure of the synthesized samples, x-ray diffraction (Rigaku Smartlab) with Cu K α radiation ($\lambda=1.15406$ Å) was used. Morphological study of the samples was carried out using SEM (Philips XL 30S). The samples were analyzed with XPS using an Al K α x-ray ($h\nu=1486.6$ eV) source and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The base pressure of the analysis chamber was 1.33×10^{-8} Pa during the measurements. The spectra were fitted using the CasaXPS using mixed Gaussian–Lorentzian peaks after subtracting Shirley-type background in order to extract the chemical bonding energies.

All the samples were located in the same measurement cell of the automated gas sensing setup for investigating the sensing properties. The volume of the measurement cell was 50 ml. The frequency of the QCMs was recorded as a function of time. The changes in the resonance frequency of the QCMs were evaluated as sensor responses. Dry air was used as reference and carrier gases. When steady state was obtained, samples were exposed to desired concentrations of gases controlled via mass flow controllers and multi gas controller device (MKS 647C). Gas cylinders were used to obtain NO₂ gas and dry air. The volatile organic compounds (VOCs) and humidity were generated through bubblers. HCN and H₂S gases were generated via Owlstone V-OVG gas generator. Details about the gas generating system were given in the

previous works [226]. The gas sensing measurements were performed at room temperature. The total flow rate per exposure was kept constant at 100 sccm. Sensors were exposed to various concentrations of gases as given in Table 6.2.

Table 6.2: Test analytes and tested concentration values.

Analyte	Concentrations (ppm) lowest to highest			
Dichlorobenzene	75	150	300	600
Toluene	170	340	680	1700
Xylene	65	130	260	520
Ethly acetate	650	1300	2600	5200
NO ₂	50	100	200	500
H ₂ S	0.85	1.65	3.3	6.6
HCN	1.1	2.2	4.4	8.8
Isopropyl alc.	85	170	340	850

6.3. Results and Discussion

6.3.1. Structural Characterization

In the electrolyte solution, KCl was used as a supporting electrode to obtain a good conductivity. However, it is well known that Cl⁻ ions might act as capping layer on polar faces by blocking the grain growth. This preferential absorption of Cl⁻ ions onto (0001) polar faces of ZnO surfaces hinders the growth along the (0001) direction (c axis) and enables faster growth along non-polar than the polar crystal planes, causing the formation of plate-like structures. ZnCl₂ concentration in the electrolyte solution also plays a key role to control the growth kinetics. Increase in concentration of ZnCl₂ in the solution is expected to cause an increase in the coverage of the surface as depicted in literature [227, 228]. SEM images of ZnO NRs are displayed in Figure 6.1(a–h). When the concentration of KCl was kept constant at 6 mM and lower concentrations of ZnCl₂ was applied, plate like structures were formed as seen in Figure 6.1(b) and (c). When the concentration of KCl was kept constant at 6 mM and the concentration of ZnCl₂ was increased from 1.25 mM to 10 mM, NRs were formed instead of plate like structures (Figure 6.1(b–e)). On the other hand, when the concentration of ZnCl₂ was kept constant at 5 mM and a lower concentration of KCl was applied, more uniform NRs were obtained as in Figure 6.1(g) and (h) (higher magnification). Thus, the growth parameters used for S7

was chosen for the further experiments and the Cu doped NRs were synthesized according to these parameters. In the rest of the text, ZnO NRs refers to undoped ZnO NRs grown with the growth parameters of S7.

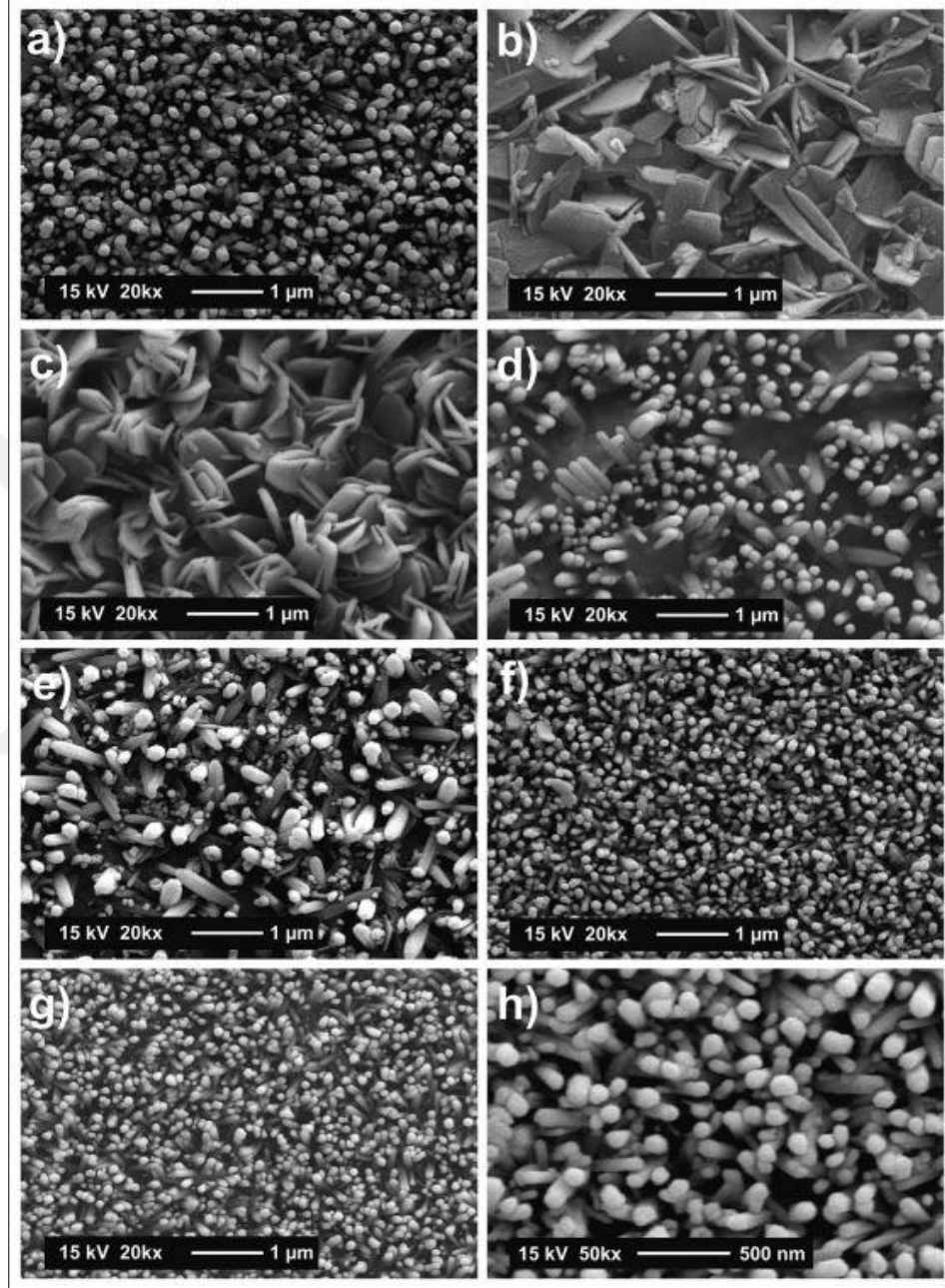


Figure 6.1: SEM images of (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6, (g) S7 and (h) higher magnification of S7.

SEM images of Cu doped ZnO NRs with different doping concentrations are shown in Figure 6.2. It is seen that the lower concentration of Cu doping does not significantly affect the morphology of the ZnO NRs as seen in 1, 2 and 3% Cu doped

samples. However, when the concentration of the Cu doping was increased above 3%, the morphology of the nanorods was distorted as seen in Figure 6.1(e–f). Thus, 1% and 3% Cu doped ZnO NRs were chosen for testing the sensors as they both maintain their original shape and the Cu contents are quite different from each other.

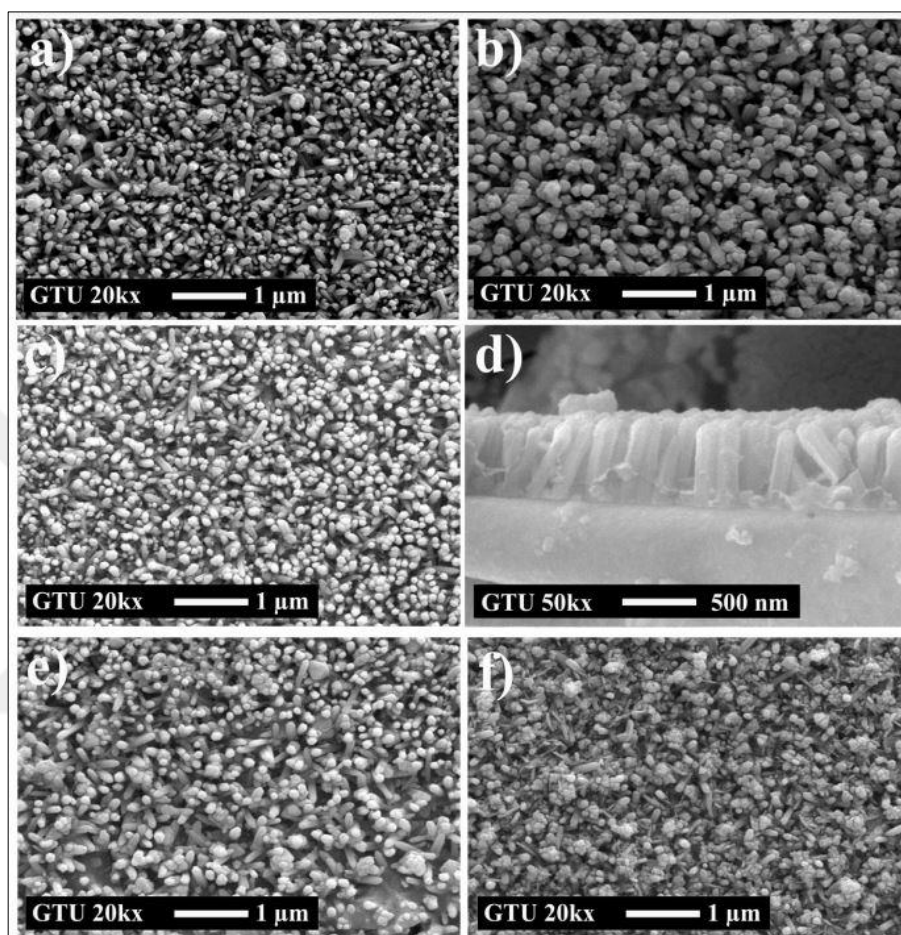


Figure 6.2: SEM images of (a) 1% Cu doped ZnO NRs, (b) 2% Cu doped ZnO NRs, (c) 3% Cu doped ZnO NRs, (d) cross sectional image of 3% Cu doped ZnO NRs, (e) 4% Cu doped ZnO NRs and (f) 5% Cu doped ZnO NRs.

The crystal structure and phase composition of electrodeposited undoped and Cu-doped ZnO NRs were investigated by XRD. Figure 6.3 shows XRD patterns of ZnO NRs (undoped S7), 1% Cu doped (1%Cu@ZnO) and 3% Cu doped (3%Cu@ZnO) ZnO NRs. The XRD peak at 34.2° and 36.4° are related with the wurtzite hexagonal phase of ZnO and can be assigned to (002) and (101) planes [219]. The observed patterns reveal a hexagonal wurtzite phase and match with the data of the Joint Committee on Powder Diffraction Standards (JCPDS) card no. 36–1451 [229]. The peak at 38.1° (111) is related to Au from the substrate [230]. Furthermore,

no other peaks corresponding to Cu or Cu oxides were detected. As a results, either Cu ions substituted Zn^{2+} ions and did not change the hexagonal wurtzite structure of the samples or Cu atoms accumulated near the surface region of the NRs and form tiny metal clusters which are difficult to detect by XRD. XPS studies are performed to identify different atoms including very small amounts since XPS is surface sensitive and chemical state sensitive technique.

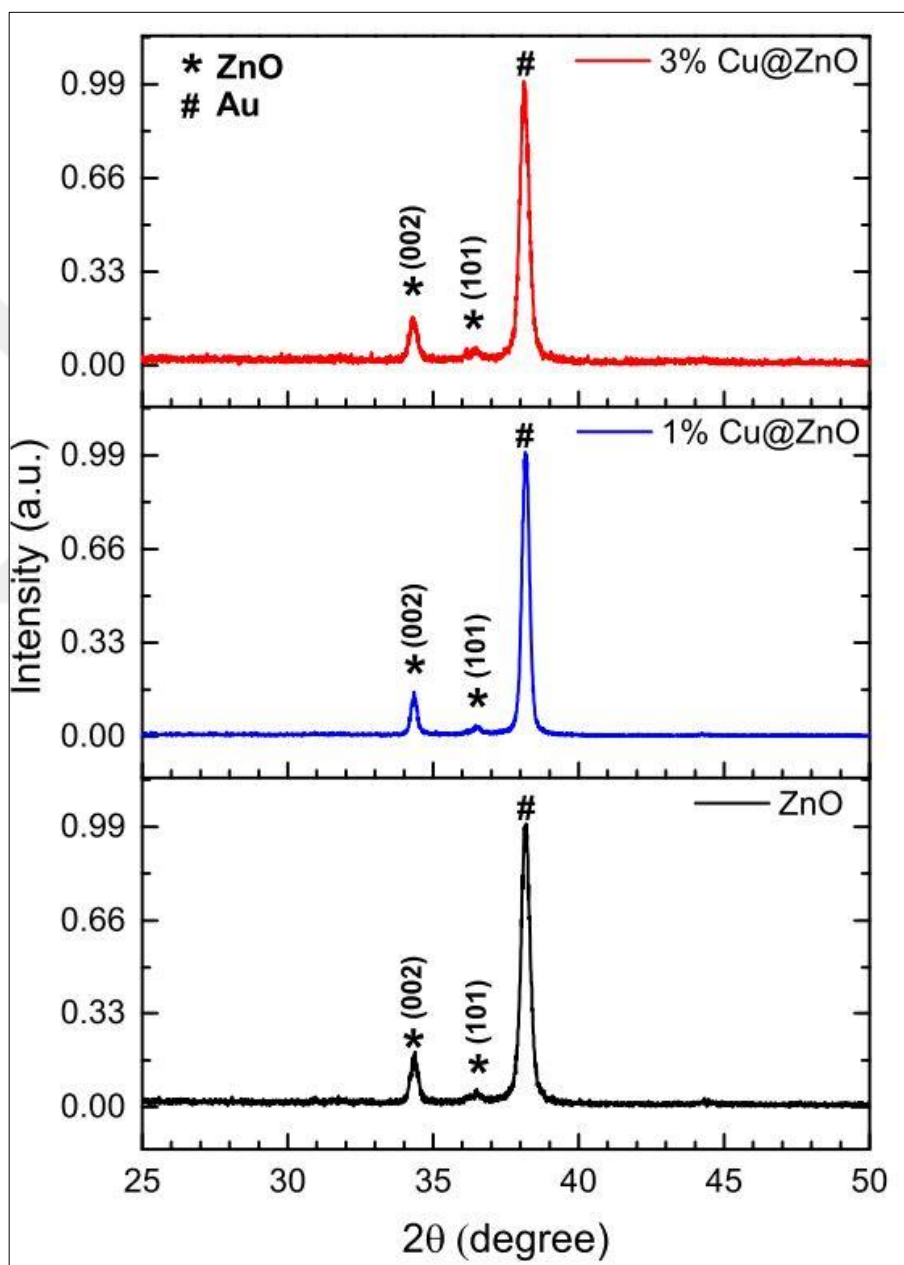


Figure 6.3: XRD patterns of Cu@ZnO NRs for different Cu content.

The XPS spectra of O 1s, Zn 2p and Cu 2p regions were analyzed to investigate the chemical state of dopant atoms in Cu-doped ZnO NRs. The binding energies of the spectra have been calibrated by the carbon C 1s peak (284.8 eV) reference. The carbon peak is due to the unavoidable air exposure as the sample is inserted in the XPS chamber. As shown in Figure 6.4, the O 1s spectra of ZnO NRs consists of the main peak at 530.46 eV associated with the Zn and Cu metal-oxide (lattice oxide) bonds, the shoulder at 531.9 eV related to defect-oxide (oxygen vacancies) and the highest energy at 533.2 eV peak related to the adsorbed oxygen species such as water, and hydroxyl groups. After Cu doping, the O 1s spectra presents similar peaks with a slight shift to lower binding energy. With the increase of Cu doping level to 3%, the binding energy of the lattice oxide peak shifted about 0.3 eV to lower energy which indicates the increase of the coordination number of O. The detailed fitting peak parameters, including peak position and $O_{\text{lattice}}/O_{\text{vacancy}}$ ratio, are concluded in Table 6.3. Comparing the area ratio of the main peaks (lattice oxide/oxygen vacancy) in the samples, it is worth noting that the lattice oxide in 1%Cu@ZnO account for 56% of the total oxygen, lower than 66% for pristine and 3%Cu@ZnO. Moreover, it can be seen from Table 6.3 that the atomic percentage of O in Cu doped ZnO NRs is slightly increased compared to that of ZnO NRs, suggesting the generation of the oxygen sites. 1%Cu@ZnO has the lowest concentration metal-oxide bond and the highest concentration of oxygen vacancies compared with those of pristine and 3%Cu@ZnO, which may contribute to the observed sensitivity enhancement [231].

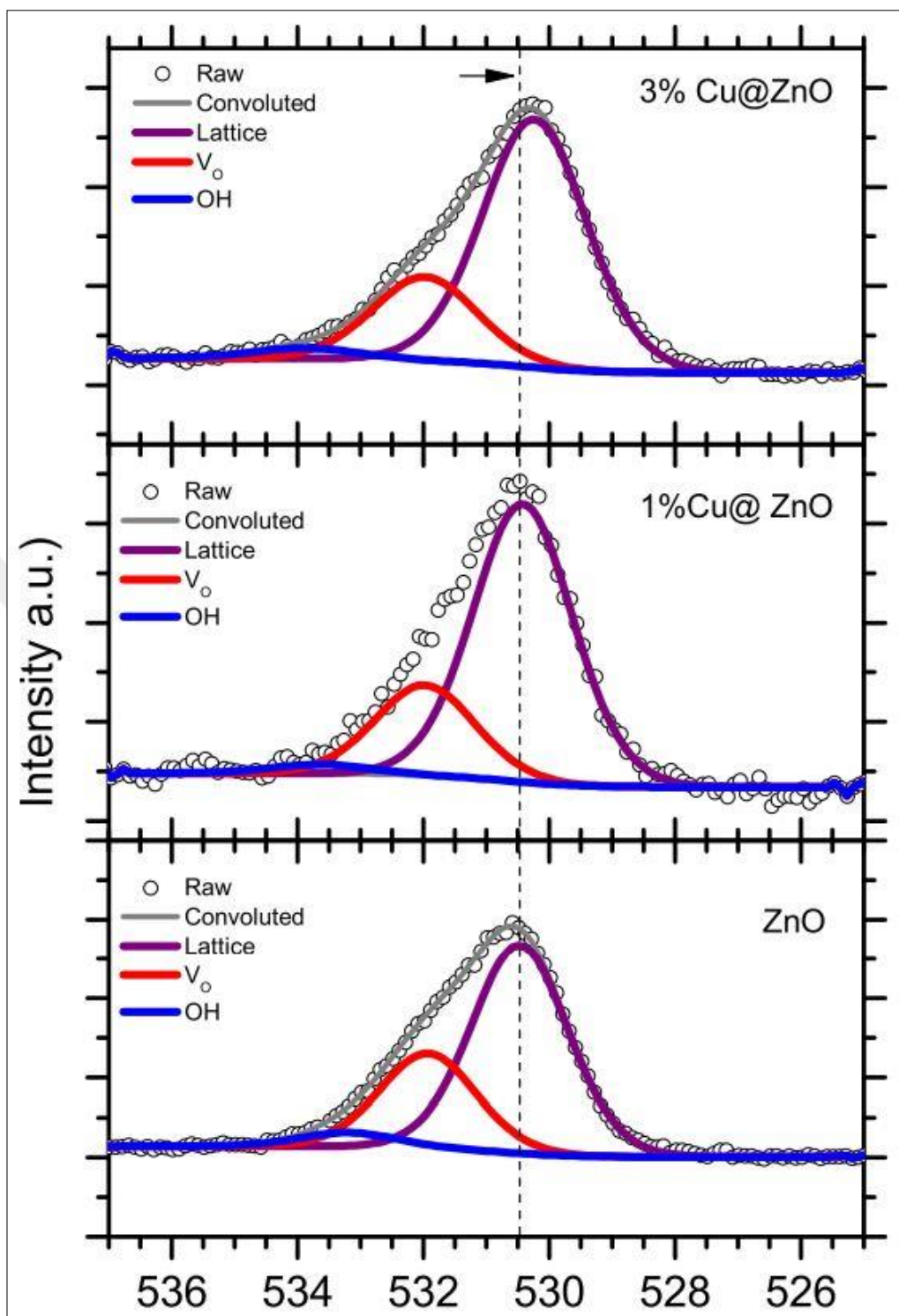


Figure 6.4: O 1s spectra of ZnO, nominal 1% and 3% Cu@ZnO NRs. The O 1s spectra are fitted with three components corresponding to O lattice (530.4 eV, purple line), O vacancy (531.9 eV, red line) and weakly bonded hydroxyl groups (533.6 eV, Blue line). The dashed lines are guide for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 6.3: XPS elemental analysis and stoichiometry of the Cu doped ZnO NRs.

Sample	O 1s Peaks		Zn 2p Peaks		Cu 2p Peaks		O/(Zn+Cu) Ratio
	Peaks	% at	Peaks	% at	Peaks	% at	
ZnO NRs	530.46eV Lattice (66%)	56	1021.6 eV Zn 2p _{3/2}	44	—	—	1.27
	531.92 eV Vacancy (29%)		1044.6 eV Zn 2p _{3/2}		—		
%1 Cu@ZnO NRs	530.32 eV Lattice (56%)	67	1021.6 eV Zn 2p _{3/2}	23	931.8eV Cu 2p _{3/2}	110	2.03
	531.73 eV Vacancy (34%)		1044.6 eV Zn 2p _{3/2}		951.6eV Cu 2p _{3/2}		
%3 Cu@ZnO NRs	530.16 eV Lattice (66%)	60	1021.5 eV Zn 2p _{3/2}	27	931.8eV Cu 2p _{3/2}	13	1.5
	531.69 eV Vacancy (27%)		1044.6 eV Zn 2p _{3/2}		951.6eV Cu 2p _{3/2}		

The Zn 2p spectra of the ZnO NRs have binding energies of 1021.6 and 1044.6 eV (Figure 6.5(a)), which are related to Zn 2p_{3/2} and Zn 2p_{1/2} lines, respectively. The separation between the Zn 2p_{3/2} and Zn 2p_{1/2} peaks is 23 eV consistent with the oxidation state of Zn²⁺ in ZnO [232]. The binding energies of Zn 2p showed almost no changes after doping, indicating that the chemical environment of Zn 2p was not affected from doping Cu into ZnO NRs [233]. Figure 6.5(b) displays a doublet located at 931.8 eV and 951.6 eV, corresponding to the core lines of Cu 2p_{3/2} and 2p_{1/2} of Cu⁺ respectively, which remains unchanged with both doping concentrations. The binding energies are comparable to those previously reported for other Cu doped ZnO nanostructures [234, 235]. Via the fine spectral contrast of Zn 2p and Cu 2p in XPS, doped Cu atoms were predicted to replace the site of Zn atoms in ZnO lattice. Due to the similar ion radius and charge numbers between Zn²⁺ and Cu⁺, Cu⁺ can substitute Zn²⁺ to occupy the regular lattice sites in ZnO. It was presumed that the some of the Zn–O bonds of pure ZnO were partially changed to Cu–O bonds. Cu atoms replaced the site of Zn in lattice and allowed more oxygen to sit in lattice site. The chemical composition analyzed by XPS shows that the doping concentration in the nominal 1% Cu doped ZnO NRs is in fact around 10 at % Cu. This might be attributed to the surface

sensitivity of the XPS method. It is likely that the doped Cu atoms prefer to locate in the close vicinity of the NRs surface.

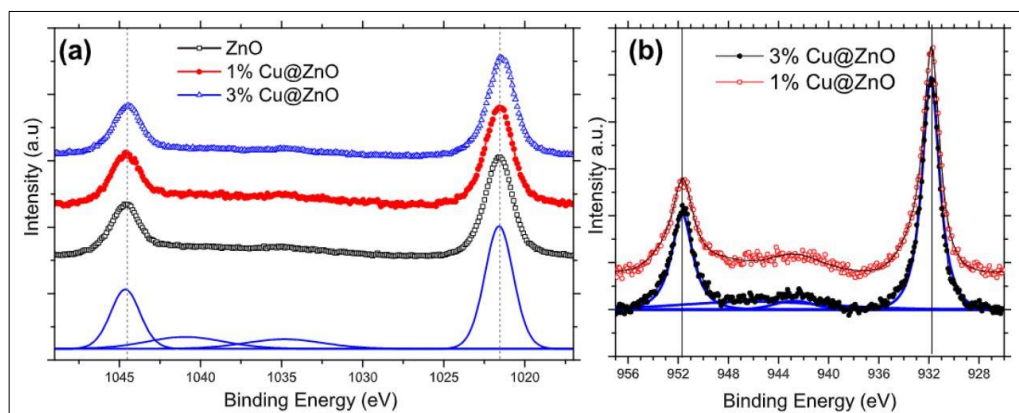


Figure 6.5: Comparison of XPS (a) Zn 2p and (b) Cu 2p spectra of ZnO, nominal 1%Cu@ZnO and 3%Cu@ZnO.

6.3.2. Gas Sensor Measurements

The gas sensing performances of ZnO, 1%Cu@ZnO and 3%Cu@ZnO coated QCM sensors were tested for the detection of various hazardous gases. Comparative time dependence on frequency shifts (sensor responses) of fabricated sensors against 6.6 ppm H₂S, 8.8 ppm HCN, 240 ppm dichlorobenzene, 850 ppm isopropyl alcohol, 350 ppm toluene, and 6000 ppm ethyl acetate is given in Figure 6.6. It is observed that the responses of all the QCM sensors were rapid and clear. The baselines of the QCM sensors were relatively stable. The noise level on QCM crystals is about 2 Hz. 1%Cu@ZnO and 3%Cu@ZnO sensors showed higher sensor responses toward all tested gases compared to ZnO. This means that the sensor responses were enhanced by Cu doping into ZnO NRs. On the other hand, pristine QCM sensor did not show response against any gases.

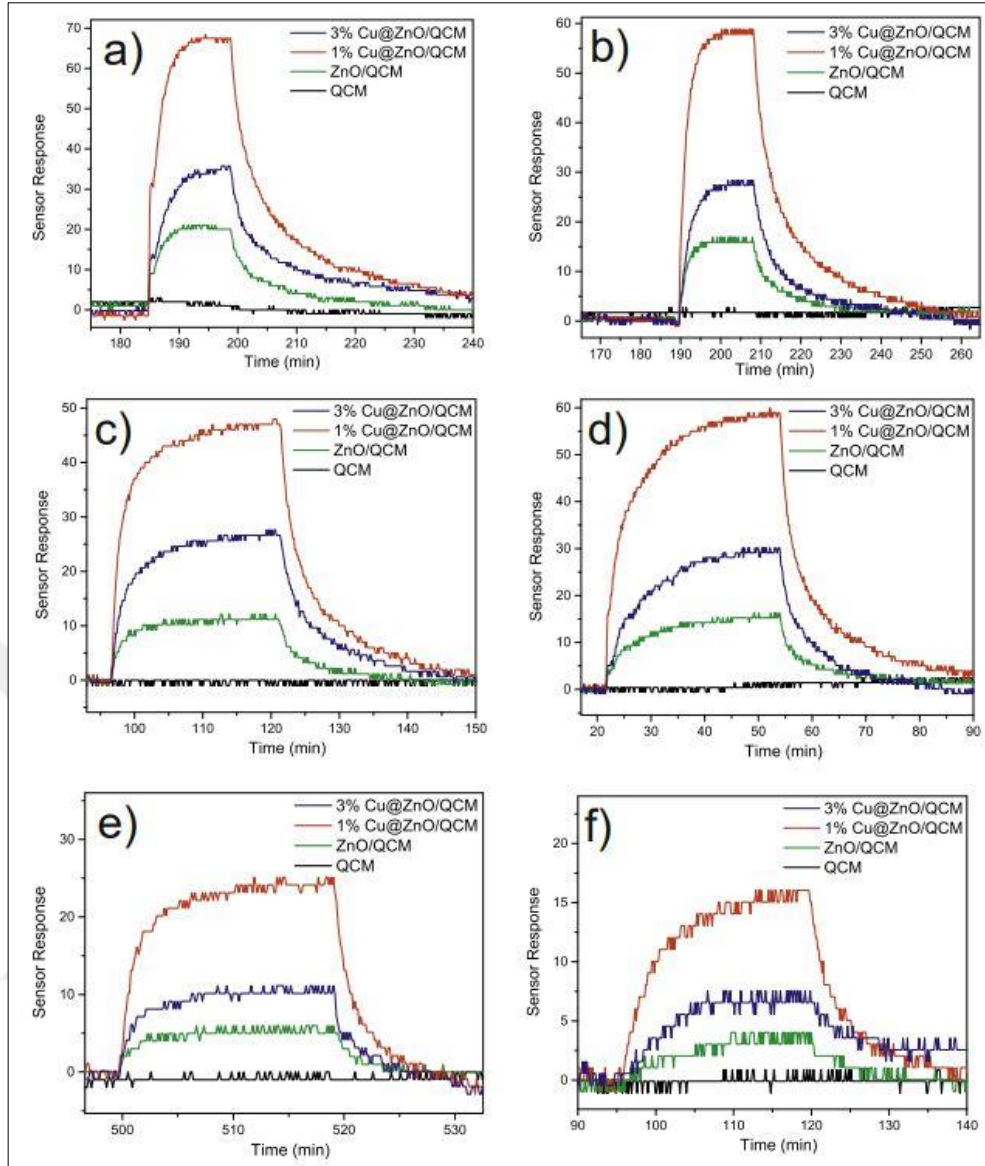


Figure 6.6: Frequency shifts of fabricated sensors against (a) 6.6 ppm H₂S, (b) 8.8 ppm HCN, (c) 240 ppm dichlorobenzene, (d) 850 ppm isopropyl alcohol, (e) 350 ppm toluene and (f) 6000 ppm ethyl acetate.

To understand the sensitivity of the QCM based sensors, the mean sensitivity values (S_m) were calculated by the following formula [236, 237]:

$$S_m = \frac{1}{n} \sum_{i=1}^n \frac{\Delta f_i}{c_i} (\text{Hz/ppm}) \quad (6.1)$$

where Δf is the frequency shift when the sensor is exposed to analyte concentration C_i , i is an index for desired gas concentration and n is the number of gas exposures for each analyte. The mean sensitivities of all sensors are given in Table 6.4. Generally,

1%Cu@ZnO sensor showed better sensitivity. Additionally, ZnO NRs based sensors have the highest sensitivity against HCN and H₂S gases. Comparison of the mean sensitivities is given in Figure 6.7(a). It is clearly understood that 1%Cu@ZnO sensor has the highest sensor response against H₂S and HCN.

Table 6.4: Mean sensitivity of the QCM based sensors for all test analytes.

Analyte	ZnO	1%Cu@Zn	3%Cu@Zn
Dichlorobenzene	0.041	0.24	0.135
Toluene	0.045	0.11	0.087
Xylene	0.07	0.34	0.16
Ethly acetate	-	0.5	0.1
NO ₂	0.01	0.1	0.07
H ₂ S	3.31	9.66	4.72
HCN	1.4	5.27	3.04
Isopropyl alc.	0.12	0.62	0.14

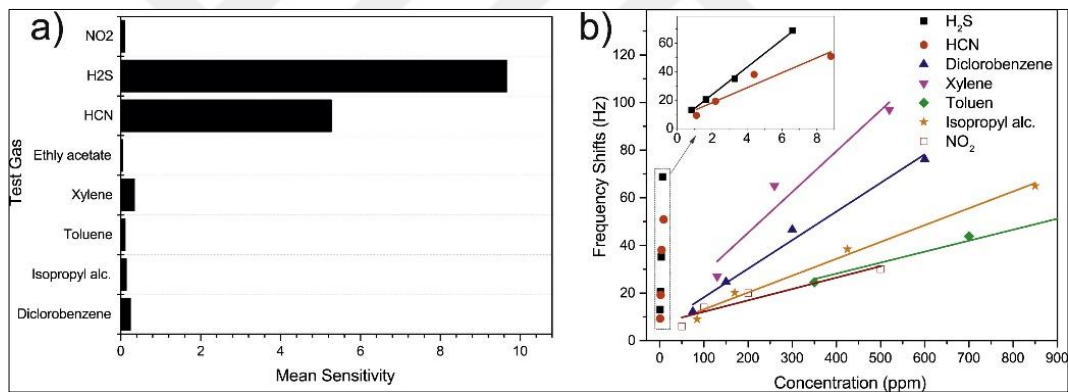


Figure 6.7: (a) Mean sensitivities and (b) calibration curves of 1%Cu@ZnO sensor.

The calibration curves fitted by the linear regression model of the 1%Cu@ZnO against all analyte gases were plotted in Figure 6.7(b). Direct ratio between gas concentration and frequency shift can be observed for all gases. It can be also understood that 1%Cu@ZnO sensor can detect lower concentrations than the measured range especially for H₂S and HCN gases.

Figure 6.8(a–b) illustrates the typical real-time response curves of 1%Cu@ZnO against HCN and H₂S gases with decreasing concentrations. The sensor showed rapid and reversible response indicating that no chemical bond formed during the adsorption process. It is observed that the sensor is able to detect HCN and H₂S gases at such low concentrations of 1.1 and 0.85 ppm, respectively. Additionally, frequency shifts

against HCN and H₂S under 40% relative humidity (R.H.) condition were given as inset in Figure 6.8 (a) and (b), respectively.

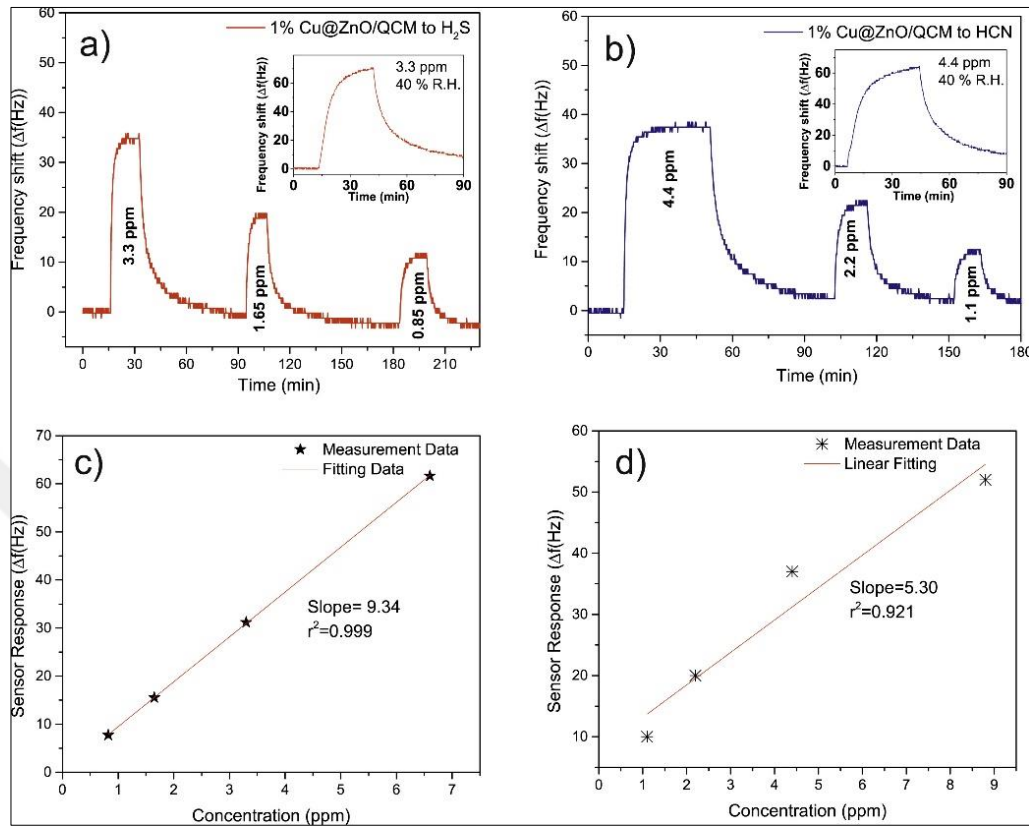


Figure 6.8: Sensor responses of 1%Cu@ZnO sensor against (a) H₂S and (b) HCN, and linear fitting of 1%Cu@ZnO sensor toward (c) H₂S and (d) HCN. Frequency shifts toward 3.3 ppm H₂S and 4.4 ppm HCN with 40% R.H. were given as inset in a and b, respectively.

To better understand of the sensor performance, the limit of detection values (LOD) were derived from the signal processing performance as the reports described [238]. The root-mean-square deviation (rmsd) was used to calculate the sensor noise. 10 data points were chosen at the baseline before analyte gas exposure. Then, rmsd value was calculated using the curve-fitting equation. Meanwhile, the sensitivities to H₂S and HCN gases were calculated via linearly fitting of sensor response (Δf) vs. concentration graphs as seen in Figure 6.8(c–d).

As a result, LOD values of 1%Cu@ZnO sensor were calculated as 79 and 169 ppb for H₂S and HCN, respectively using the following equation;

$$DL(ppm) = 3(rmsd/sensitivity) \quad (6.2)$$

6.3.3. Sensing Mechanism

It is important to understand the sensing mechanism of the ZnO functionalized QCM oscillator sensors. Gas molecules and atoms are absorbed by MOX surface in two ways: chemical and physical sorption. In chemical sorption, there is an electron transfer between the target gas and MOX surface. However, in physical sorption mechanism, the analyte molecules are adsorbed via weak physical bonding such as van-der Waal forces, dipole-dipole interactions, etc. [201]. At low temperatures (<100°C), physical sorption mechanism is more dominant than chemical sorption mechanism [187]. Because ZnO is an amphoteric molecule, its surface contains both Lewis acid and base sites which are responsible for adsorption of analyte molecules on the surface. Metiu et al. performed density functional theory (DFT) calculations to understand the chemistry of oxide surfaces [239]. They reported that a Lewis base formation on the oxide surface can be achieved by modification with low-valence dopants, which form oxygen vacancies [215, 239]. In the physical adsorption mechanism, analyte molecule can interact with cation centers (metal atoms; Zn^{2+} etc.) or anion centers called Lewis base on ZnO surface. As can be understood from the XPS results (see Table 6.3), doping ZnO with Cu atoms creates surface oxygen vacancies, which is equivalent to turning the surface of the oxide into Lewis base because the formation of an oxygen vacancy produces two unpaired electrons. Our sensor testing results showed that Cu doped ZnO NRs (both 1% and 3% doped) has better sensor response than un-doped ZnO NRs sensor (as seen in Figure 6.6). The doping process increased surface oxygen vacancies of ZnO NRs, thus increased the adsorption sites. Also, 1%Cu@ZnO has the highest percentage of oxygen vacancies which justifies the highest sensor performance obtained from 1%Cu@ZnO sensor (Figure 6.4 and Figure 6.6).

6.4. Conclusion

As a chemical sensor, ZnO NRs were successfully synthesized on the Au metal electrode of the QCM oscillators by using electrochemical deposition process. By electrodeposition route, Cu^{2+} was successfully doped in substitutional positions of Zn^{2+} in hexagonal wurtzite structure of ZnO NRs. It was observed that Cu doping advanced the sensor performance of ZnO NRs against all tested gases. 1%Cu@ZnO

sensor showed the highest sensor response compared to 3%Cu@ZnO and ZnO sensor. It can be explained with favorable surface properties that can be proven with XPS analysis. Among the tested gases, the highest responses were measured against H₂S and HCN at room temperature. Moreover, the limit of detection values of 1%Cu@ZnO NRs sensor were calculated as 79 and 169 ppb for H₂S and HCN, respectively.



7. ENHANCED ETHANOL SENSING PERFORMANCE OF Cu-DOPED ZnO NANORODS

Cu-doped ZnO ($\text{Zn}_{1-x}\text{Cu}_x\text{O}$, $x=0, 0.01, 0.02, 0.03$, and 0.04) nanorods (NRs) were grown on glass substrates by a seed-mediated hydrothermal method for gas sensing applications. The morphological and structural characterizations were performed by X-ray diffraction method (XRD) and scanning electron microscopy equipped with electron dispersive spectroscopy (EDS). Fabricated sensors were tested against H_2 , NO_2 , ethanol, acetone, xylene and toluene at different operation temperatures. It was found that Cu doping enhanced the sensor response of ZnO NRs especially towards ethanol. The highest sensor response against the ethanol were obtained with 2% and 3% Cu-doped ZnO NRs. Moreover, Cu-doping allowed us to operate ZnO NRs sensors at lower temperatures. Although pristine ZnO NRs did not show any sensor response at 100°C , 2% Cu-doped sensors exhibited selective sensor behavior towards ethanol among the other tested gases.

7.1. Introduction

Nowadays, there is a strong demand for gas sensors in many applications such as health-care industry, military applications, human daily life, etc [6, 240-243]. For the fulfillment of this demand, several kinds of sensor materials have been developed such as conductive polymers [244], graphene [245], metal-organic-frameworks (MOFs) [246], transition metal di-chalcogenides [247] and semi-conductor metal-oxides (MOXs) [5]. Among them, MOXs based gas sensors have attracted great interest due to their superior sensing abilities, low cost, and ease of use. The sensing mechanism of MOX based gas sensors can be explained by the reaction between gas molecules and the surface chemisorbed oxygen species, which causes a change in the surface conductivity [248]. The sensing performance is closely related with the morphology, surface properties and composition of the sensing materials [249].

*This chapter has been submitted as a O. Alev, I. Ergün, Özdemir, L. Ç. Arslan, S. Büyükköse, Z. Z. Öztürk “Enhanced ethanol sensing performance of Cu-doped ZnO nanorods”, Mater Sci Semicond Process, (2021).

Therefore, it is important to advance the functionality of the sensing material to obtain a high performance gas sensors.

Zinc oxide (ZnO) nanostructures have been intensively studied for gas sensing applications due to their high surface-to-volume ratio and extraordinary chemical or physical properties [250-252]. Another important advantage of ZnO is the existence of a variety of methods to obtain its nanostructures (nanorods, nanowires, nanofibers, etc.) such as hydrothermal [253], electrodeposition [5], chemical vapor deposition (CVD) [254] and physical vapor deposition (PVD) [255]. In addition, different effective approaches have been applied to ZnO nanostructures to improve their sensing abilities such as hybrid heterostructures [256], and functionalization with noble metals [222, 257].

Doping of different transition metals into the ZnO nanostructures is one of the most effective methods to alter the carrier concentration, the distribution of oxygen species, the grain size and the lattice structure [220, 258-261]. Various elements such as Al, Mg, Cu, Ni, In etc. were investigated as dopant into the ZnO nanostructures to improve gas sensing properties [218, 262, 263]. Among these dopants, Cu was found to be an attractive dopant element due to its similar ionic radius to that of Zn^{+2} ion (0.74 Å) and the created localized impurity levels for gas sensing applications [210]. In our previous work, Cu doped ZnO NRs were fabricated by electrochemical deposition technique for mass-sensitive based sensor applications. It was observed that Cu doping enhanced the sensing abilities of ZnO NRs [5]. Patil et al. reported that the low addition of Cu into ZnO lattice is beneficial for the enhancement of sensing properties [264]. Nimbalkar et al. observed that Cu-doped ZnO thin films (TF) grown by sol-gel coating showed better sensing properties in terms of sensitivity, response and recovery times and selectivity than those of pristine ZnO TF [265]. Ganesh et al. observed that Cu doping enhanced the sensing properties of ZnO nanostructures towards ammonia gas [266]. Corlu et al. reported that the selectivity and response of the sensor were significantly improved with the Cu doping [267].

Although there is a broad range of literature reports on doped ZnO materials for gas sensing applications, there is a limited number of systematic studies on the gas sensing properties of Cu doped ZnO nanostructures. According to the literature, substitution limit of Cu into ZnO is below 5 at.% [225, 268]. Thus, Cu-doped ZnO ($\text{Zn}_{1-x}\text{Cu}_x\text{O}$) NRs were synthesized by a seed mediated hydrothermal route with $x = 0.00, 0.01, 0.02, 0.03$ and 0.04 . Then, the effect of doping content on the gas

sensing performance were systematically studied. Pristine and Cu-doped ZnO NRs were tested towards NO₂, H₂, acetone, ethanol, xylene and toluene at different operation temperatures.

7.2. Experimental Details

Pristine and Cu-doped ZnO NRs were synthesized by a seed-mediated hydrothermal route on glass substrates. All chemicals used in this study including zinc acetate (CH₃CO₂)₂Zn (Merck, purity of 99.99%), zinc nitrate hexahydrate Zn(NO₃)₂•6H₂O (Merck, purity of 98%), copper nitrate trihydrate Cu(NO₃)₂•3H₂O (Merck, purity of 99%), ethanol (C₆H₁₂O, Merck-purity of 99.99%) and hexamethylenetetramine (HMTA; C₆H₁₂N₄, Sigma Aldrich, purity of 99.0%) are commercially available. Glass substrates were cleaned with acetone, isopropyl alcohol and deionized (DI) water for 10 min in ultrasonic bath, respectively. For the seed layer solution, 0.01 gr zinc acetate was dissolved in 50 ml ethanol under magnetic stirring for 1 h (pH 7–7.5). The prepared solution was coated on glass substrates by spin coater at 1000 rpm. Then, ZnO film coated glass substrates were annealed at 130°C for 5 min. This step was repeated 5 times and final ZnO seed layer films were annealed at 300°C for 1 h [269]. Hydrothermal solution was prepared by dissolving zinc nitrate hexahydrate and copper nitrate trihydrate in DI water [269]. Copper nitrate trihydrate was used as Cu source and the molar concentration ratio of Cu to Zn was changed between 0%–4% in steps of 1% (pH values were 6.5–7 for the undoped solution and 7–7.5 for doped solutions). The seed layer coated glass substrates were immersed in a sealed glass container contains the prepared solution and kept for 3 h at 90°C in a temperature controlled furnace. Then, the samples were rinsed with DI water. Sample codes and the molar ratio of the samples were given in Table 7.1. Schematic illustration of the fabrication steps is given in Figure 7.1.

Table 7.1: Sample codes and the corresponding molar ratios.

Sample Code	Zn _{1-x}	Cu _x
ZnO	1.00	–
1CZnO	0.99	0.01
2CZnO	0.98	0.02
3CZnO	0.97	0.03
4CZnO	0.96	0.04

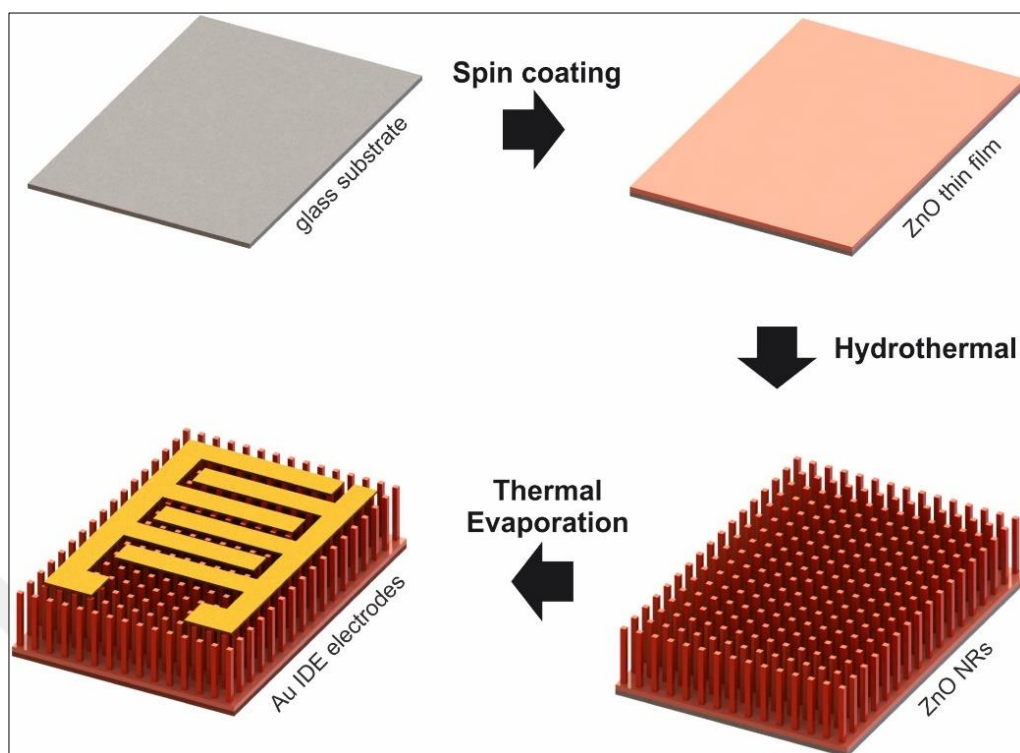


Figure 7.1: Schematic view of the sensor with interdigitated Au electrodes deposited on ZnO NRs grown on a glass substrate.

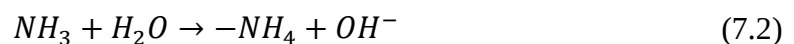
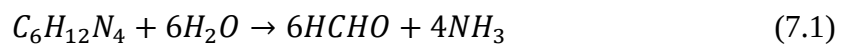
To investigate the crystal structure of the synthesized samples, X-ray diffraction (Rigaku Smartlab) with Cu K radiation ($\lambda = 1.15406 \text{ \AA}$) was used. Morphological study of the samples was carried out using SEM equipped with EDS (Philips XL 30S). The average mean diameters of NRs were measured from several images by counting 20 nanorods using ImageJ software (National Institutes of Health, USA). The samples were analyzed with XPS using an Al $K\alpha$ X-ray ($h\nu = 1486.6 \text{ eV}$) source and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The base pressure of the analysis chamber was $1.33 \times 10^{-8} \text{ Pa}$ during the measurements. The spectra were fitted using the CasaXPS using mixed Gaussian–Lorentzian peaks after subtracting Shirley-type background in order to extract the chemical bonding energies. The binding energies of the spectra were calibrated by the carbon C 1s peak (284.8 eV) reference. To perform sensor measurements, Au interdigital electrodes (IDEs) with a thickness of 200 nm were grown on the NRs via thermal evaporation method. Samples were mounted on a 1 L home-made stainless-steel chamber, which is connected to the gas lines. Temperature controller (Lakeshore 34) and electrometer (Keithley 6517 A) were used to control the operation temperature

and to measure the direct current of the sensors, respectively. During the measurements, 1 V constant bias voltage was applied to the samples. High purity dry air flowed (200 sccm) through the sensors until the current reached a steady value (baseline), and then the sensors were exposed to the target gases. NO₂ and H₂ were obtained from gas cylinders. For volatile organic compound (VOC) generation, dry air (200 sccm) was purged through gas washing bottles filled with the VOCs and the bottles were immersed in a thermostated bath to maintain a constant temperature (−10°C). Thus, the gas stream was saturated with VOCs [270]. The actual gas concentrations were calculated by using the saturated vapor pressure values in Antoine's equation [162].

7.3. Results and Discussion

7.3.1. Structural Characterizations

The SEM images of the fabricated samples with two different magnifications are given in Figure 7.2(a-j). The SEM images showed that the undoped NRs are vertically aligned and have a hexagonal shape. It can be seen that Cu doping did not affect the shapes of the NRs; however, the diameter and the density of the NRs were changed with the doping level. ImageJ software was used for size calculation of the NRs. The calculated mean diameters were 46, 83, 59, 55 and 66 nm for ZnO, 1CZnO, 2CZnO, 3CZnO and 4CZnO, respectively. The average NR length was 500 nm as seen in Figure 7.2(a) inset. The change in size might be explained with the change of nucleation sites and pH values with Cu doping into ZnO structures [271]. The chemical reactions taking place during hydrothermal process can be described as follow [272, 273]:



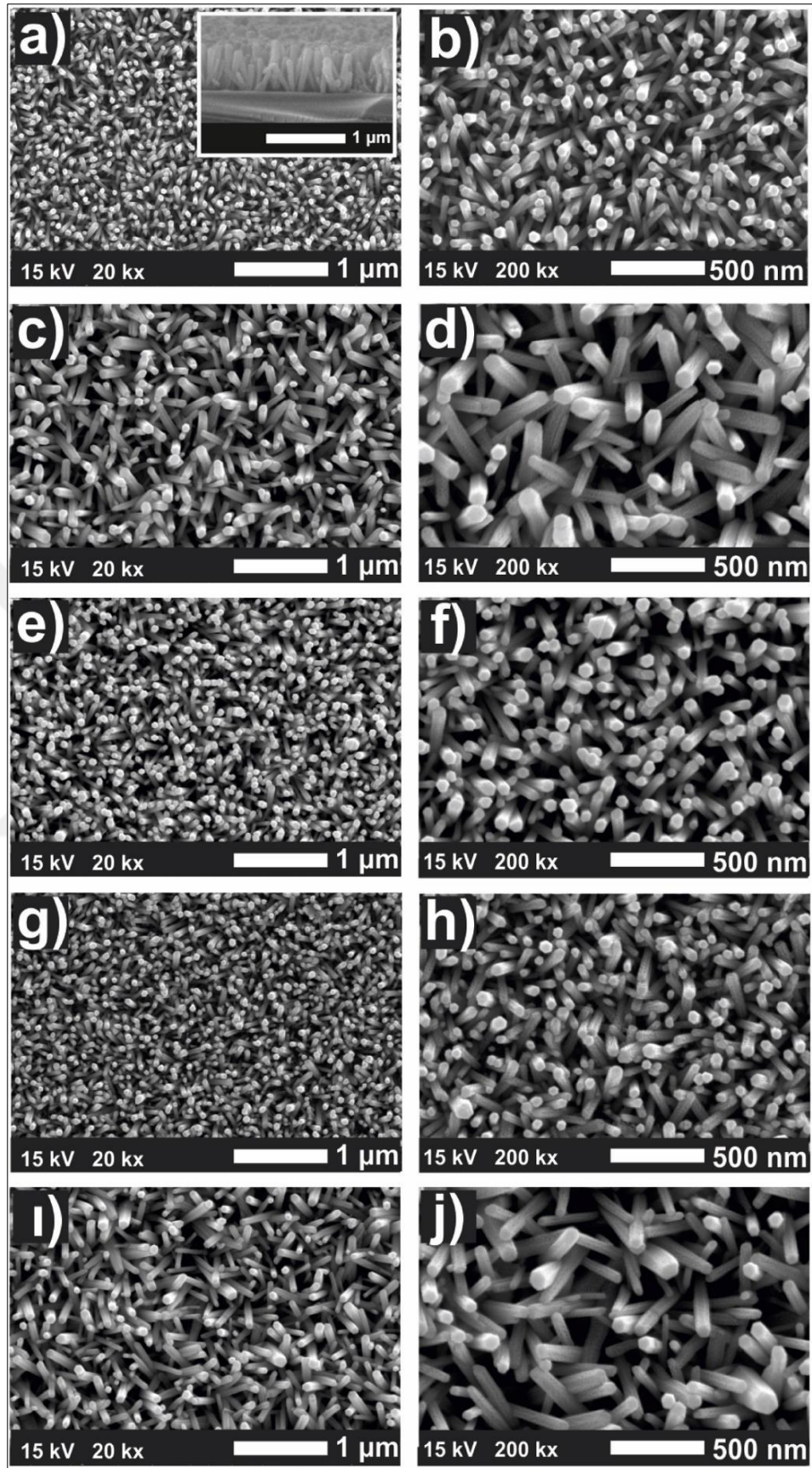
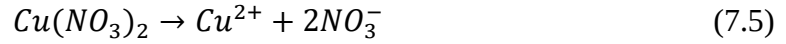


Figure 7.2: Sem images of (a–b) ZnO, (c–d) 1CZnO, (e–f) 2CZnO, (g–h) 3CZnO and (i–j) 4CZnO.

The equilibrium in these reactions can be shifted by changing the physical parameters, temperature, precursor concentration and pH [272]. Moreover, while precursor concentration affects the density of the NRs, pH value affects the aspect ratio. Therefore, the presence of Cu during the NRs growth can increase the nucleation density and increase the growth rate with the following reaction [271]:



The anions (NO_3^-) resulting from this reaction decrease the concentration of OH and the growth rate [271]. Thus, an enlarging and aggregation of the NRs were observed.

EDS was performed to identify the elemental distribution on the surface of samples. Atomic ratios of Cu were measured to be 0.28, 0.36, 0.58 and 0.83 for Cu doping concentrations of 1%, 2%, 3% and 4%, respectively. Also, detailed atomic concentrations obtained from EDS analysis were given in Table 7.2. EDS mapping images and spectrums of 1% and 4% Cu doped ZnO NRs are given in Figure 7.3. In the mapping images, blue points represent O, pink represents Zn and green represents Cu. It is clearly observed that Cu is homogenously distributed on the surface.

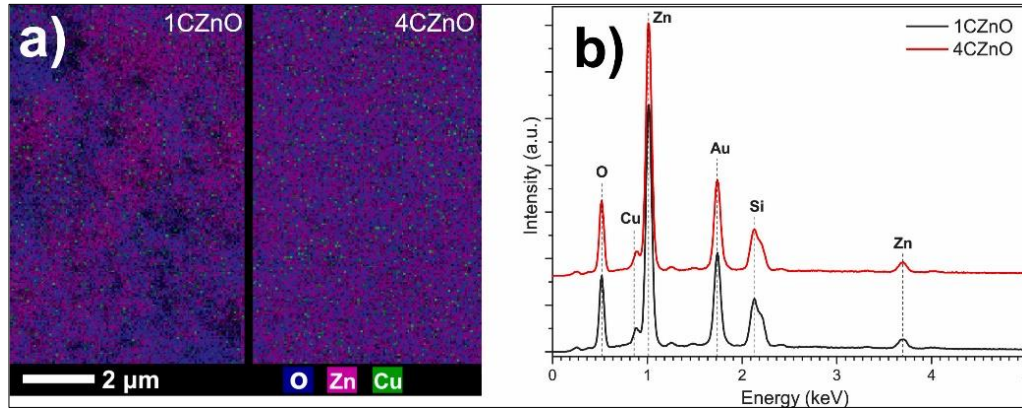


Figure 7.3: (a) Elemental mapping images 1CZnO and 4CZnO, and (b) EDS spectra of 1CZnO and 4CZnO.

The XRD patterns of the pure and Cu-doped ZnO NRs are shown in Figure 7.4(a). Diffraction peaks at 31.1° , 34.4° , 36.3° , 47.6° , 62.8° and 72.6° correspond to the direction of (100), (002), (101), (102), (103) and (004), respectively [274, 275]. All the diffraction peaks can be indexed to wurtzite crystal structure of ZnO [276]. No

other peaks corresponding to copper were observed at such low doping concentrations. In addition, a small shift of (002) peak towards lower angle was detected with the insertion of Cu into ZnO NRs, as shown in Figure 7.4. This shift can be attributed to the difference between Zn^{+2} and Cu^{+2} ionic radius [271, 277]. The shifting in diffraction peaks can be associated with the incorporation of Cu ions into the interstitial and substitutional sites of ZnO matrix [220, 278]. Additionally, the lattice strains (ϵ_s) were calculated by Williamson–Hall estimation [279, 280].

$$\beta_{hkl} = \frac{k\lambda}{D\cos\theta} + 4\epsilon\sin\theta \quad (7.6)$$

where D is the crystallite size (nm), k is the shape factor ($k = 0.9$), λ is the wavelength of the X-rays ($\lambda = 1.54056 \text{ \AA}$ for Cu $K\alpha$), θ is Bragg diffraction angle and β is the broadening of the diffraction peak measured at the full-width half-maximum (FWHM, in radians). $\beta\cos\theta$ was plotted with respect to $4\sin\theta$ for the preferred orientation peaks of doped and undoped ZnO NRs with the wurtzite hexagonal phase. Accordingly, the slope of the fitted line represents strain [279]. As seen in Table 7.2, no change in strain was observed depending on the doping concentration. More detailed information about the chemical environment of atoms is given XPS analysis.

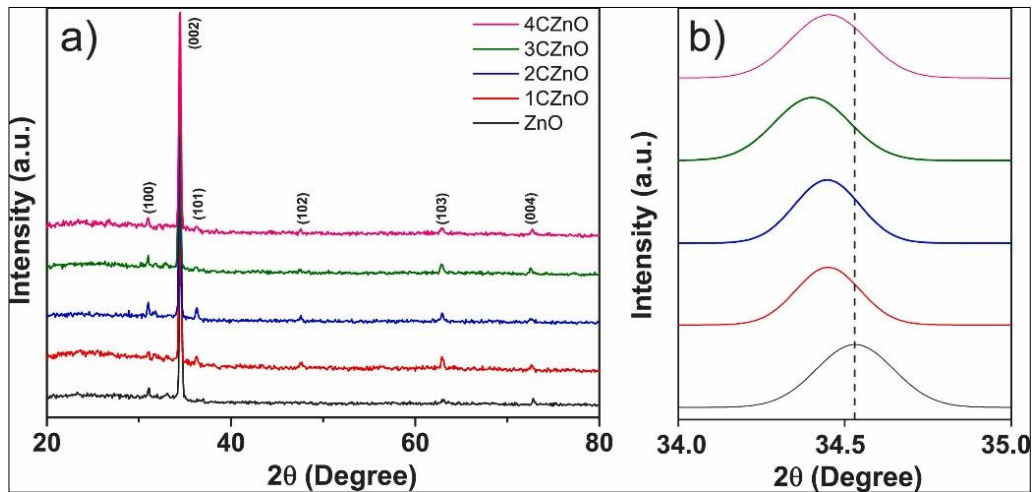


Figure 7.4: (a) Full range of XRD patterns and (b) high-resolution of (002) peak of pristine and Cu-doped ZnO NRs.

We explored the gas sensing properties of Cu doped ZnO NRs by core level XPS to monitor the surface chemical composition alongside the valence states of the elements, which highly affect the electrical resistance. The XPS survey spectra confirmed the existence of Zn, Cu, and O in the samples, as well as the presence of carbon contaminants. The carbon peaks appear due to exposure of the samples to the ambient atmosphere. After Ar sputtering for 20 min at 3 keV, no adventitious carbon element (C1s) was detected. All the data was collected from the samples which were either (i) pre-exposed to ambient air prior to loading into the XPS instrument to mimic realistic device conditions, or (ii) Ar⁺ ion-etched to remove surface oxides resulting from the air exposure during sample transfer to determine the elemental composition in the near-surface region. Since the native oxides and carbon contaminants could have a considerable impact on the relative atomic percentage, the atomic concentrations of each element were obtained by fitting all the spectra obtained after surface etching and using the appropriate relative sensitivity factors (RSFs) for scaling. The surface Cu doping concentrations derived by XPS are substantially lower compared to nominal values of Cu in ZnO similar to EDX results (see Table 7.2).

Table 7.2: Atomic concentrations obtained in EDS and XPS, and the lattice strain of Cu doped ZnO NRs.

Sample	XPS			EDS			Lattice strain ϵ_s (%)
	Zn (%)	O (%)	Cu (%)	Zn (%)	O (%)	Cu (%)	
ZnO	46.34	53.66	–	35.41	64.59	–	0.344
1CZnO	47.02	52.61	0.19	46.13	53.6	0.28	0.337
2CZnO	46.32	53.43	0.25	48.92	50.71	0.36	0.355
3CZnO	42.84	56.75	0.41	26.01	73.41	0.58	0.339
4CZnO	47.03	52.47	0.50	59.48	39.7	0.83	0.349

Figure 7.5 shows Zn 2p and Cu 2p core level spectra of Cu doped ZnO NRs before surface etching. In Figure 7.5(a), the binding energy of the symmetric Zn 2p peak for pure ZnO NRs appears at 1021.6 eV with the spin–orbit splitting value of 21.07 eV, which indicates that Zn at ZnO surface mainly exists in the divalent state [281]. It is clear that the Zn peak of samples shows a slight shift to high binding energy up to doping concentrations of 3% copper, and then moves towards lower binding energy with further Cu incorporation. The gradual blue shift of the binding energies is

due to the electron transfer from Cu dopants occupy the interstitial sites to ZnO. However, the red shift with the further increase of Cu doping concentration can be associated with Cu atoms residing at mostly substitutional lattice sites. Since the electronegativity of Cu is higher than Zn, the weaker Cu–O bonds increase the electron density around Cu atoms, and the binding energy decreases, leading to a red shift in the peak position. Figure 7.5(b) displays the Cu 2p_{3/2} region of Cu doped ZnO NRs. The Cu shake-up satellite lines which are attributed to Cu²⁺ are not present until reaching 4% doping concentration. The weak appearance of the satellite line for only 4% Cu doped NRs indicates the fact that some fraction of the surface copper is oxidized in a divalent state.

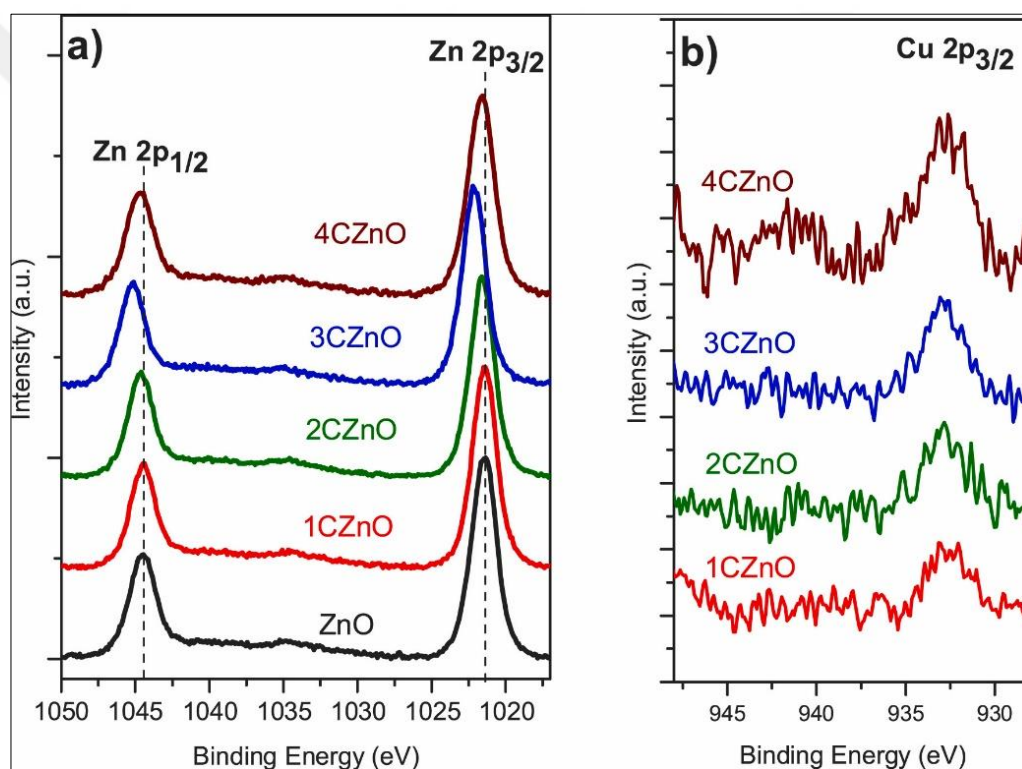


Figure 7.5: (a) Zn 2p_{1/2} and Zn 2p_{3/2}, and (b) Cu 2p_{3/2} XPS spectra for Cu doped ZnO NRs at different concentrations.

The O 1s XPS spectra in Figure 7.6 demonstrates similar line shapes for unspattered ZnO NRs with different Cu content, and the O 1s peak in each spectrum can be deconvoluted into three symmetric (Gaussian–Lorentzian) components. The lower binding energy peak is assigned to lattice oxygen, the wider peak centered around 531.5 ± 0.2 eV is attributed to non-lattice oxygen indicating vacancy or metal deficiency in the films and the highest binding energy peak located at 532.3 ± 0.3 eV

can be attributed to the oxygen absorbers such as hydroxides. FWHM of lattice oxide peak is set to 1.5 ± 0.1 eV while the non-lattice oxygen peak is set to 2.3 ± 0.2 eV, this variance is allowed due to the narrower expected chemical state distribution for lattice oxide bonding compared to the oxygen defects. Similar to the shifting trend of Zn 2p_{3/2}, the crystal lattice oxygen peak also gradually shifts from 530 eV to 530.5 eV as the amount of Cu in NRs increases up to 3%. It is known that the oxygen vacancies can lead to band bending, which will also affect the optoelectronic properties of the NRs [282]. As can be seen Fig. 6f, the atomic ratio of lattice oxygen and oxygen defects of all the NRs were calculated to be 0.92, 0.98, 0.57, 0.58 and 1.33 for samples ZnO, 1CZnO, 2CZnO and 4CZnO before surface etching, respectively. Although it follows the same trend, the increase in the ratio of O_{lat}/O_{def} before and after Ar⁺ etching is due to a decrease of absorbed native oxide overlayer in the NRs surfaces. The amount of deficient oxygen decreases slightly after introducing very low Cu. The ratio of O_{lat}/O_{def} decreases with doping concentrations up to 3%, whereas it increases with further Cu doping. Therefore, the number of oxygen defects at Cu doping concentrations of 2% and 3% has been increased due to the incorporation of Cu atoms at the interstitial sites of ZnO lattice, whereas, due to increasing doping concentration, Cu ions favorably substitute Zn ions rather than taking the interstitial sites of the ZnO lattice. The formation of stable Cu–O bonds reduces oxygen defects. Moreover, higher oxygen deficiency leads to the enhancement of the active sites to adsorb oxygen atoms on the surface. Consequently, concentrations of such adsorbed oxygen ions improve the effective sensing performance of the developed sensor, which is further confirmed by the sensor characterizations.

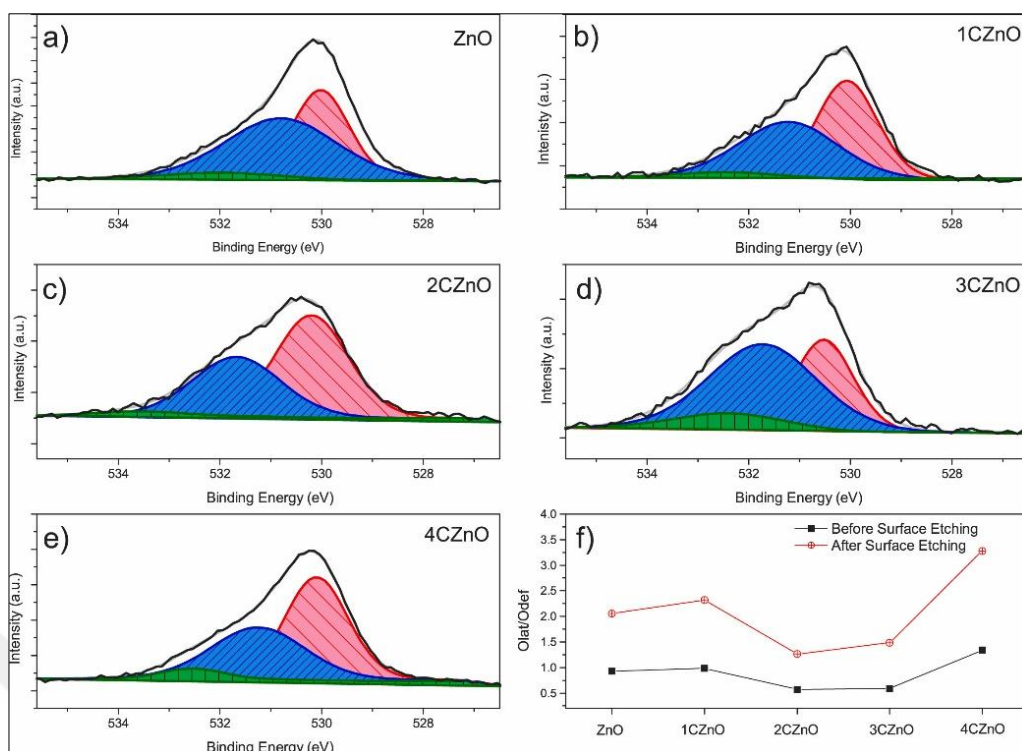


Figure 7.6: Core level XPS spectra and deconvoluted peaks of O 1s state in (a) undoped and (b–e) nominally 1%–4% Cu doped ZnO NRs, and (f) Relative weight percentage of lattice oxygen and oxygen defects as a function of copper concentration.

7.3.2. Gas Sensor Measurements

The gas responses of undoped and doped ZnO NRs based sensors to various gases including acetone, ethanol, toluene, xylene, H_2 , and NO_2 at $50^\circ C$, $100^\circ C$ and $200^\circ C$ were investigated. It was observed that optimum operation temperature is $200^\circ C$ for all sensors. A significant increase in sensor response to ethanol was observed with Cu doping into ZnO NRs (especially for 2% and 3%), as seen in Figure 7.7. 3CZnO sensor showed the highest sensor response, which is 5.5 times higher than that of undoped ZnO. Although ZnO NRs with 4% Cu doping showed lower sensor response than that of 2% and 3% Cu doped ZnO NRs, all the Cu doped ZnO sensors presented better sensor response compared to pristine ones. The results show that 3% Cu doping was the optimum concentration for ethanol detection. Moreover, while undoped sensor did not show sensor response towards H_2 , Cu doped sensors were able to detect H_2 especially at doping concentrations higher than 2%. On the other hand, Cu doping did not make a significant difference in response to NO_2 . While undoped ZnO sensor did not show any response to ethanol, 3CZnO sensor were able to sense

ethanol with a sensor response of 0.1 at 100°C. However, the sensor signal obtained at 100°C was too noisy. Moreover, none of the sensors showed a response at 50°C.

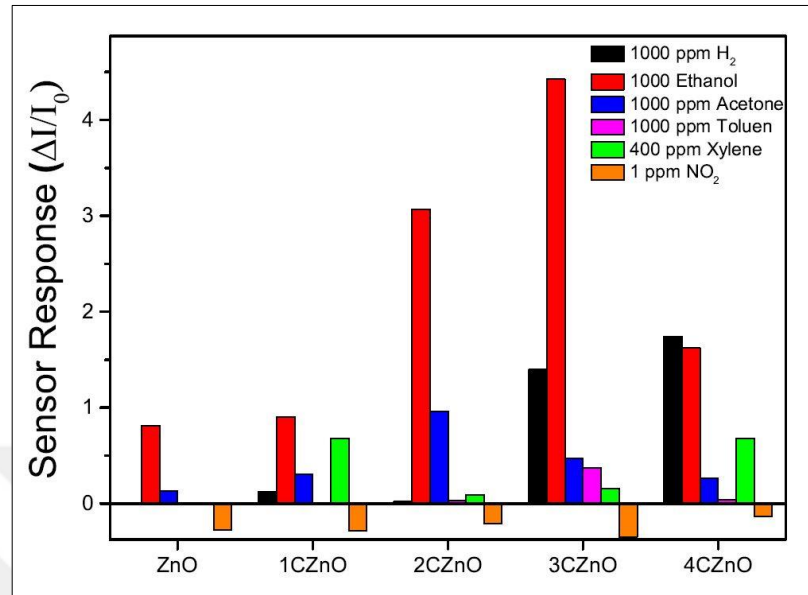


Figure 7.7: Sensor responses of fabricated samples at operation temperature of 200°C.

The sensor response curves of five sensors to 1000 ppm ethanol at 200°C are shown in Figure 7.8(a). The results showed that all the sensors exhibited clear sensor responses. Moreover, sensor signals recovered to their initial baseline values after the removal of ethanol gas. The sensor response values to 1000 ppm ethanol were 0.7, 0.9, 3.0, 4.3 and 1.6 towards 1000 ppm ethanol for ZnO, 1CZnO, 2CZnO, 3CZnO and 4CZnO, respectively. It is clearly seen that 3% Cu doped sensor showed the highest sensor response to ethanol. Figure 7.8(b) shows the dynamic sensor response of 3CZnO sensor against different concentrations of H₂ and ethanol. It is clearly seen that even when the sensor was exposed to hydrogen and ethanol gases in succession, the sensor exhibited repeatable and stable sensor responses. The sensor had sensor responses of 4.3, 3.0 and 1.5 against 1000, 500 and 250 ppm ethanol, respectively. Also, limit of detection (LOD) values of 3CZnO sample were calculated as 107 ppm and 40 ppm for hydrogen and ethanol, respectively based on previous works [5, 238, 283]. Additionally, it is observed that operation temperature of ZnO sensor decreased with Cu doping. Sensor characteristics of ZnO based gas sensors against ethanol are in line with literature and show promising results as given in Table 7.3.

Table 7.3: Comparison of Cu doped ZnO NRs sensor with the reported ZnO based ethanol gas sensors.

Sensing material	Operation Temp. (°C)	Sensor response	Concentration (ppm)	Ref.
Mn doped ZnO	300	0.01	300	[284]
Co doped ZnO	300	0.57	300	[284]
Ni doped ZnO NRs	370	0.313	500	[285]
Bi doped ZnO thin-film	400	0.05	1000	[286]
Cr doped ZnO	300	18	400	[287]
Pd decorated ZnO NRs	260	0.81	500	[288]
Cu doped ZnO NRs	200	4.3	1000	This study

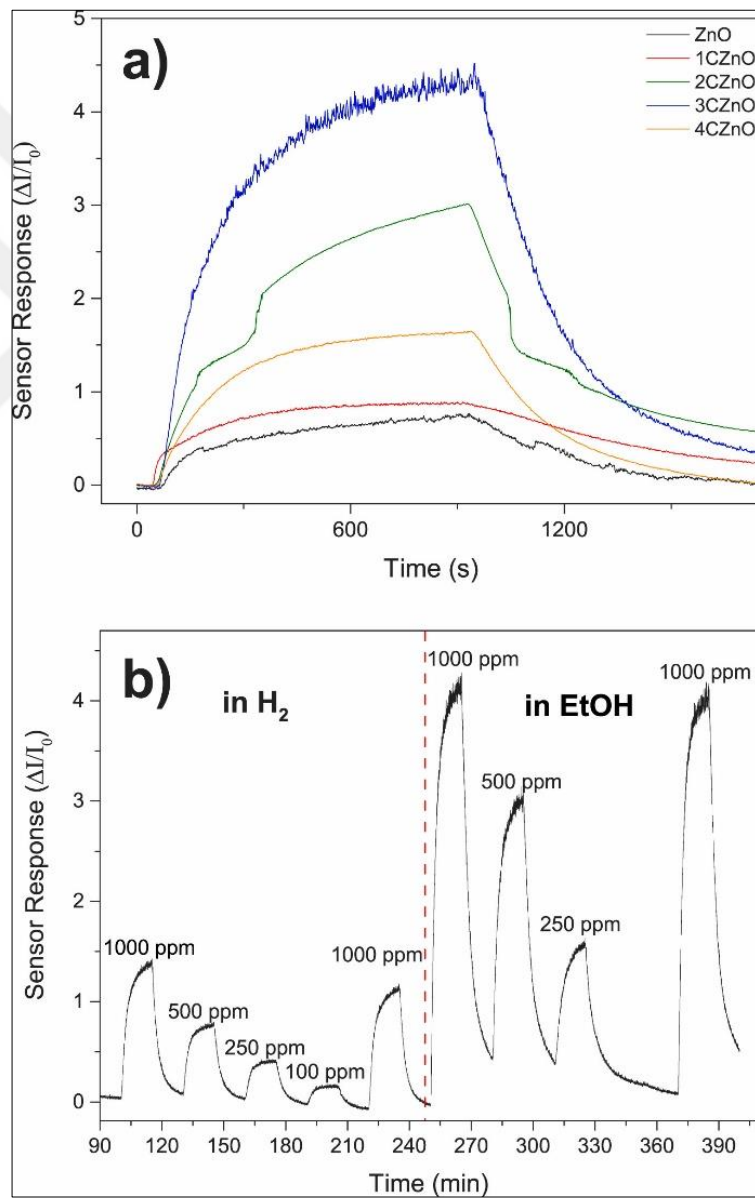


Figure 7.8: Dynamic sensor responses of (a) all sensors against 1000 ppm ethanol and (b) 3CZnO sensor against different concentrations of hydrogen and ethanol at operation temperature of 200°C.

The activation energy is an important factor to determine the reactions between target gas molecules and the surface of MOXs [289, 290]. The activation energy is the thermal energy to carry the electrons to the conduction band from valance band [264]. The electrical conductivity (σ) versus inverse temperature in the range of 423–473 K were given in Figure 7.9. The activation energies were calculated using the following equation:

$$\sigma = \sigma_0 e^{\frac{-E_A}{kT}} \quad (7.7)$$

where σ is the pre-exponential factor, k is the Boltzmann constant, and T is the absolute temperature. Activation energy of 3% Cu doped ZnO was calculated as 0.417 eV which is lower than that of undoped ZnO (1.021 eV).

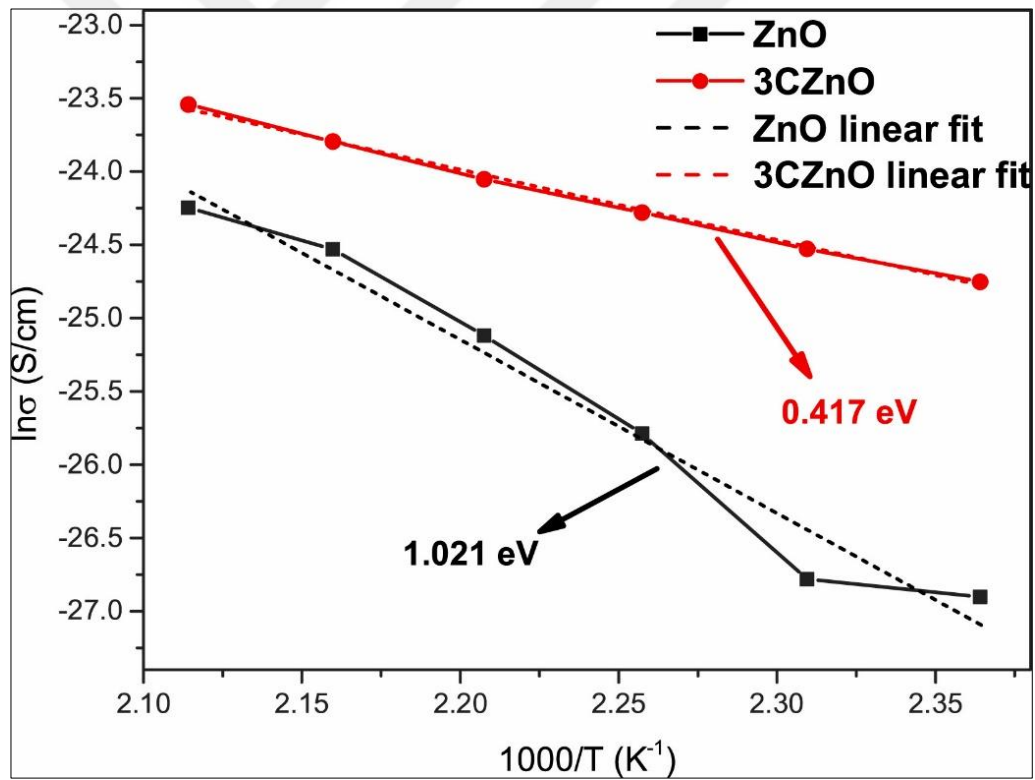
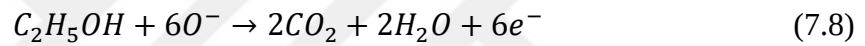


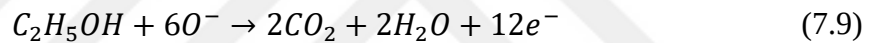
Figure 7.9: The electrical conductivity (σ) as a function of inverse temperature.

7.3.3. Sensing Mechanism

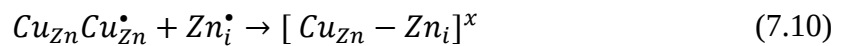
It is well known that the sensing mechanism of semi-conductor MOXs is explained with the reaction between target gas molecules and adsorbed oxygen species [248]. Figure 7.10 illustrates the sensing mechanism of undoped and Cu doped ZnO towards ethanol gas. In air atmosphere, oxygen species (O^- , O^{2-} and O_2^-) are absorbed onto the surface of ZnO. Thus, a depletion region forms and conductivity decreases due to the trapped electrons by surface adsorbed oxygen species [291]. In this study, O^- and O^{2-} are expected to be dominant oxygen species due to relatively low operation temperatures ($<300^\circ\text{C}$) [264]. When the sensor is exposed to ethanol, ethanol molecules react with the surface adsorbed oxygen on the surface and trapped electrons released back to the conduction band, which results in an increase in surface conductivity, as described in Equations [292, 293]:



or



In the case of Cu doping into ZnO structure, Cu^{+2} ions substitutes with the Zn partially in the ZnO structure. This substitution provides more electrons to the conduction band due to the formation of Cu–Zn complex defects [294].



Consequently, the Cu dopants cause the formation of more surface absorbed oxygen because of increasing charged oxygen vacancies. In our study, this fact is observed as the highest sensor response from 3CZnO sensor due to the highest O defect concentration as compared to the other sensors (see Figure 7.6). Then, the number of active adsorption sites increases, therefore more gas molecules can be detected and the activation energy decreases [264]. A thick depletion region is formed due to increasing barrier height and resistance (see Figure 7.10). In ethanol atmosphere, the barrier height and the depletion region are decreased, depending on the doping material and adsorbed oxygen as shown in Figure 7.10. As a result, the incorporation of Cu into ZnO exhibited a positive effect on gas sensing performance.

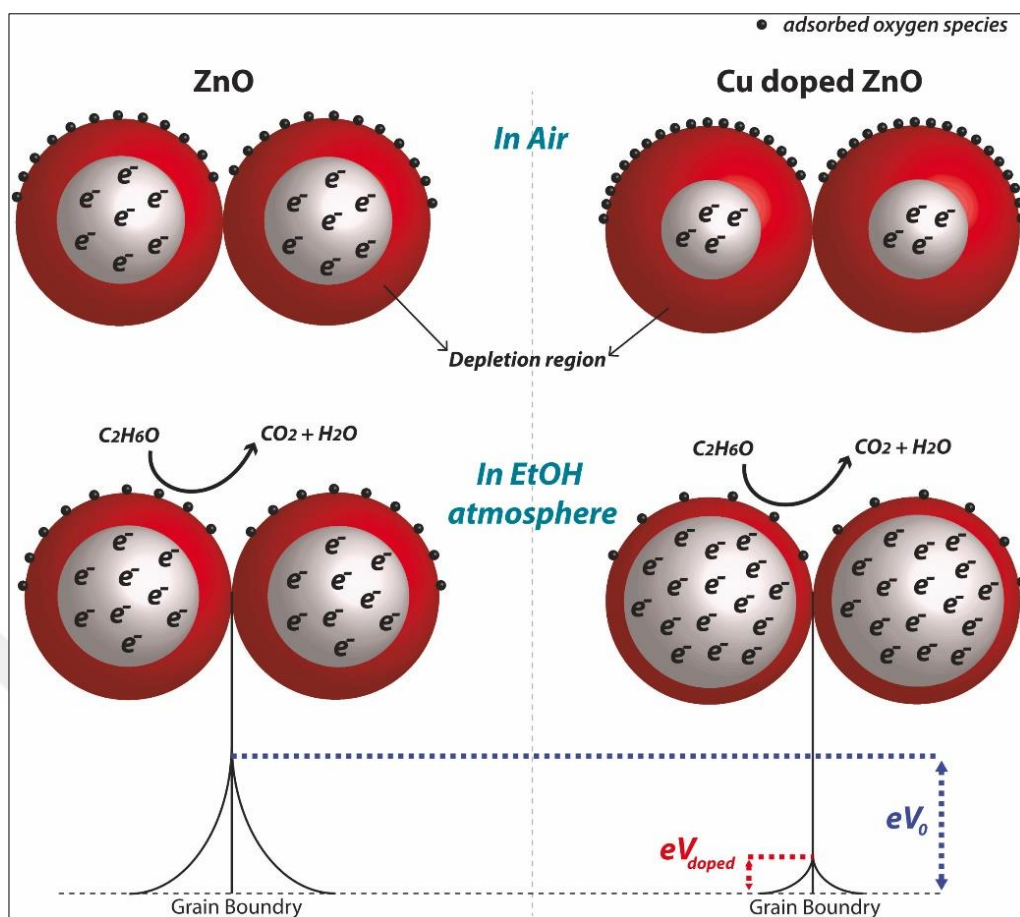


Figure 7.10: The schematic illustration of gas sensing mechanism of undoped and Cu doped ZnO NRs.

7.4. Conclusion

In conclusion, undoped and Cu doped ZnO NRs have been successfully synthesized by a seed-mediated hydrothermal method. Fabricated sensors were tested against ethanol, acetone, toluene, xylene, hydrogen, and NO_2 . It was observed that the sensitivity of ZnO NRs to ethanol is significantly changed with Cu doping. The 3% Cu doped ZnO NRs exhibited the highest sensor response to ethanol, which is 5.5 times higher than undoped ZnO. Moreover, 3CZnO sensor was able to detect ethanol gas even at $100^\circ C$ while the undoped sensor was not. Improved sensor performance of the NRs can be attributed to the increased number of surface oxygen species and lower activation energy due to doping of Cu.

8. CONCLUSION

In this thesis, nanostructured materials were fabricated by different techniques such as electrochemical deposition, RF magnetron sputter, hydrothermal, and ALD. Structural and morphological characterizations were performed in different spectroscopic techniques. These nanostructures were grown on QCM and chemi-resistive transducers for sensor measurements.

In the fourth chapter, ZnO thin films were fabricated by the ALD method. The thin films were characterized by AFM, XPS, SEM, EDS, and Uv-Vis. Then, the thin films were grown on QCM oscillators to perform biosensor measurements. In this respect, the sensor surface was modified with the antibodies (specific MAM TRC2) of the transferrin to show selectivity against the target analyte. The fabricated sensors were tested against different concentrations of human transferrin (hTF). ZnO thin films homogeneously covered the entire substrate surface. While the number of cycles and pulse times do not affect the morphology, the increasing temperature of the reaction chamber increases the size of granular structures. There is a direct ratio between the number of cycles and the surface porosity. However, no relation was observed between precursor pulse time and the film porosity. According to the XPS results, it was observed that the surface defects increase significantly with the decrease of the film thickness. The antibody (TRC2) immobilizations on the ZnO surfaces were successfully performed. In static biosensor measurements, TRC2 immobilized ZnO/QCM platform exhibited sensor response to hTF in the range of 100-1000 ng. TRC2 immobilized ZnO/QCM sensor showed lower sensor response to hTF in the dynamic measurements than that of static measurements. Also, since QCM frequency is highly affected by environmental factors, it has been observed that there are differences between measurements performed at different times.

In the fifth chapter, WS₂ thin films were grown on QCM oscillators via the RF magnetron sputtering technique. Structural and morphological properties of the fabricated thin films were investigated by SEM and XPS. WS₂ coated QCM sensors were tested toward nine different hazardous gases including DMMP, which is known as a simulant of sarin nerve agent, in a dry and humid atmosphere at RT. The sensors showed the highest sensitivity to DMMP gas. Moreover, WS₂ based sensor was able to detect DMMP gas at a concentration as low as 175 ppb. The detection limit of the

sensor for DMMP gas was calculated as 5 ppb which is quite below the threshold limit value. WS₂/QCM sensor exhibited superior sensor performance in terms of sensitivity, selectivity among measured gases, repeatability, and durability at RT. The sensing mechanism of WS₂ thin films is associated with the physical adsorption of DMMP through the oxygen defects located on the surface. In a conclusion, our results indicate that WS₂-based QCM sensor has the potential for the detection of nerve agents in real-time applications.

In the sixth chapter, Cu-doped ZnO NRs were fabricated by the electrochemical deposition method. The effect of Cu doping in ZnO NRs was systematically studied, and the mechanism behind the improvement in sensor properties was explained. By electrodeposition route, Cu²⁺ was successfully doped in substitutional positions of Zn²⁺ in hexagonal wurtzite structure of ZnO NRs. It was observed that Cu doping advanced the sensor performance of ZnO NRs against all tested gases. 1% Cu doped ZnO NRs sensor showed the highest sensor response compared to 3% Cu-doped ZnO and ZnO sensor. It can be explained by favorable surface properties that can be proven with XPS analysis. Among the tested gases, the highest responses were measured against H₂S and HCN at room temperature. Moreover, the limit of detection values of 1% Cu doped ZnO NRs sensor were calculated as 79 and 169 ppb for H₂S and HCN, respectively.

In the seventh chapter, undoped and Cu doped ZnO NRs have been successfully synthesized by a seed-mediated hydrothermal method for chemi-resistive gas sensor applications. The nanorods were investigated by XRD, XPS, SEM, and EDS. The sensors were exposed to various gases and the Cu doping effect on gas sensing properties was investigated. Fabricated sensors were tested against ethanol, acetone, toluene, xylene, hydrogen, and NO₂. It was observed that the sensitivity of ZnO NRs to ethanol is significantly changed with Cu doping. The 3% Cu doped ZnO NRs exhibited the highest sensor response to ethanol, which is 5.5 times higher than undoped ZnO. Moreover, the 3% Cu doped ZnO NRs sensor was able to detect ethanol gas even at 100°C while the undoped sensor was not. Improved sensor performance of the NRs can be attributed to the increased number of surface oxygen species and lower activation energy due to the doping of Cu.

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