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**THE GROWTH AND CHARACTERIZATION OF Sn DOPED
Al/ZnS/p-Si STRUCTURES**

**Ph.D. THESIS
IN
ENGINEERING PHYSICS**

**BY
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**Ph.D. Thesis
in
Engineering Physics
Gaziantep University**

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March 2022**



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ABSTRACT

THE GROWTH AND CHARACTERIZATION OF Sn DOPED Al/ZnS/p-Si STRUCTURES

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Ph.D. in Engineering Physics

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In this study, undoped and Sn (tin) doped ZnS (zinc sulfide) solutions were coated on glass and p-type Si (silicon) crystal using the sol-gel method. The Sn contribution amount changed between 0%-10%. The films are coated 15 layers on glass and 6 layers on crystal. Optical parameters such as thickness d , forbidden band gap E_g and refractive index n of the materials were investigated by using UV-vis-NIR measurements of thin films coated on glass. The crystal structure of the materials was determined with help of XRD spectrum. According to the results obtained, it was observed that the films grown on both glass and crystal crystallize as a cubic structure. Current-voltage I - V measurements of doped and undoped ZnS/p-Si structures were taken at room temperature in the dark, and diode properties of the samples were investigated with the help of these measurements. Diode parameters such as ideality factor n , barrier height ϕ_b and series resistance R_s were calculated using Thermionic emission (TE), Norde, Lien and Cheung-Cheung methods. In addition, capacitance-voltage C - V measurements of doped and undoped ZnS/p-Si in the frequency range of 10kHz-1.5MHz were taken and diode parameters were determined in detail by using these measurements. In addition, illuminated I - V measurements of doped and undoped ZnS/p-Si structures were determined under 100mW/cm² illumination power in order to investigate photodiode characteristics of the samples.

Key Words: ZnS, p-Si, Sol-gel, Diode Characteristic, Thin Film.

ÖZET

Sn KATKILI Al/ZnS/p-Si YAPILARIN BÜYÜTÜLMESİ VE KARAKTERİZASYONU

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Bu çalışmada katkısız ve Sn (kalay) katkılı ZnS (çinko sülfür) çözeltileri sol-jel yöntemi kullanılarak cam ve p-tipi Si (silisyum) üzerine kaplanmıştır. Sn katkı miktarı %0-%10 arasında değiştirildi. Filmler cam üzerine 15 kat, kristal üzerine ise 6 kat kaplanmıştır. Cam üzerine kaplanan ince filmlerin UV-vis-NIR ölçümlerinden yararlanılarak malzemelerin kalınlık d , yasak enerji aralığı E_g ve kırılma indisi n gibi optiksel parametreleri incelenmiştir. XRD spektrumu yardımıyla malzemelerin kristal yapısı belirlenmiştir. Elde edilen sonuçlara göre hem cam hem de kristal üzerine büyütülen filmlerin kübik yapıda kristallendiği görülmüştür. Oda sıcaklığında ve karanlıkta katkılı ve katkısız ZnS/p-Si yapıların akım-voltaj I-V ölçümleri alınmış ve bu ölçümler yardımıyla numunelerin diyot özellikleri incelenmiştir. Termoyonik emisyon (TE), Norde, Lien ve Cehung-Cehung yöntemleri kullanılarak ideallik faktörü n , bariyer yüksekliği ϕ_b ve seri direnç değeri R_s gibi diyot parametreleri hesaplanmıştır. Ayrıca 10kHz-1.5MHz frekans aralığında katkılı ve katkısız ZnS/p-Si yapısının kapasitans-voltaj C-V ölçümleri alınmış ve bu ölçümler kullanılarak diyot parametreleri detaylı olarak belirlenmiştir. Ayrıca, numunelerin fotodiyot özelliklerini incelemek için 100mW/cm^2 ışık şiddeti altında, katkılı ve katkısız ZnS/p-Si yapıların aydınlık I-V ölçümleri alınmıştır.

Anahtar Kelimeler: ZnS, p-Si, Sol-jel, Diyot Özellikleri, İnce Film.



'Dedicated to my family'

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LIST OF SYMBOLS

A	Effective diode area
A*	Richardson constant
C	Capacitance
D	Film thickness
D	Average crystallite size
E	Electron charge
eV	Electron volt
E_f	Fermi energy level
E_g	Optical band gap
E_m	Maximum electric field
h	Planck constant
hν	Photon energy
I	Current
I₀	Saturation current
k	Boltzmann constant
m_e	Electron mass
m_e*	Effective mass of electron
n	Ideality factor
n	Refractive index of the film
N_A	Acceptor concentration
N_V	Intensity of the effective states in the valence band
N_{ss}	Density of interface states
R_s	Series resistance
V	Voltage
V₀	Intercept potential
V_d	Diffusion potential
W_D	Depletion length

$\Delta\phi_b$	Schottky barrier lowering
δ	Thickness of the insulator layer
ϵ_i	Dielectric constant of the insulator
ϵ_s	Dielectric constant of the semiconductor
Φ	Work function
ϕ_b	Barrier height
χ	Electron affinity
λ	Wavelength
θ_{hkl}	Bragg's angle



LIST OF ABBREVIATIONS

AC	Alternative Current
C-V	Capacitance-Voltage
DC	Direct Current
FE	Field Emission
I-V	Current-voltage
MS	Metal/semiconductor
MIS	Metal/insulator/semiconductor
RCA	Radio Corporation of America
TE	Thermionic Emission
TFE	Thermionic Field Emission
UV-vis-NIR	Ultraviolet-visible-near infrared
XRD	X-ray Diffraction

CHAPTER I

INTRODUCTION

1.1 Motivation of Study

Semiconductor materials are the basis of technological devices and are used in the manufacture of many electronic devices. The study of the English scientist Michael Faraday in 1833 is in the literature as the first documented observation study about the semiconductor materials. In this study, it was found that the coefficient of variation of the resistance of the silver sulfide (AgS) material against temperature changed inversely. It has been observed that AgS material provides better conductivity when its temperature decreases [1]. In 1839, it was observed that a potential difference occurred between the electrodes when light was thrown on the surface of one of the two electrodes placed in the same electrolyte by the French scientist E. Becquerel [2]. Photoconductivity in solids was discovered in 1873 by British engineer W. Smith. In 1876, Smith observed that the resistivity of selenium was sensitive to light and its conductivity changes [3]. Scientist Karl Ferdinand Braun discovered in 1874 that the electrical interaction between metal and semiconductor contacts such as copper, iron and sulfide is asymmetrical. Thanks to this, these electronic circuit elements started to be used as detectors in the first radio experiments [4].

One of the first practical semiconductor circuit elements is Schottky diodes, which are attributed to W. Schottky for his detailed work on metal/semiconductor structures [5]. In 1930, Spenke and Schottky improved the rectification theory based on the carrier diffusion through the energy barrier [6]. In 1932, the quantum mechanical tunneling theory was developed by Wilson for metal/semiconductor diodes and tried to explain the reverse polarity for rectification [7]. In the 1940s, Bethe made an important contribution to Schottky diode studies with thermionic emission theory (TE) and developed the Schottky diffusion theory [8]. Later, Crowell and Sze combined these two theories and presented the current conduction mechanism in ideal Schottky diodes

as thermionic diffusion emission theory [9]. Metal/oxide/semiconductor (MOS) or metal/insulator/semiconductor (MIS) structures are obtained by adding various interfaces to metal/semiconductor (MS) structures to increase the durability of the structure against external factors and its electrical conductivity and improve its overall performance [10]. In the preparation of structures such as MS, MIS or MOS, metals such as silver (Ag), aluminum (Al) and gold (Au) are generally used in high purity and silicon (Si) is generally preferred as a semiconductor because it is cheaper and more stable. During the preparation of these structures, attention should be paid to the work function of the metal. When making a rectifier contact, the metal with appropriate work function should be selected by considering providing the semiconductor used is n-type or p-type. In these structures, the selection of the layer to be placed between the semiconductor and the metal is very significant to increase a performance and regulate the interface charge transitions. When choosing these interfacial layers, attention is paid to the selection of materials with high dielectric constants that will passivate the surface, minimize the leakage current, realize a controllable current transmission mechanism and approach the rectifier property [11].

II-VI binary semiconductors have been studied for many years without losing their importance for researchers [12, 13]. One of the II-VI group compound semiconductors is zinc sulphide (ZnS) [14]. ZnS exhibits an n-type semiconductor properties and its wide and direct band gap, non-toxicity, chemical stability, high resistivity and refraction values are the main reasons for its widespread use. [15, 16]. Sulphide surface defects cause ZnS to exhibit photo degradation activity [17]. ZnS can crystallize both hexagonal wurtzite and cubic structures and its forbidden band gap value ranges from 3.5 to 3.9 eV [18, 19]. The main usage areas of ZnS are; photovoltaic devices [20], light-emitting diodes [21], lasers [22], photocatalyst [23], biosensors [24].

It is possible to use different techniques to produce ZnS thin films. Spray pyrolysis, chemical bath deposition (CBD), radio frequency (RF) sputtering and sol-gel dip coating are some of these methods [25-30]. Doping atoms can change characteristics of ZnS semiconductor such as; optical, morphological, structural and electrical [31].

Wanjala et al. [32] fabricated ZnS thin films and they used Sn as dopant. They examined that increasing Sn doping concentration caused increasing of the electrical resistivity. In addition, they said Sn doped ZnS thin film with low concentration, is

suitable for Solar Cell applications. Kumar et al. [33] prepared Sn doped varied 0%-8% ZnS nanopowders using solid state reaction and they found that the optical band gap varied between 3.51 eV and 3.58 eV. They observed that the optical absorption value decreased with Sn concentration, also. Mukherjee and Mitra [34] investigated 2.5% and 5% Sn: ZnS thin films. According to the XRD results, structures crystallized hexagonal ZnS structure and the major peak was shifted through lower angles with Sn doping. They said that this shifting because of the difference between the ionic radius value of Sn^{2+} and Zn^{2+} ions. Abu Sayeed et al. [35] deposited Sn doped ZnS thin films on glass and observed that the optical band gap and the dielectric constant values depend on Sn concentration. Besides, transmittance was approximately 85% in the NIR. Ramki et al. [36] prepared undoped and Sn doped ZnS nanoparticles. They said that the films crystallized as cubic zinc blende. Since the dopant concentration was small, there were no impurity peaks in the XRD spectrum. In addition, they studied on photoluminescence properties of the films and they observed that the emission spectra were covered violet to blue region.

Farid et al. [37] coated Cu (copper) and In (indium) doped ZnS thin films by dipping method and observed that although the forbidden band gap value increased with In doping, it decreased with Cu doping. In addition, In doping caused decreasing of the resistivity, Cu doping, however, increased it. Ke et al. [38] fabricated Cu doped ZnS thin films with different thickness and they said that since the ionic radius of Zn^{2+} are close to that of Cu^{2+} , the position of diffraction peak and the lattice constant value did not changed with increasing film thickness. Ortiz-Ramos et al. [39] prepared Cu:ZnS thin films using CBD technique. The addition of Cu caused a slight decreasing in the optical band gap value. Besides, 1% and 1.5% Cu:ZnS thin films exhibit p-type conductivity.

Mohamed Bakr Mohamed [40] studied Co (cobalt), Mn (manganese), and Fe (ferrum) doped ZnS and reported while Co:ZnS caused blue emission only, Mn:ZnS shown blue-green emission and Fe doped ZnS exhibited violet emission also. Poornaprakash et al. [41] prepared Co, and Er (erbium) co-doped ZnS nanoparticles and according to the XPS spectrum, there was no impurities in the particles. Besides, the optical band gap value reduced from 3.52 to 2.56eV for Co-Er co-doped ZnS nanoparticle.

Benamra et al. [42] fabricated Al (aluminum) doped ZnS films. The addition of Al caused decreasing the resistivity of the films. Kityk et al. [43] studied the effect of In, Sn and Al concentration on the non-linear parameters of the ZnS thin films. Al doped ZnS caused the maximum change in the photoinduced spectrum, a less effect was observed for In doped ZnS and Sn doped caused the lowest effect on the photoinduced spectrum. Jrad et al. [44] studied on Al:ZnS thin films and they said the addition of Al caused decreasing crystalline quality because of the difference between ionic radius of Al^{3+} and Zn^{2+} . Zhu et al [45] fabricated Al doped ZnS/p-Si (100) and the electrical resistivity of the films firstly decreased and then increased with Al content. They investigated photoluminescence properties of the structures also and the emission intensity firstly rised and then sharply reduced with increasing Al content. Jebathew et al. [46] prepared doped ZnS thin films using Sb, Al and Sn as dopant by nebulized spray pyrolysis and they observed the effect of doping atoms on the photo-sensing characteristics of the films. They observed that the photo current value nearly two orders greater than dark current value measured at 5V. The responsivity values were found in the mA/W level and Sn doped ZnS had the maximum responsivity value.

E. M. Nasir [47] prepared Al doped ZnS/p-Si structures and observed the built-in potential decreased with increasing Al concentration. Tapan et al. [48] investigated photodiode characteristics of the ZnS/Si isotype heterojunction. Ji et al. [49] fabricated ZnS/p-Si heterojunction using CBD technique and investigated photovoltaic characteristic. Similarly, Qiu et al [50] using WO_3 as hole selector contact, fabricated ZnS/p-Si diode and studied on the power-loss of the structure. Senados et al. [51] growth ZnS thin film on p-type Si (100) crystal. The sample was annealed 500°C at 2h and they reported that the structure exhibit good rectifying behavior. Huang et al. [52] prepared ZnS/p-Si heterojunction and studied on photoresponse properties. They said that ZnS/p-Si heterojunction had good crystallinity. The sample can crystallize both cubic and hexagonal wurtzite because there is only one peak in the XRD spectrum and the angle of the cubic (111) reflection and that of the hexagonal (002) reflection are nearly same angle. They found the forbidden band gap value as 3.52 eV with the help of transmittance spectrum. The heterojunction was illuminated at 330 and 450 nm. According to the illuminated I-V measurements, while there is no significant change under forward bias conditions after illumination, the current value rised under reverse bias.

ZnS can be an insulator layer because of the low field resistivity value (10^{12} ohm.cm) in the Al/p-Si structures [53]. Sands et al. [54] investigated C-V and I-V properties of ZnS/p-Si heterojunction. In addition they observed the density of interface states value of the structure is very high. Simons et al. [55] studied on capacitance and conductance characteristics of ZnS:Mn/p-Si heterojunctions. They observed that the sample annealed at 500° - 600° showed non-ideal C-V characteristics. On the other hand, the sample heated at 700° exhibited normal C-V behavior.

Coating condition can also affect the film characteristics. Kurnia et al. [56] growth ZnS thin film under vacuum and N_2 gas. While the film grown under vacuum crystallized as the zinc blende phase, the film grown under N_2 gas formed as wurtzite structure.

In this study, undoped, and Sn doped ZnS thin films coated on p-type Si (111) and glass substrates using sol-gel dipping method. The reason for using Sn as the doping atom is that the ionic radius values of Sn and Zn atoms are very close to each other (for $Sn^{4+}=0.071nm$ for $Zn^{2+}=0.074nm$) [57]. Thus, it was thought that the defects in the crystal structure of the material would be less. In addition, Sn has 4 valance electrons and this provides extra electrons for the electrical conduction. Optical parameters such as thickness d , forbidden band gap E_g and refractive index n of the materials were investigated by using UV-VIS-NIR spectrum of the thin films coated on glass. The crystal structure of the materials was determined with help of XRD spectrum. Current-voltage (I - V) measurements of doped and undoped ZnS/p-Si structures were taken under illuminated and dark conditions at room temperature. Diode and photodiode characteristics of the structures were determined with the help of these measurements. Diode parameters such as ideality factor n , series resistance R_s , barrier height ϕ_b , and saturation current I_0 were calculated using Thermionic emission (TE), Norde, Lien and Cheung-Cheung methods. Photodiode parameters such as detectivity D , photosensitivity PS and photoresponse R values were calculated. In addition, capacitance-voltage (C - V) measurements of doped and undoped ZnS/p-Si in the frequency range of 10kHz-1.5MHz were taken and diode parameters were determined in detail by using these measurements.

CHAPTER II

THEORETICAL BACKGROUND

2.1 Types of Solids

Solid materials are classified as amorphous, polycrystalline and crystalline according to the arrangement of atoms or molecules. A crystal is a homogenous solid surrounded by smooth faces formed by the combination of atoms or groups of atoms in a periodic order in three-dimensional space. The single crystals are known as grains. Grain boundaries allow each grain to be separated from each other. Amorphous solids, on the other hand, are solids that are composed of random particles of various sizes and do not have a definite regular structure [58, 59]. Figure 2.1 illustrates types of solids.

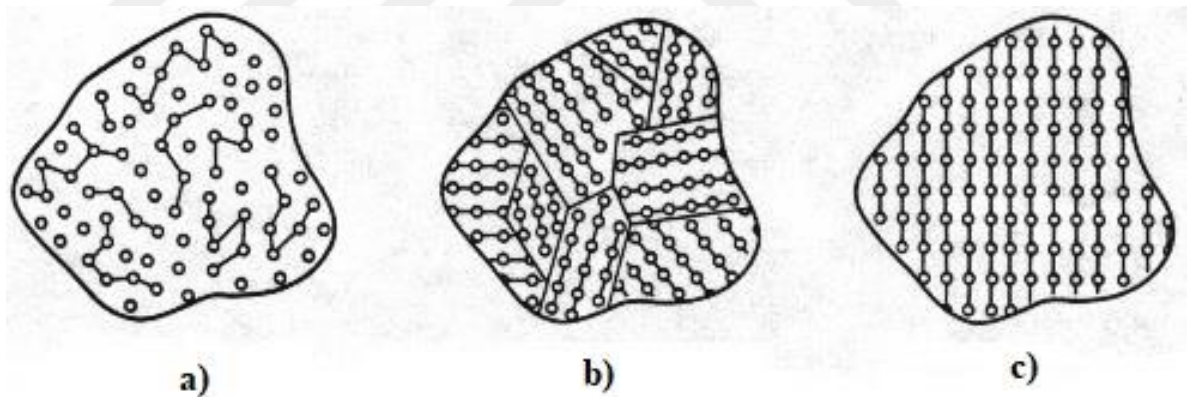


Figure 2.1 Schematics of three general types of crystals. **a)** amorphous, **b)** polycrystalline, **c)** crystalline [59].

The particles forming the crystal in a crystal are arranged according to a certain order in a three-dimensional crystal lattice. The smallest piece of lattice that has all the properties of a whole lattice is known as a unit cell. When this unit cell is moved in various directions at equal distance to its own dimensions, it forms the crystal lattice. Crystal lattices are considered within seven general crystal systems. Figure 2.2 shows unit cell and crystal lattice

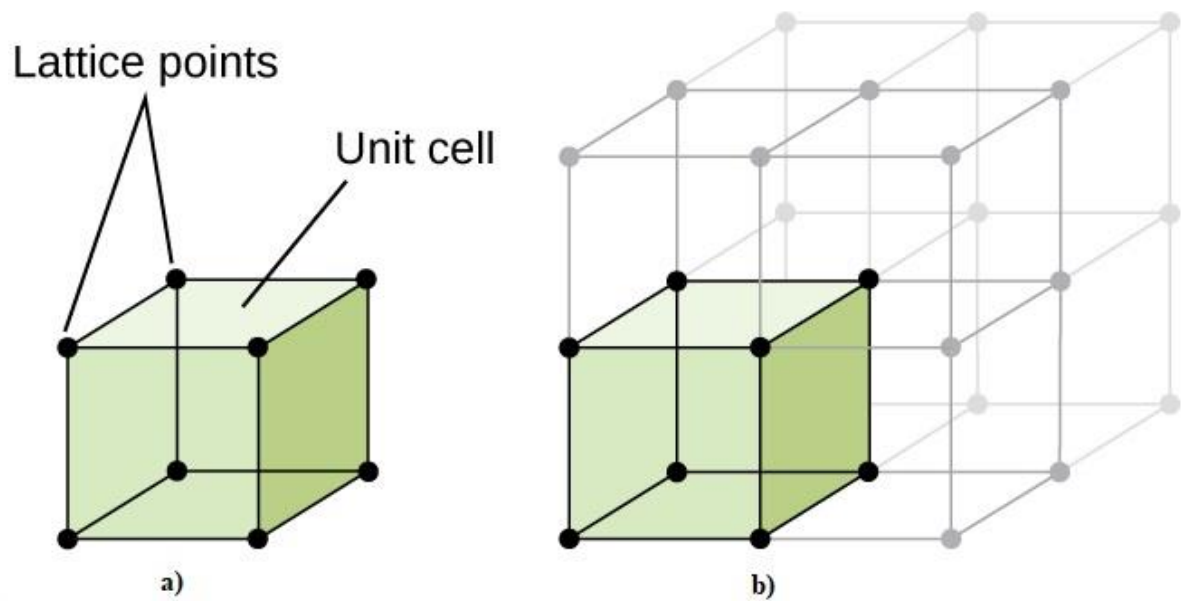


Figure 2.2 The illustration of **a)** unit cell and **b)** crystal lattice [60].

2.2 The Crystal Structure

The properties of crystals change depending on the crystal structure of the material, and the spatial arrangement of atoms, ions, or molecules. There are seven crystal systems and fourteen different lattices or Bravais lattices according to the positions of atoms in different positions within these crystal structures themselves in three-dimensional space [61]. Figure 2.3 gives Bravais lattice types.

By dividing space into three sets of planes, we can obtain various types of unit cells, depending on the way we choose these planes. Depending on the different values that the unit cell parameters can take, it is seen that the unit cells come in seven different shapes and sizes in order to represent all crystals found in nature. A crystal is defined by the three side lengths of the a , b , c axes and the angles α , β , γ between these axes.

Most of the commonly used metals generally have hexagonal close packed, body centered cubic and face centered cubic.

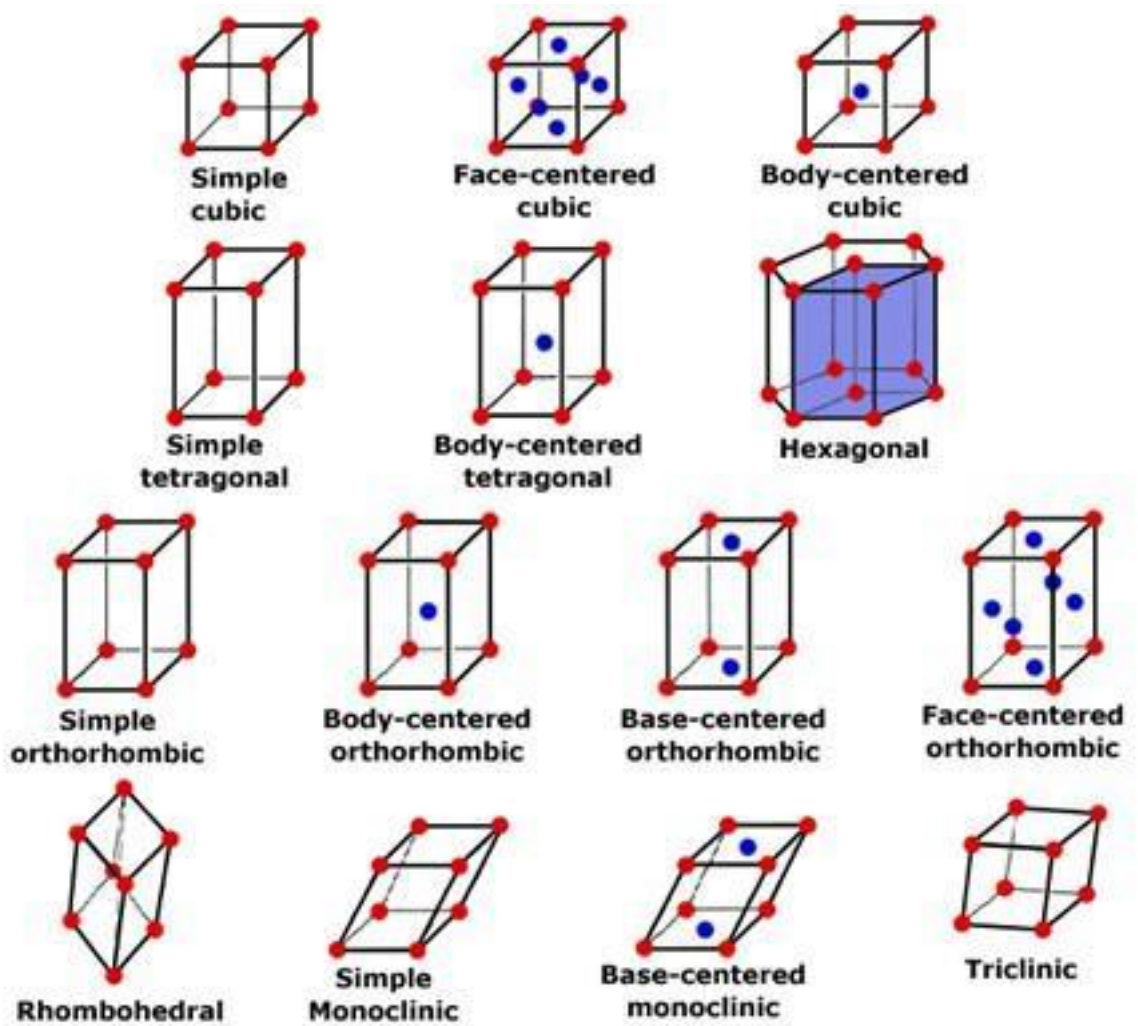


Figure 2.3 Bravais lattice types [62].

2.2.1 The Cubic Crystal Structure

In the cubic crystal system, the lattice geometry is in the form of a cube with equal sides, and the atoms are arranged in three different ways, forming a simple cubic, body centered cubic and face centered cubic structure [63].

In the simple cubic lattice structure, the atoms are existed in each corner of the cube. Due to an unstable atomic arrangement, there is no substance in nature that fits this structure. There is a total of 1 atom in the unit cell of a simple cubic lattice.

In the body centered cubic (BCC) structure, there is an atom in the middle of the cube and in each corner. Iron has this structure at room temperature. There are 2 atoms in the unit cell of the body centered cubic structure. Figure 2.4 shows the body centered cubic structure.

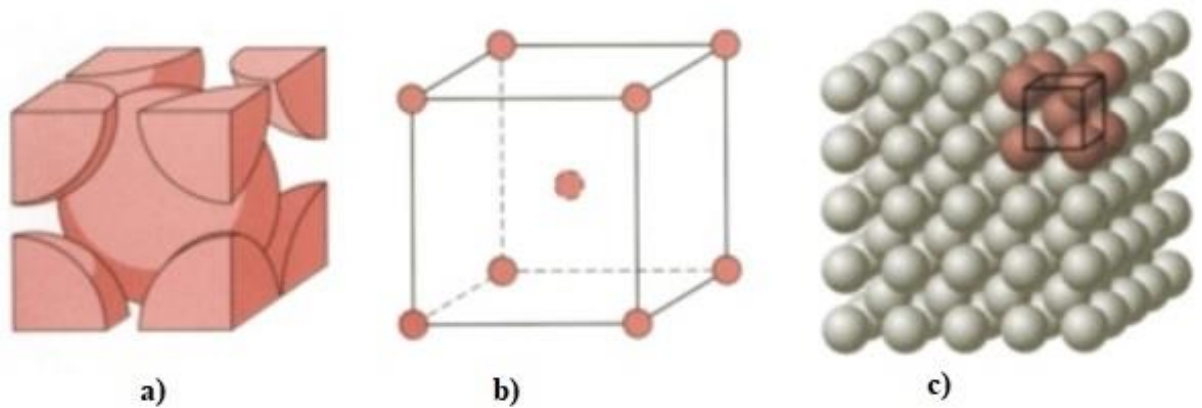


Figure 2.4 The Body Centered Cubic Crystal structure **a)** hard sphere unit cell **b)** a reduced sphere unit cell **c)** an aggregate of many atoms [64].

In a face centered cubic (FCC) structure, atoms are existed in each corner and surface of the cube. There are a total of 4 atoms in the unit cell of a face centered cubic lattice. Aluminum, gold, copper and silver are some of the metals that crystallize in this structure. Figure 2.5 gives the face centered cubic structure.

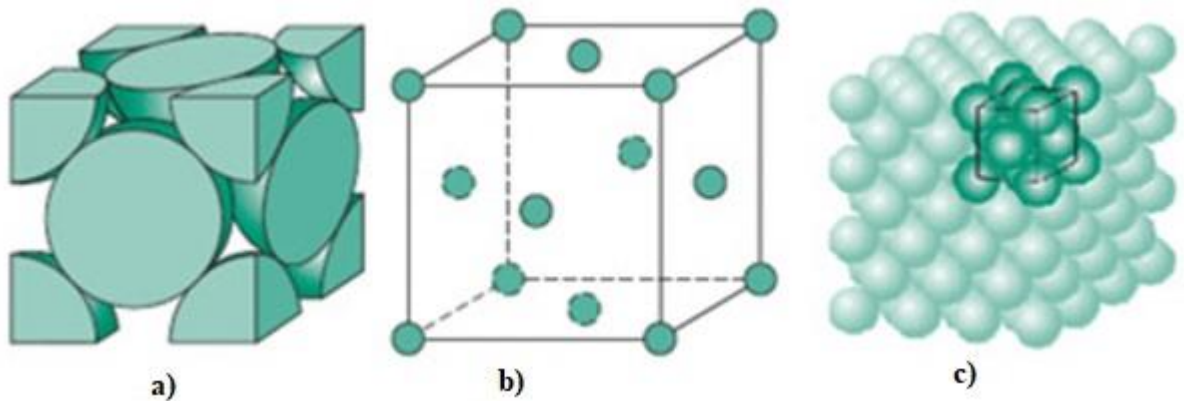


Figure 2.5 The Face Centered Cubic Crystal Structure **a)** hard sphere unit cell **b)** a reduced sphere unit cell **c)** an aggregate of many atoms [65].

2.2.2 The Hexagonal Crystal Structure

The unit cells of all metals are not arranged in cubic symmetry. Some have a unit cell that is hexagonal. Figure 2.6 displays the hexagonal close packed crystal structure (HCP).

The upper and lower faces of the unit cell consist of six atoms forming regular hexagons and surrounding a single atom in the center. Another plane, which provides

three additional atoms to the unit cell, lies between the upper and lower planes. Atoms in this midplane have nearest neighbor atoms in both of the two adjacent planes. Each unit cell contains the equivalent of six atoms; One sixth each of the 12 upper and lower face corner atoms, half each of the 2 center face atoms, and all 3 midplane inner atoms. If a and c represent, respectively, the short and long unit cell dimensions of figure 2.6, the c/a ratio should be 1.633; however, for some HCP metals this ratio deviates from the ideal value [61].

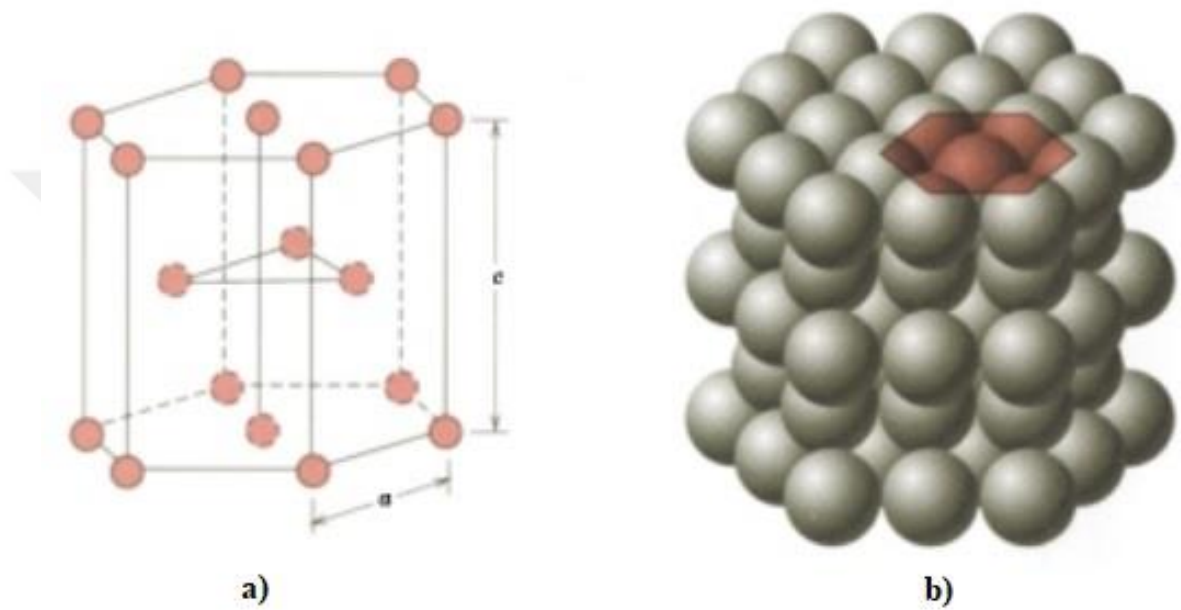


Figure 2.6 The Hexagonal Close Packed Crystal Structure **a)** a reduced sphere unit cell **b)** an aggregate of many atoms [64].

2.3 Ceramic Crystal Structure

Ceramics have a more complex crystal structure than metals because ceramics are made up of two or more elements. The crystal structure of ceramics is mainly determined by the size ratio of the ions that make up the compound and the electrical charge of the ions. When we talk about how the size ratio of ions affects the crystal structure, we do not consider the size of the atoms, but the size of the atoms after they gain an electric charge by sharing electrons, that is, when they are ionized. Since ions have a different number of electrons than atoms in the neutral state, they also vary in size. The metal atoms that make up the ceramic compounds lose their outer orbital electrons and become cations. Nonmetal atoms gain electrons to their outer orbits and become anions. Generally, anions are observed to be larger than cations, since cations

get smaller by giving up some of their electrons, and anions grow by taking electrons from cations. When we consider a crystal structure, we see that it does not contain any electrical charge. In order for this condition to be met, while ceramic compounds are formed, anions and cations must come together at a rate that will zero each other's electric charge.

2.3.1 AX Type Crystal Structure

Some well-known ceramic materials containing equal numbers of anions and cations are called AX compounds. There are AX compounds with different crystal structures. Here A is cation and X is anion. Compounds with the same crystal structure are grouped under the name of the most familiar material.

2.3.1.1 Rock Salt Structure

The most common AX crystalline element known is the rock salt, also called sodium chloride (NaCl). The crystal structure of sodium chloride or rock salt has high ionic bonding. To maintain charge neutrality, the Na^+ and Cl^- ions are in equal numbers. The Cl^- ions are located at the FCC atom lattice points, while Na^+ cations are located in the intermediate places between the FCC atoms. Since each Na^+ cations is surrounded by six Cl^- anions, the structure has octahedral association, that is, the coordination number is 6, and therefore the cation-anion radius ratio is between approximately 0.414 and 0.732. Some of the common ceramic materials that form with this crystal structure are NaCl, FeO, MnS, MgO and LiF [66].

2.3.1.2 Cesium Chloride Structure

In this crystal structure; the number of Cs^+ and Cl^- ions is equal. The coordination number is 8 for both ion types. There is only one cation at the center of the cube, while anions are at each corner of the cube and the ion radius ratio of Cs^+ and Cl^- are 0.94. Since there are two different types of ions, this crystal structure is not BCC. The ionic compounds in the CsCl structure are CsBr, TlCl and TlBr. Intermetallic compounds such as AgMg, LiMg and AlNi also have this structure [66].

2.3.1.3 Zinc Blende Structure

A third AX structure is zinc sulfide. Zinc sulfide has the chemical formula ZnS, and the unit cell shown in figure 2.7 has four zinc and four sulfur atoms. It is a structure

with a coordination number of 4; that is, all ions are tetrahedral coordinated. This is called the zinc blende or sphalerite structure also.

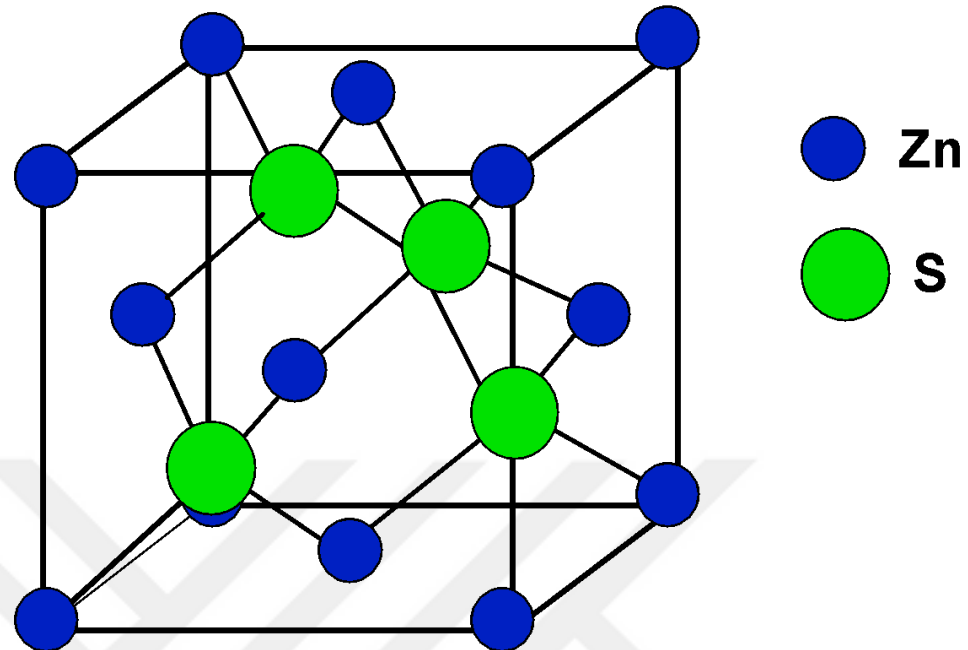


Figure 2.7 A unit cell for the zinc blende (ZnS) crystal structure [67].

As shown in figure 2.7, Zn atoms are in the tetrahedral region and S atoms are located in all corner and face regions of the cubic. According to the Pauling equation, the Zn-S bond is 87% covalent. An equivalent structure is formed if the positions of the Zn and S atoms are hidden. Thus each Zn atom is bonded to four S atoms. It has many semiconductor zinc sulfide structures such as CdS, InAs, InSb and ZnSe.

2.4 Diamond Crystal Structure

Silicon and Germanium the group IV elements and have a diamond crystal structure. The unit cell of the diamond structure is given in figure 2.8. We can examine the diamond structure by considering the tetrahedral structure. This structure is simply a body centered cubic (BCC) structure missing four of its corner atoms. Each atom in the tetrahedral structure has 4 nearest neighbor atoms and this structure forms the diamond structure. The diamond structure is a lattice in which all atoms are of the same type, as in Si and Ge. The difference between the zinc blende structure and the diamond structure is that the lattice contains two different types of atoms [59].

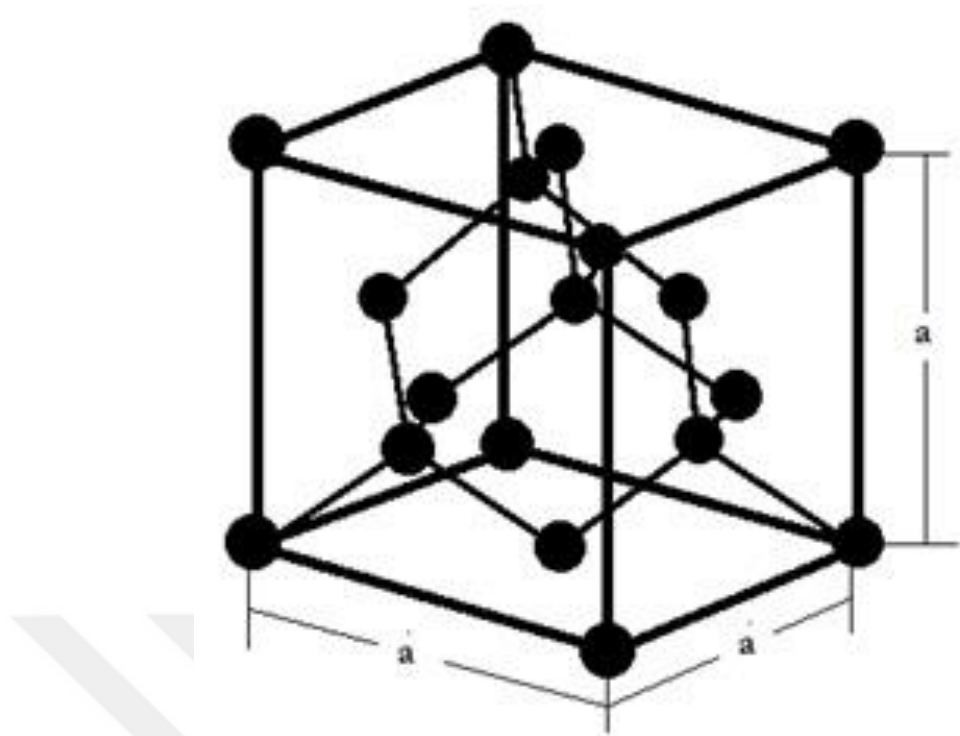


Figure 2.8 A unit cell for the diamond crystal structure [68].

2.5 The Miller Indices in a Crystal

A crystal plane in space with three points not on the same line determines. This is done by using Miller indices (hkl) in a crystal. The Miller indices of the plane are shown in brackets (hkl) and the Miller indices of the directions are shown with square brackets in the form $[hkl]$. Figure 2.9 and 2.10 show some The Miller indices of the planes and the Miller indices of the directions, respectively. To determine Miller indices, the points where the plane intersects the crystal axes are determined in terms of lattice constants. These numbers are reduced to obtain the smallest integer with the same ratio by taking their inverses. If a plane intersects one of the axes on the negative side, the corresponding index becomes negative and is indicated by placing a (-) sign on the index [69].

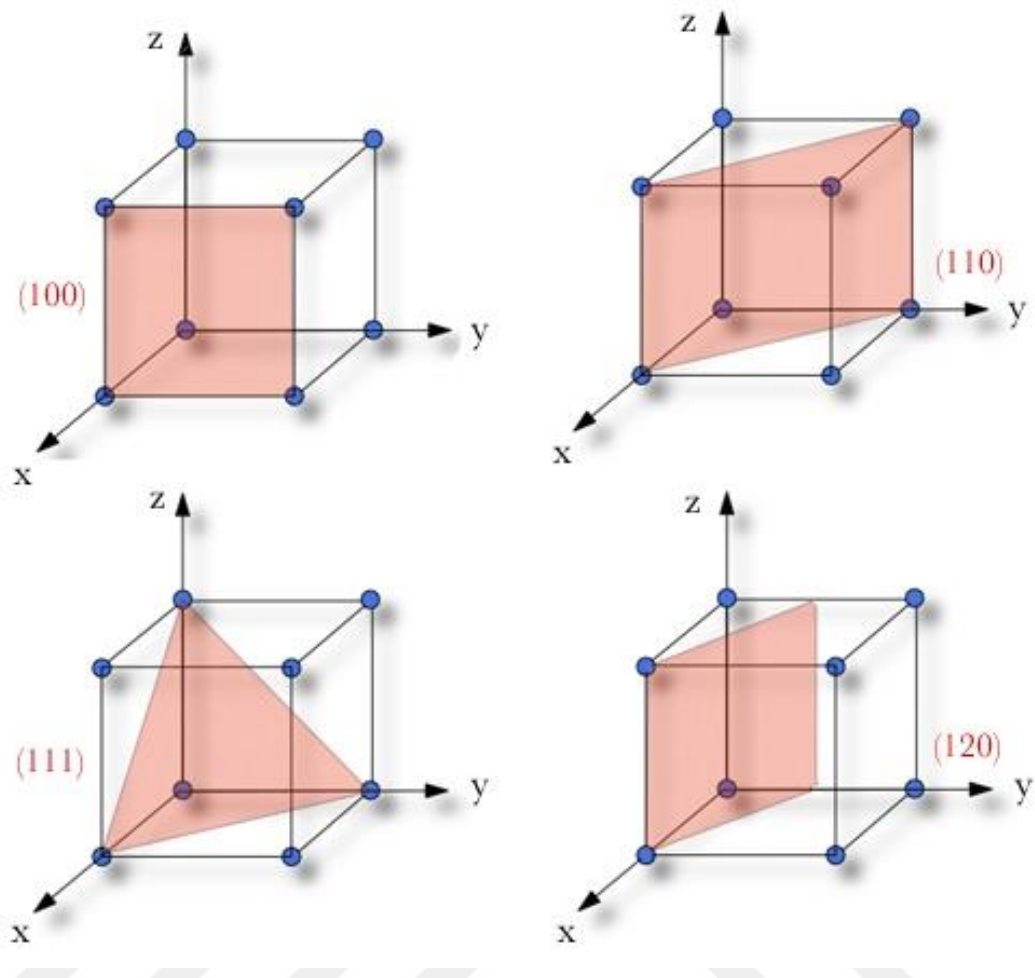


Figure 2.9 The Miller indices of the planes [69].

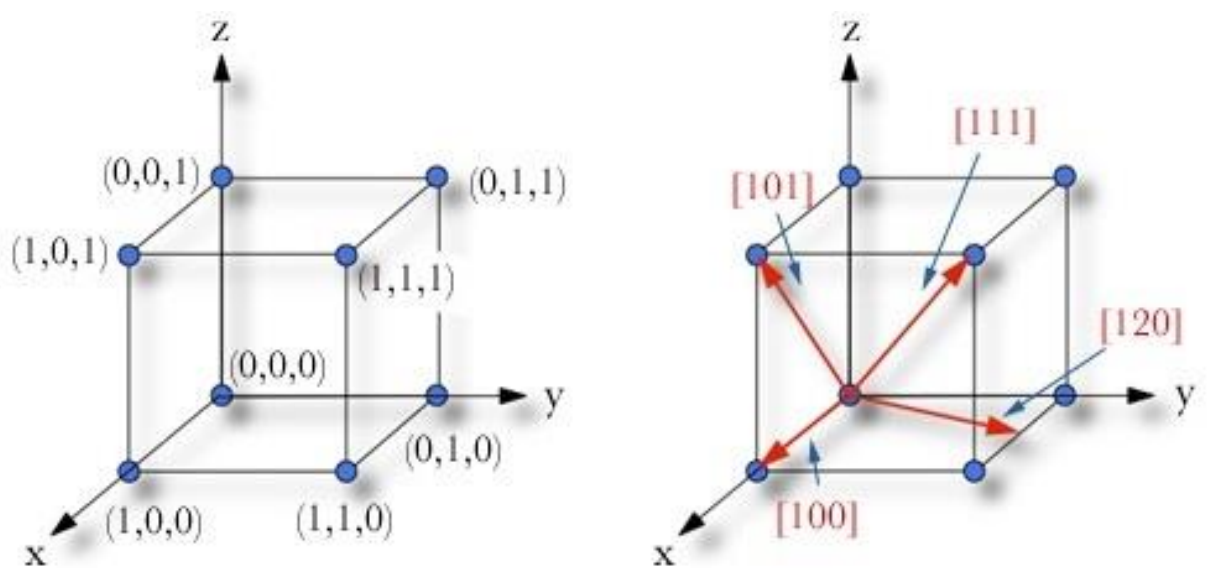


Figure 2.10 The Miller indices of the directions [69].

2.6 X-Ray Diffraction

XRD is one of the non-destructive techniques to understand the characteristics of the materials. With this technique, the unit cell parameters, the position of various atoms in the crystal structure, crystal defects, average grain size, strain, crystallinity can be determined [70-73]

XRD is used to determine the nature of the materials as amorphous or crystalline. XRD pattern of amorphous is broad, whereas crystalline has sharp peak [74, 75]. Figure 2.11 shows typical diffraction spectra of amorphous and crystalline structures.

XRD is a result of the scattering phenomenon and can be easily explained by Bragg's law. Consider a monochromatic beam of X-rays hitting the crystal. The crystal consists of atoms in planes arranged one above the other with exactly equal spatial distance between them. This beam scatters at specific angles from each set of lattice planes. If scattering results in constructive interference, XRD peaks are produced. The atomic position in the lattice planes defines the peak intensities [70, 75]. Figure 2.12 [77] displays schematic diagram of reflection from the lattice planes.

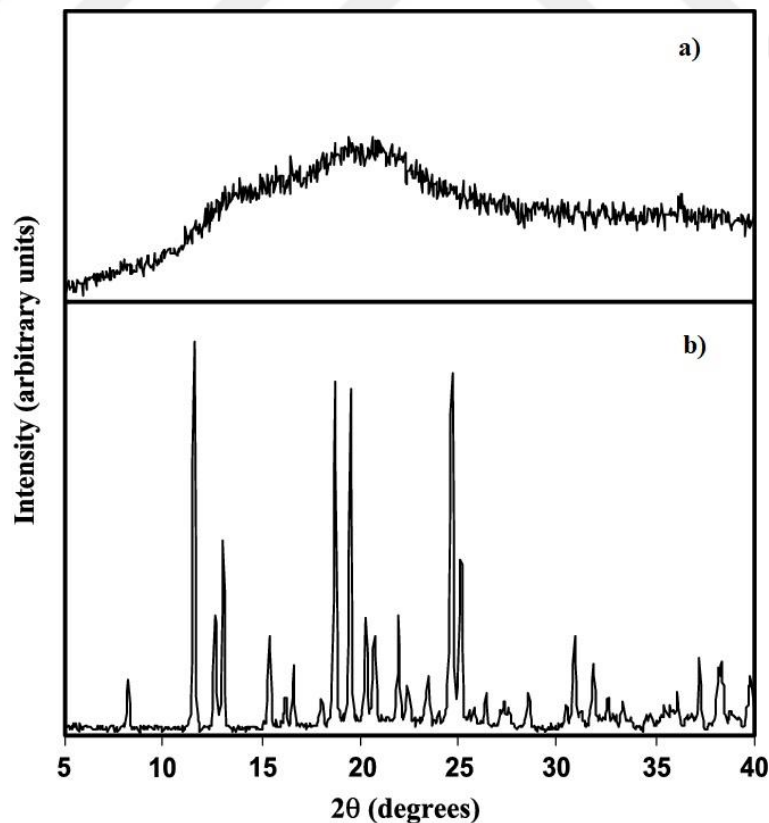


Figure 2.11 Typical XRD spectra of **a)** amorphous structure **b)** crystalline structure [76].

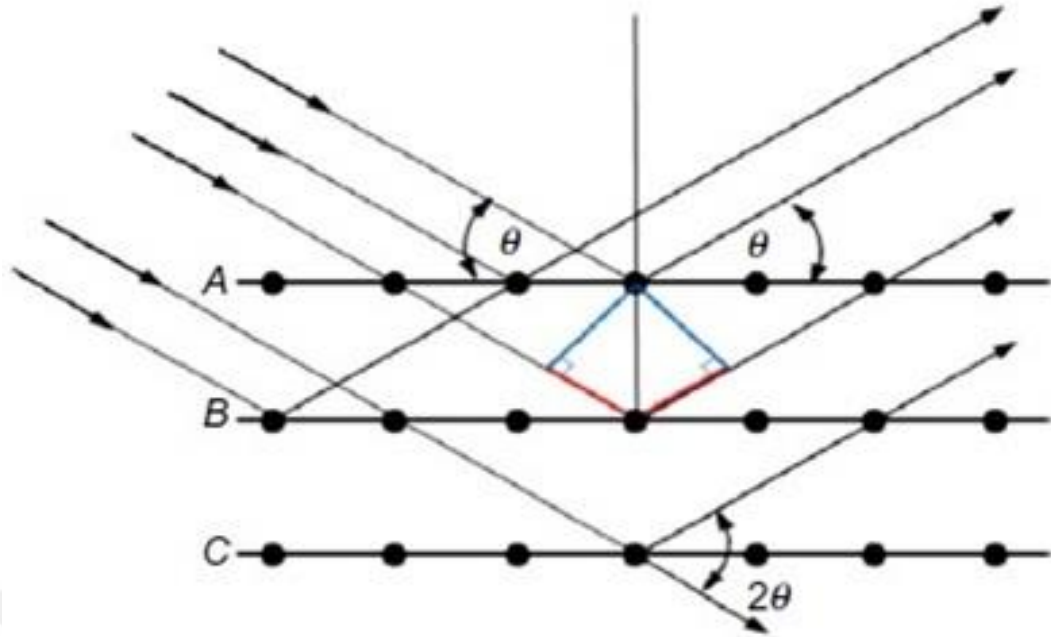


Figure 2.12 Schematic diagram of reflection from the lattice planes [77].

Bragg's law is given below equation.

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \quad (2.1)$$

where n known as the order of the reflection and denotes an integer number, λ is known as the wavelength of the monochromatic beam, d is the perpendicular distance between lattice planes and θ_{hkl} is described as the Bragg's angle. The beam which is scattered below planes takes a path that is exactly n wavelengths longer than those the ray above and this results in constructive interference. Waves scattered in other directions are in opposite phase and destruct each other. When n is equal 1, the diffracted beam is or the first order. Since the incoming and outgoing beams both make the same angle θ with the crystal planes, this process look like a mirror reflection from the plane and is often known as reflection. However, it differs from reflection because it occurs only when the Bragg equation is satisfied.

In X-ray spectrometry, the values of θ is changed and θ values at strong reflection serve to identify the corresponding strong components in the spectra by means of Bragg's law. By scanning a particular region of angles and continuously measuring the corresponding reflection intensities, the spectrum can be plotted.

Lattice constant can be calculated for a cubic phase using equation (2.2).

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.2)$$

The crystallite size of structures can be determined using Debye-Scherrer's formula [78].

$$D = \frac{0.96\lambda}{\beta \cos \theta_{hkl}} \quad (2.3)$$

herein β is described as full width at half maximum (FWHM) of the main diffraction peak.

The dislocation density δ is calculated using equation (2.4) [79].

$$\delta = \frac{1}{D^2} \quad (2.4)$$

The micro strain ε and the lattice mismatch values are calculated using the following equations [80, 81].

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (2.5)$$

$$\frac{\Delta a}{a} = \frac{2(a_2 - a_1)}{(a_2 + a_1)} \quad (2.6)$$

Where a_1 and a_2 are the lattice constant of the thin film and the crystal, respectively. For p-Si crystal the lattice constant is 0.54309 nm.

2.7 Determination of Optical Parameters of the Thin Films

The basic equation to obtain interference fringes is given following equation.

$$2nd = m\lambda \quad (2.7)$$

Here m is a half integer for minima and an integer for maxima transmittance peak, n is described as the refractive index of the films and d is the film thickness.

In order to obtain the refractive indices and the film thicknesses a method was developed by Swanepoel [82]. According to this method, the interference pattern is enclosed in an envelope and there are minima values corresponding to each maxima

Using average value of the thickness (d_{avr}), now the order numbers (m) for the extremes can be found using equation (2.7). m values have to be integer for maxima or half-integer for minima transmittance value. Taking m values integer or half-integer, d , d_{avr} and n can be calculated again. Thus, it can be said the accuracy in the results increases.

The values of the refractive index n can be fitted to Cauchy dispersion relation given by equation (2.11). By extrapolating it to shorter wavelengths using this relation, a theoretical function that generalizes the spectrum is obtained.

$$n(\lambda) = a + b/\lambda^2 \quad (2.11)$$

Here a and b denote constants. The constant b is found from the slope of the n/λ^2 graph. Also, by extrapolating the graph to the n -axis, the values of the constant a are found. When the constants a and b are known, the value of the refractive index for any wavelength can be found with greater accuracy with the help of the relation.

m and d values can also be obtained using simple graphical method. For the first extreme, suppose the order number is m_1 . Equation (2.7) can be written again, for the extremes of the spectrum.

$$2nd = (m_1 + l/2)\lambda \quad l = 0,1,2,3 \dots \quad (2.12)$$

The graph of $l/2$ versus n/λ is linear and the slope of the graph gives $2d$ and cut-off point on the y -axis gives $-m_1$ value.

Equation (2.13) gives the absorption coefficient relation.

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{x} \right) \quad (2.13)$$

here d is the thin film thickness and x is the transmittance value as a percent. After calculation of the absorption coefficient value, the forbidden band gap value is determined using Tauc method [83].

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n \quad (2.14)$$

Where $h\nu$ is photon energy and n is 0.5 for direct transition.

2.8 Semiconductor Materials

A group of materials having conductivities between those of metals and insulators are known as semiconductor materials. Semiconductors are divided into two groups, elemental and compound semiconductor materials. While the elemental semiconductor materials are in group IV of the periodic table, the compound semiconductor materials are formed special combinations of group III and group V or group II and group VI elements [59].

Semiconductors can be found in nature as pure as well as in compound structures. Silicon (Si), germanium (Ge) are the leading semiconductor materials of electronic technology and they are elemental semiconductors. Zinc oxide (ZnO), copper oxide (CuO), gallium arsenid (GaAs) and zinc sulfide (ZnS) are some of the compound semiconductors. GaAs is in the III-V group and ZnS is in the II-VI group.

2.8.1 Band Diagram

Solid materials are categorized according to their conductivity. These are conductors, semiconductors and insulators. Whether these materials are conductors, semiconductors and insulators is explained by the band theory of solids.

Atoms come closer to each other to form the crystal and their outer orbitals are intertwined. According to the Pauli principle, since two electrons with equal four quantum numbers cannot be found in the same atom, each energy level of the atoms forming the crystal is divided into levels very close to each other and a band image is formed.

In semiconductor solids, the valence band is the filled band and the conduction band is the empty band and lies above the valence band. The energy that the electron has to jump from the valence band to the conduction band is known as a band gap [84].

Figure 2.14 displays energy diagrams of insulators, semiconductors, and conductors.

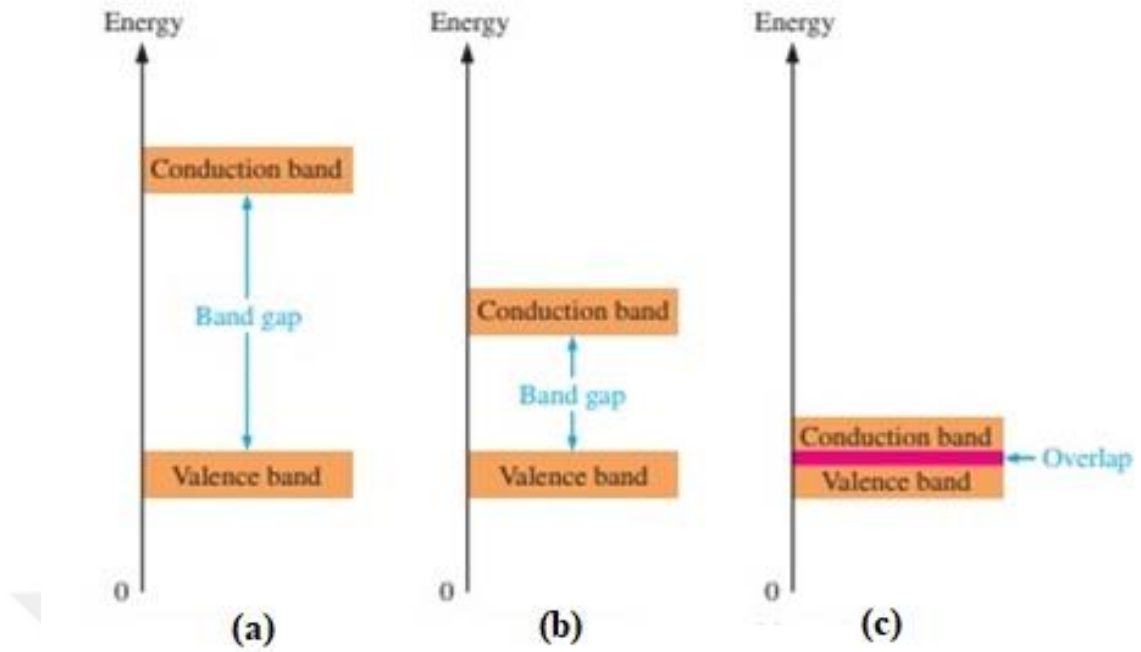


Figure 2.14 Energy diagram for **a)** insulator, **b)** semiconductor, **c)** conductor [85].

2.8.2 Intrinsic Semiconductor

If there is no impurities in the crystal, this semiconductor known as an intrinsic semiconductor. Silicon and germanium are example for intrinsic semiconductor. The atomic structures of silicon and germanium are shown in figure 2.15. There are four valence electrons in the outer or valence shell in both Si (silicon) and Ge (germanium).

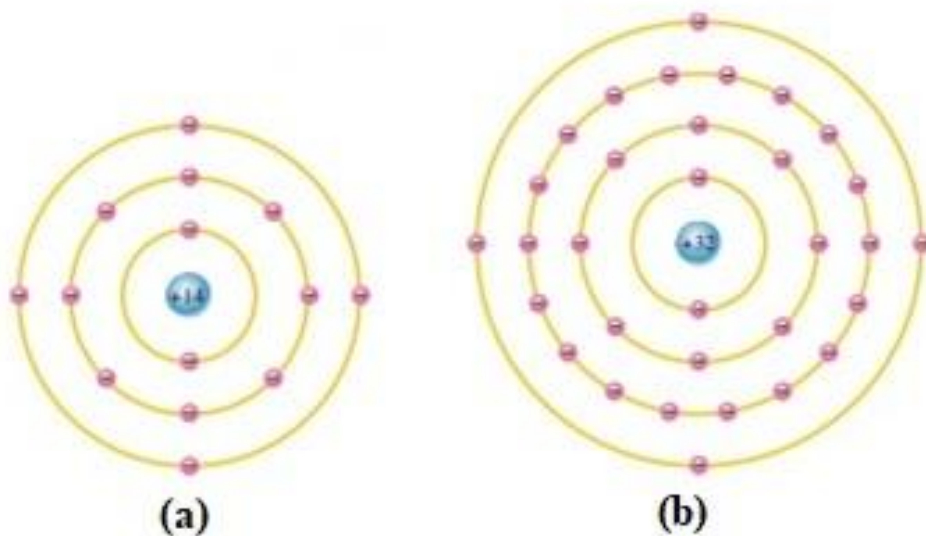


Figure 2.15 Diagrams of **a)** silicon and **b)** germanium atoms [86].

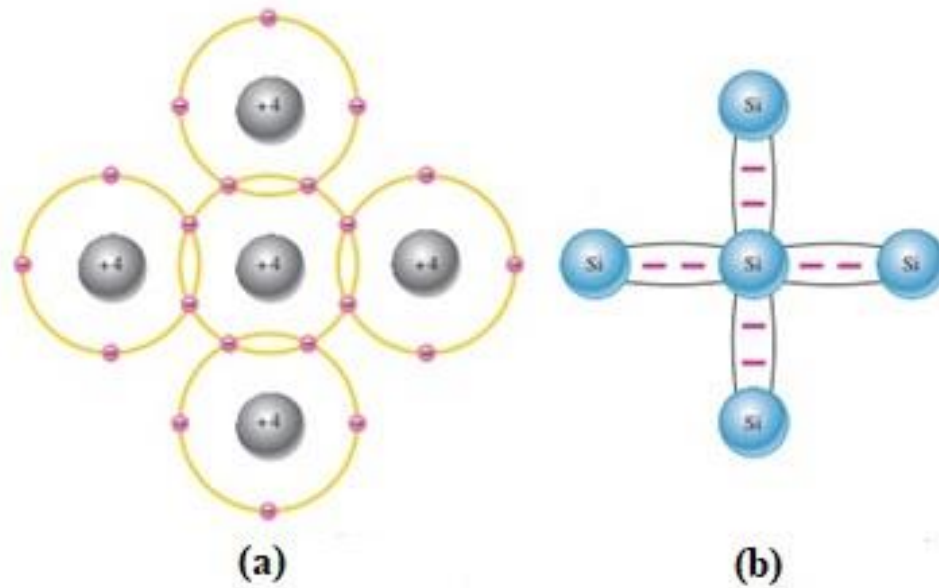


Figure 2.16 The schematic diagram of covalent bonds for silicon [87].

In a silicon crystal, each silicon atom is enclosed by four other silicon atoms as shown in Figure 2.16. Each silicon atom forms a covalent bond by sharing its valence electrons with these four neighboring silicon atoms and it appears that there are no free electrons [84].

2.8.3 Electron Hole Pairs

When an intrinsic silicon crystal at room temperature, due to the thermal energy, a small part of the bond electrons take enough energy to break the bond and begin to move freely in the silicon, becoming free electrons. Free electrons are known as conduction electrons and they can carry electric current. This is illustrated figure 2.17 [88].

When the electron breaks the bond and leaves the atom, a vacancy is left behind. This vacancy in the valance band within the crystal is called a hole. The hole can be displaced, that is, it is mobile and can carry electric current due to being mobile. But when carrying current, the direction of movement is opposite to the direction of movement of electrons. Thus, it is called a positive charge carrier. The electrons which jump the conduction band and the holes is defined electron-hole pairs [88].

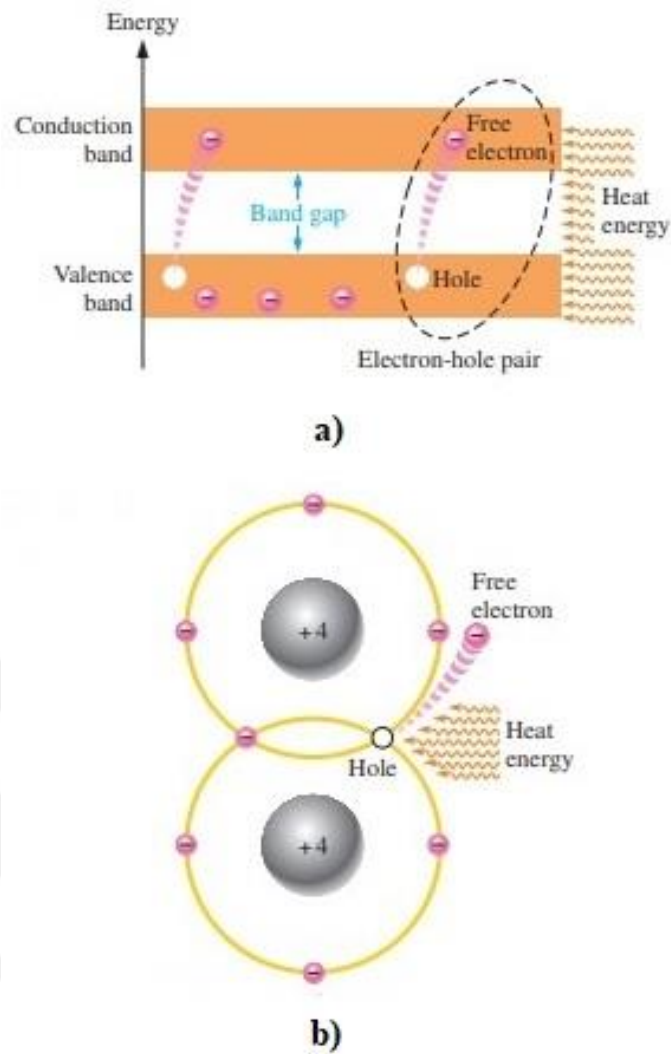


Figure 2.17 Creation of electron-hole pairs in Si crystal **a)** energy band diagram, **b)** bonding diagram [87].

2.8.4 Extrinsic Semiconductors

In order to increase the conductivity of the semiconductors, the impurities can be added into the intrinsic semiconductors. This process is described as doping. There are two types of impurities are p-type and n-type.

2.8.4.1 n-Type Semiconductor

If a pentavalent atom such as antimony (Sb), arsenic (As), bismuth (Bi), and phosphorus (P) is placed in a silicon crystal, this foreign atom forms a covalent bond with its four closest neighbors and one valence electron remains. That is, the fifth valence electron of the doping atom cannot enter the bond and becomes freely moveable in the crystal as a conduction electron. In this case, the doping atom becomes

positively charged as it loses an electron as shown in figure 2.18. The impurity atom that can donate an electron to the semiconductor is called a donor [89].

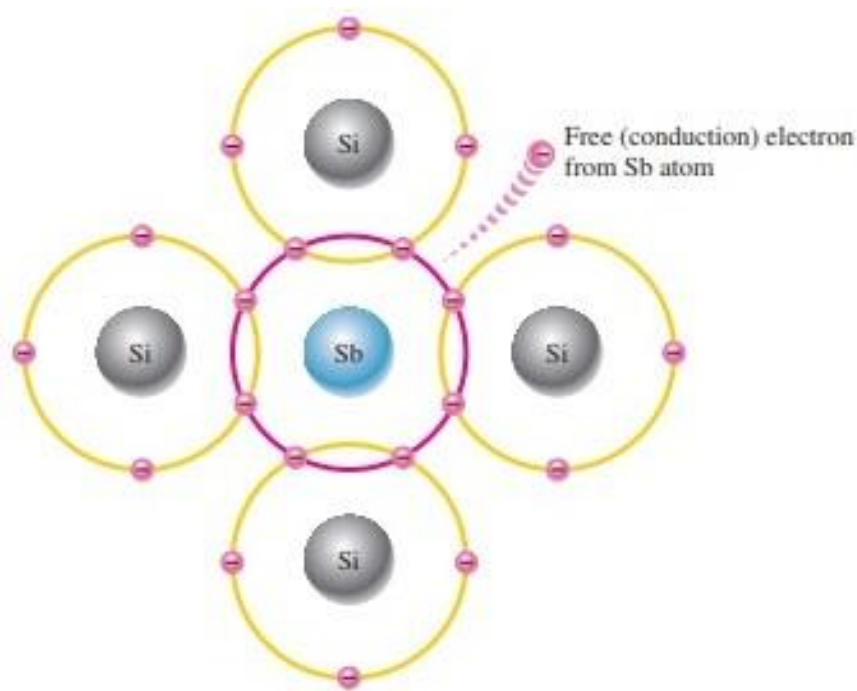


Figure 2.18 The illustration of Sb doped Si [87].

Semiconductors with higher electron density than hole density are called n-type semiconductors. In n-type semiconductors, with the ionization of the donor atom, no holes are formed in the valence band in response to the electrons leaving the donor energy level to the conduction band. Depending on the donor density, since the electron density in n-type semiconductor materials will be greater than the hole density, the contribution from electrons to the electrical conductivity will be greater. Therefore, electrons are known as majority carriers and holes are known as minority carriers in n-type semiconductors [90].

2.8.4.2 p-Type Semiconductor

If trivalent atoms such as indium (In), boron (B), and gallium (Ga) is added to the silicon crystal, this foreign atom forms a covalent bond with its four closest neighbors but one of the four covalent bond is missing an electron. This vacancy is filled by an electron leaving another bond. Thus, a hole is formed where the electron leaves. As a result, the boron atom gains electrons. The hole is freely movable inside the crystal as

shown in figure 2.19. Since the trivalent dopant atom must gain an electron to complete the tetrahedral bond, this atom is called an acceptor [91].

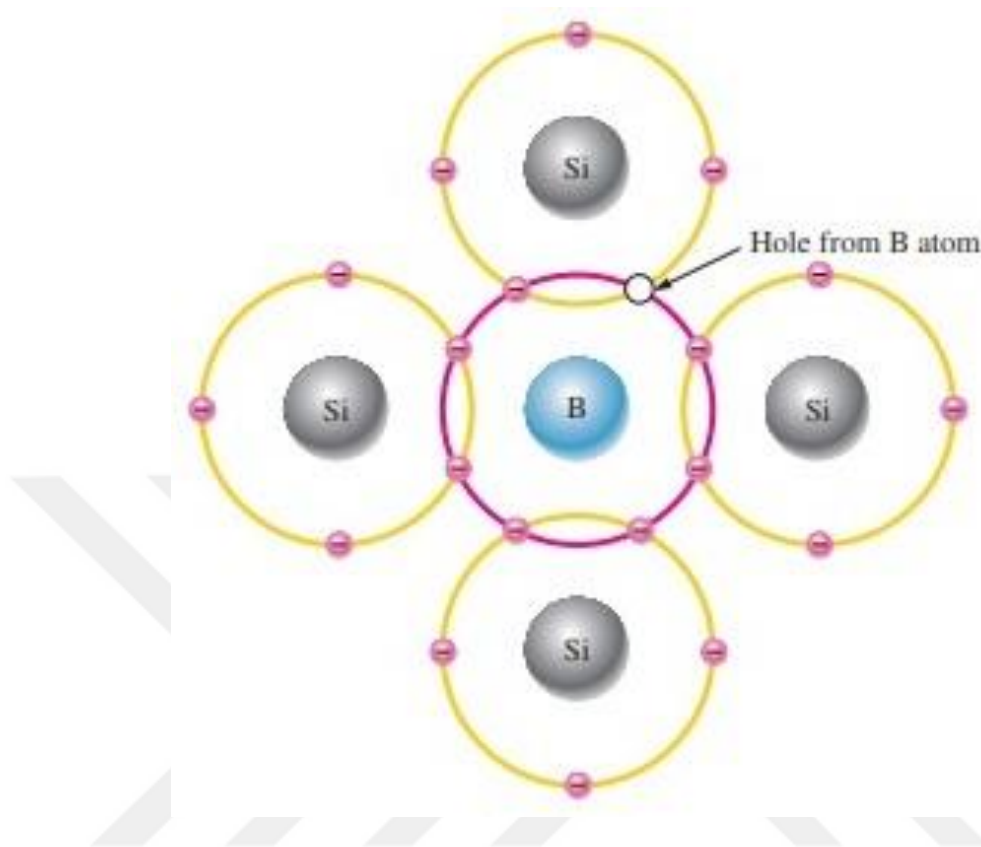


Figure 2.19 The illustration of B doped Si [87].

Semiconductors with a hole density higher than the electron density are called p-type semiconductors. Depending on the acceptor density, the hole density will be greater than the electron density, so the contribution from the hole to the electrical conductivity will be greater in p-type semiconductor materials [90].

2.9 The pn Junction

Fermi energy level is close to the conduction band in n-type semiconductors, while it is close to the valence band in p-type semiconductors. When these two materials come together, some of the conduction electrons are on one side of the junction and the majority of holes are on the other side of the junction. In this case, some of the electrons pass to the p-side and this phenomenon is called diffusion. Similarly, the holes pass to the n-side of the junction as in figure 2.20. In the meantime, electrons and holes combine with each other to form an area called the depletion region, where there is no moving charge around the junction. This diffusion process continues until the Fermi

levels of the two semiconductor regions become equal. Due to this diffusion in the junction region, there is no longer equal charge in this region, only ionized additive atoms are found in the depletion region. This creates a zone of opposite charged on both sides of the junction region. These fixed oppositely charged ions also generate a barrier potential that effectively opposes the movement of free charge carriers from the junction to the other side. Every free charge carrier entering the junction region encounters a force pushing it back from the depletion region. In other words, an electric field is formed due to the unbalanced charge originating from the ionized donor and acceptor atoms in the junction region. Since the Fermi level of a p-n junction must be constant across the junction in thermodynamic equilibrium, a band bending occurs in the junction. Free charge carriers need extra energy to overcome the electrical force created by the stationary ions in the junction to cross the depletion region. In other words, the junction acts as a barrier against the charge flow [84, 92]. This barrier is illustrated in figure 2.21 by the bending of the conduction and valence bands in the depletion region.

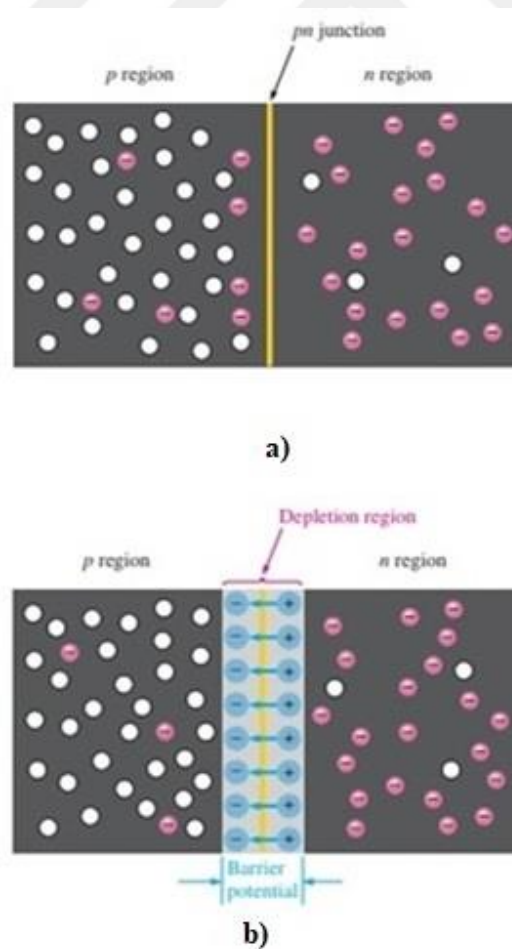
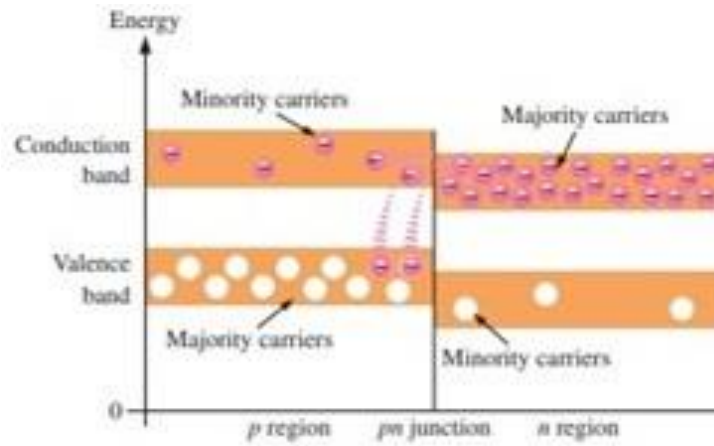
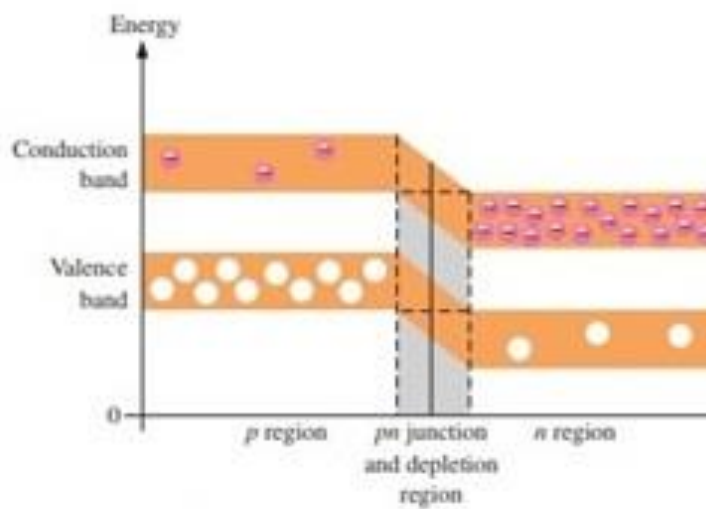


Figure 2.20 Formation of the depletion region [87].



a)



b)

Figure 2.21 Energy diagrams illustrating the formation of the pn junction and depletion region **a)** at the instant of junction formation, **b)** at equilibrium [87].

2.10 Metal/Semiconductor Contacts

When metal and semiconductor are connected with each other, there is transporting of charge both from metal to semiconductor and from semiconductor to metal until thermodynamic equilibrium is established, that is, until the Fermi energy levels of both materials are equal. Therefore, a potential barrier height ϕ_B is formed by the separation of charges at the metal-semiconductor interface. This region is called Schottky barrier. According to the Schottky-Mott theory, the barrier height arises from the difference between the work functions of the two materials.

The minimum energy required to flow an electron from the Fermi level to the vacuum level is defined as the work function, and the work function of the metal is denoted by ϕ_m and the work function of the semiconductor is indicated by ϕ_s . The Fermi energy level depends on the amount of acceptor and donor atoms in the material. On the other hand, electron affinity is an important parameter for semiconductors and it does not change with dopant atoms. Electron affinity is the amount of energy required to move an electron from the top of the conduction band to the vacuum level and it is denoted by χ_s . Figure 2.22 shows the energy level diagram between metal and semiconductor.

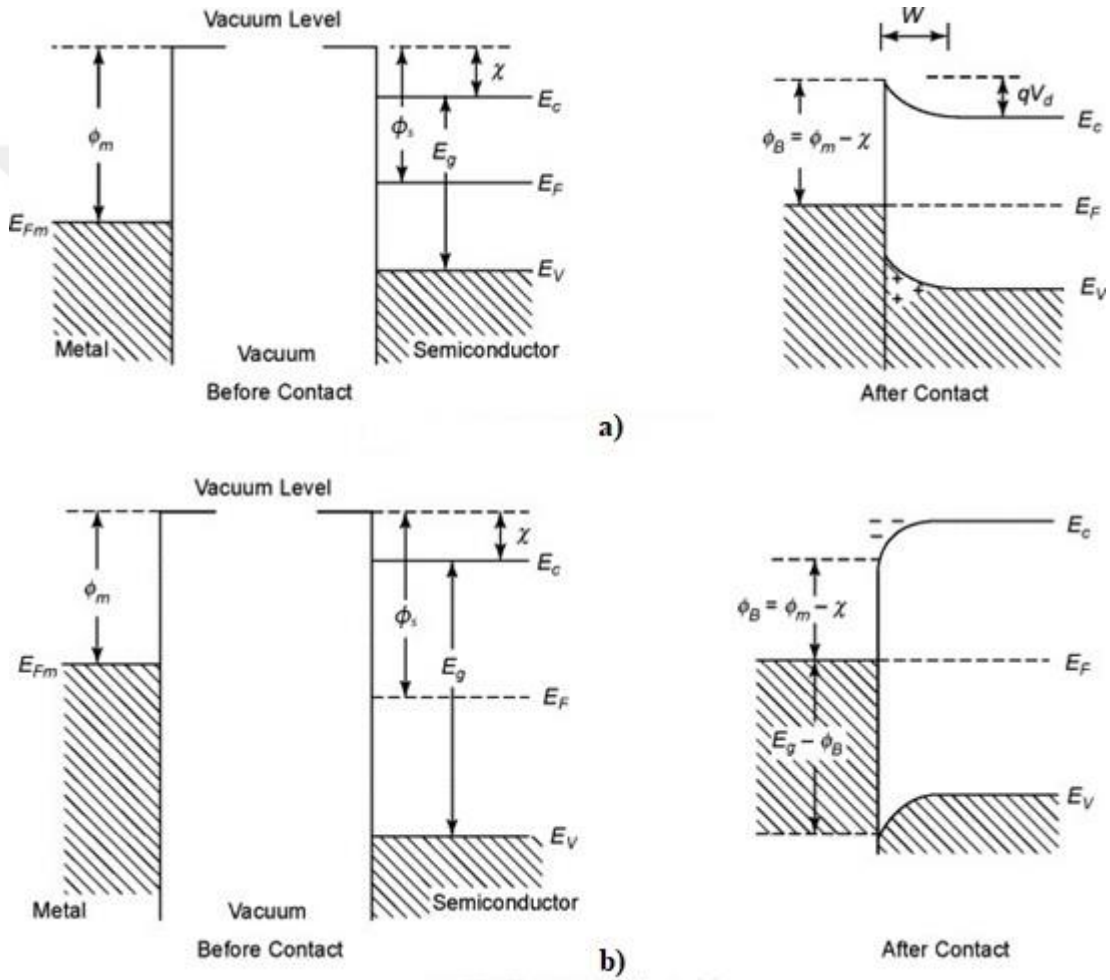


Figure 2.22 Energy level diagram between metal and semiconductor **a)** $\phi_m > \phi_s$ **b)** $\phi_m < \phi_s$ [93].

There are two types contact in metal-semiconductor contacts; rectifier and ohmic. Whether the contact is ohmic or rectifier contact depends on the work functions of the metal and semiconductor. In metal/n-type semiconductor contacts, a rectifier contact occurs if $\phi_m > \phi_s$ and an ohmic contact occurs if $\phi_m < \phi_s$. On the other hand, in metal/p-

type semiconductor contacts, a rectifier contact occurs if $\phi_m < \phi_s$ and an ohmic contact occurs if $\phi_m > \phi_s$ [93].

As the Figure 2.23, the fact that the work function of the metal is greater than the work function of the n-type semiconductor ($\phi_m > \phi_s$) indicates that the number of free electrons is less in the metal and more in the semiconductor. In other words, the Fermi level in metal is lower than that of semiconductor [94].

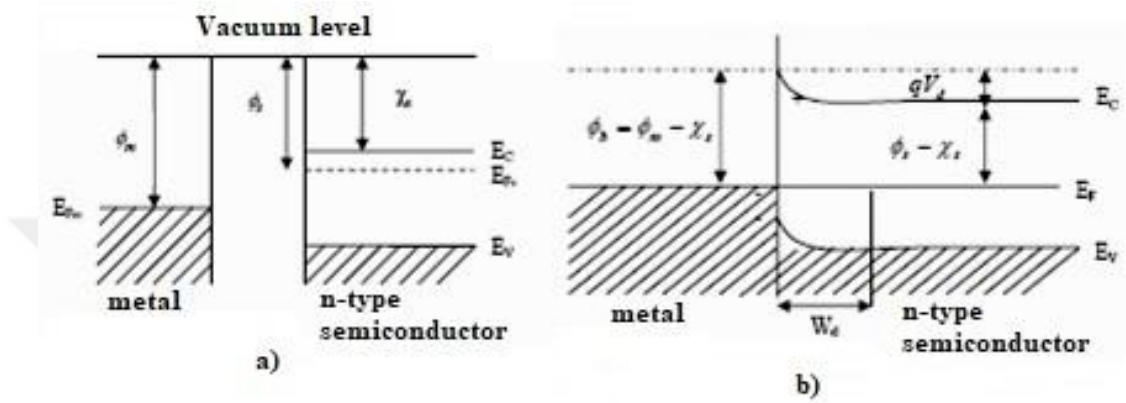


Figure 2.23 The energy band diagram between metal and n-type semiconductor **a)** before contact, **b)** after rectifier contact [95].

When the metal is contacted with n-type semiconductor, the electrons in the semiconductor move to the metal and while making this transition, they leave behind ionized charge centers called donors. These positive charge centers form a space charge distribution. While the number of electrons on the semiconductor side decreases, it increases on the metal side. Increasing the number of electrons on the metal side does not change the Fermi energy level of the metal. The decrease in the number of electrons on the semiconductor side causes the Fermi energy level to shift downward on the semiconductor side. As a result of this, a potential barrier spreading towards the semiconductors is formed. The barrier height in the semiconductor side is given [59];

$$qV_d = \phi_m - \phi_s \quad (2.15)$$

Where V_d is defined as the diffusion potential or the barrier height. The barrier height in the metal side of the contact is given;

$$q\phi_b = \phi_m - \phi_s \quad (2.16)$$

As seen in figure 2.23.b, electrons in the conduction band of the semiconductor encounter the barrier ($qV_d = \phi_m - \phi_s$) while passing to the metal. The potential barrier rising vertically on the metal side has width W_d inside the semiconductor, so that a charge-free region is formed on the semiconductor side and is called the Schottky region, barrier region or space charge region [96]. This intermediate region exhibits capacitance and behaves like a capacitor. This is called the Schottky capacity. The thickness of the barrier layer depends on the number of ionized donors and the diffusion barrier height.

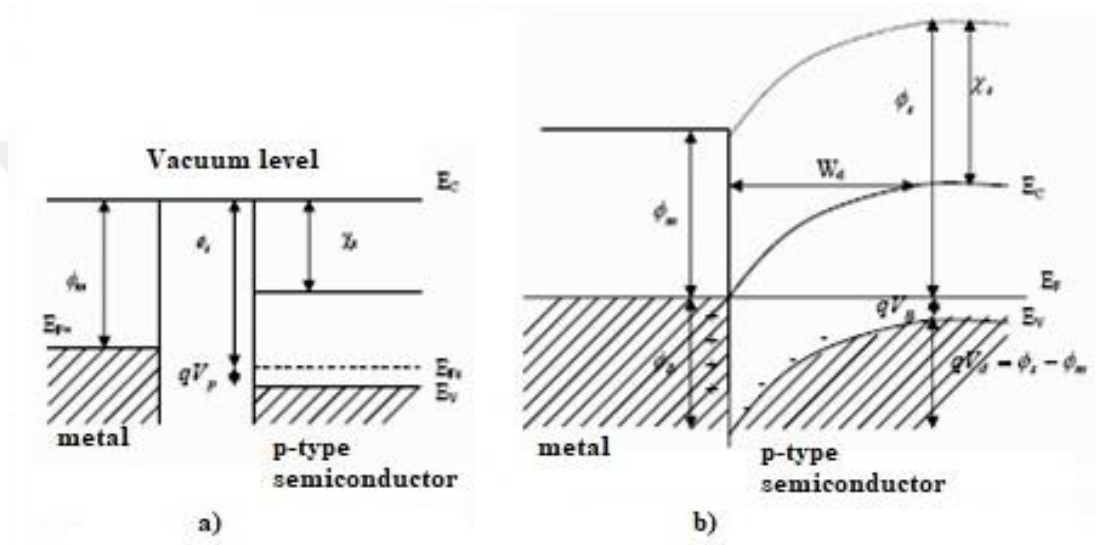


Figure 2.24 The energy band diagram between metal and p-type semiconductor **a)** before contact, **b)** after rectifier contact [95].

The figure 2.24 shows the energy band diagram between the metal and p-type semiconductor before and after contact. Before contact, the Fermi energy level of the semiconductor is below that of the metal by $(\phi_s - \phi_m)$. After contact, electrons flow from the metal into the semiconductor until the Fermi levels of the metal and the semiconductor become equal. The density of the holes in the space charge region is very small relative to the density of the acceptors and can be neglected. For this reason, a depletion layer with a thickness W_d is formed in the semiconductor side of the contact. Thus, the space charge region is filled with ionized acceptor atoms. For holes in the semiconductor side, the barrier height is defined [59];

$$qV_d = \phi_s - \phi_m \quad (2.17)$$

Figure 2.25 shows the metal/n-type contact at the forward and reverse bias condition. When a positive voltage is applied to the metal side of the contact, the situation is defined as the forward bias and the barrier height on the metal side remains the same, while the potential barrier on the semiconductor side decreases due to the space charge density in this region. Since the energy levels in the conduction band increased by qV_F , the potential barrier decreases by qV for electrons moving from the semiconductor to the metal and the electron transition from the metal to the semiconductor becomes easier. The current through the contact increases exponentially with the applied voltage [97].

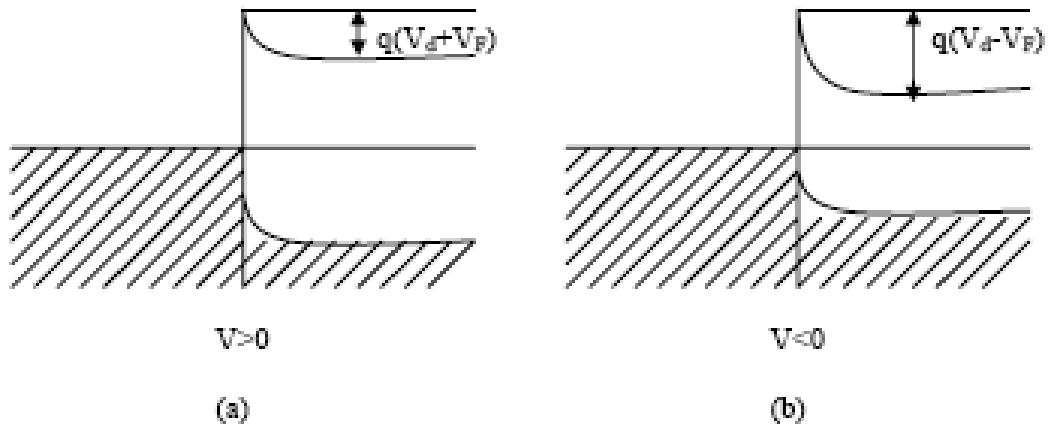


Figure 2.25 Energy band diagram of rectifier metal/n-type contact under **a)** forward bias, **b)** reverse bias conditions [95].

When a negative voltage is applied to the metal side of the contact, this situation is called reverse bias. The part of the barrier on the semiconductor side rises with the applied voltage. This makes it difficult for electrons to pass and the current from the contact semiconductor to the metal decreases. Since there will be no electron transfer from the semiconductor to the metal after a certain reverse bias, only electrons that from the metal to the semiconductor via the thermionic emission causes the current passing through the contact [97].

2.11 The Current Transport Mechanism in Metal/Semiconductor Contacts

Thermionic emission (TE), diffusion, Thermionic emission-diffusion, Thermionic field emission (TFE), Field emission (FE), Minority carrier injection, Generation-

recombination and Tunneling are the main current-transport mechanisms in MS contacts. The current transportation is provided by the majority carriers. Figure 2.26 gives the current transport mechanism in metal/n-Si under forward bias. In the Figure, (1), (2), (3), (4) and (5) show thermionic emission, tunneling, recombination, diffusion of electrons, diffusion of holes, respectively [98].

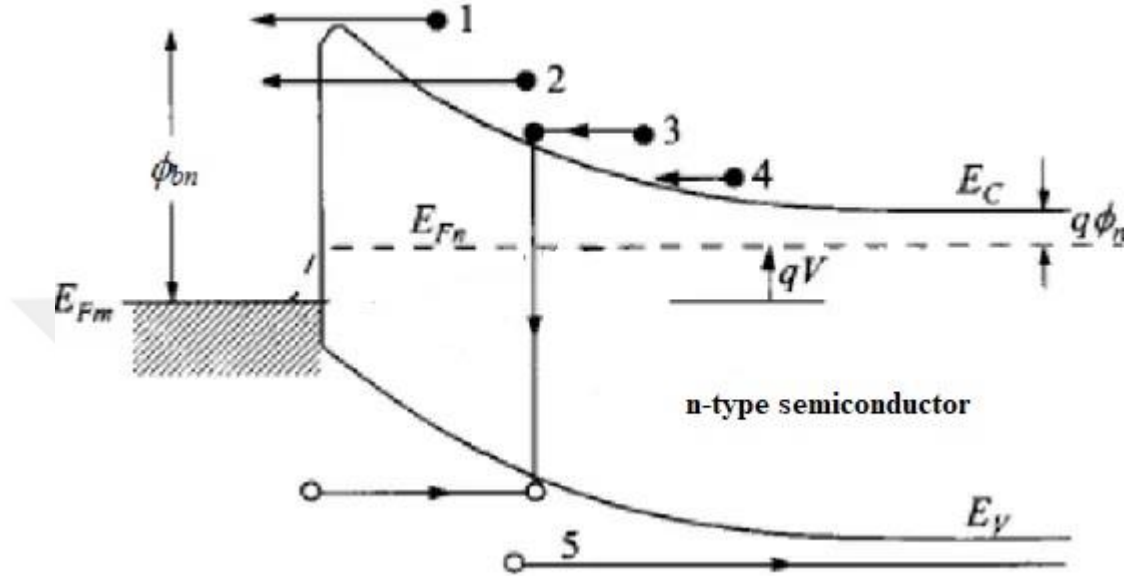


Figure 2.26 The current transport mechanisms in semiconductor under forward bias [95].

2.11.1 Thermionic Emission Theory

The transition of carriers that gain sufficient thermal energy in Schottky contacts from semiconductor to metal or from metal to semiconductor is known as TE phenomenon. The basic assumption of the TE theory, which Bethe established by accepting that the current is transmitted by majority carriers in MS contacts, are as follows [99]:

- The barrier height ($q\phi_B$) is much larger than the kT energy.
- The thermal balance has been established and the flow of net current does not affect this balance.
- The shape of the barrier profile is unimportant and the current depends on the barrier height.
- There are no carrier collisions in the Schottky region. That is, the mean free paths of the carriers are greater than the thickness of the Schottky zone.
- The effect of image forces is neglected.

The current density from the semiconductor to the metal is determined depending on the energy and orientation of the electron distribution with enough energy to exceed the potential barrier. The current $I_{s \rightarrow m}$ from the semiconductor to the metal is expressed by the number of electrons that have enough energy to cross the potential barrier and their velocity;

$$I_{s \rightarrow m} = \int_{\phi_F + q\phi_b}^{\infty} qv_x A dn \quad (2.18)$$

Where, $\phi_F + q\phi_b$ is the minimum energy required for thermionic emission into the metal, v_x is the carrier velocity and A is the effective area. Using these expressions, the current for electrons passing from the semiconductor to the metal is expressed as;

$$\begin{aligned} I_{s \rightarrow m} &= \left(\frac{4\pi q m^* k^2}{h^3} \right) A T^2 \exp \left[-\frac{q(V_n + V_p)}{kT} \right] \exp \left(\frac{qV}{kT} \right) \\ &= A A^* T^2 \exp \left(-\frac{q\phi_b}{kT} \right) \exp \left(\frac{qV}{kT} \right) \end{aligned} \quad (2.19)$$

Here in, k is Boltzmann constant, h is Planck constant, m^* is described as an effective mass and ϕ_b is known as the barrier height ($\phi_b = V_n + V_d$). A^* is Richardson constant and it is defined following equation and it is 32 A/cm^2 for p-type Silicon.

$$A^* = \frac{4\pi q m^* k^2}{h^3} \quad (2.20)$$

Since the barrier height remains the same for electrons moving from the metal to the semiconductor, the current density flowing into the semiconductor is not affected by the applied voltage. This current density is equal to the current density passing from the semiconductor to the metal at equilibrium ($V=0$). Accordingly, the current passing from the metal to the semiconductor is;

$$I_{m \rightarrow s} = -A A^* T^2 \exp \left(-\frac{q\phi_b}{kT} \right) \quad (2.21)$$

The total current density is sum of the equations (2.19) and (2.21).

$$I_n = \left[A A^* T^2 \exp \left(-\frac{q\phi_b}{kT} \right) \right] \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] = I_0 \left[\exp \left(\frac{qV}{kT} \right) - 1 \right] \quad (2.22)$$

Where I_0 is the saturation current and is defined using equation (2.23).

$$I_0 = AA^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2.23)$$

2.11.2 Diffusion Theory

Diffusion is known as the charge transfer from a region of higher density region to a region of lower density. The diffusion theory given by Schottky is based on the following assumptions [99]:

- The barrier height is much larger than the kT energy.
- The collision effect of electrons in the barrier region is taken into account.
- Carrier concentrations at $x=0$ and $x=W$ have thermal equilibrium values and are not affected by diffusion by the following current.
- The current is limited by diffusion and drift.
- The impurity concentration in the semiconductor is not degenerate.

Since the current depends on the area and density difference in the depletion region, the current density equation is used.

$$J_x = J_n = q \left[n(x)\mu E(x) + D_n \frac{dn}{dx} \right] = qD_n \left[\left(-\frac{qn(x)}{kT} \right) \left(\frac{dV(x)}{dx} \right) + \frac{dn}{dx} \right] \quad (2.24)$$

Here in; $n(x)$, μ , D_n and $E(x)$ are electron density, mobility, diffusion constant and electric field in Schottky region, respectively. The current expression is given following equation for diffusion theory;

$$J = J_{SD} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (2.25)$$

Here in; J_{SD} is saturation current density and it is determined as;

$$J_{SD} = \left(\frac{q^2 N_C D_n}{kT} \right) \left[\frac{q(V_d - V) 2N_D}{\epsilon_s} \right]^{1/2} \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2.26)$$

Where; N_C , N_D , V_d and ϵ_s are the carrier density in the conduction band, the donor concentration, the diffusion potential and the permittivity of semiconductor. The expressions obtained from thermionic emission and diffusion theories are very similar.

However, the saturation current density of diffusion theory changes more quickly with voltage, but its temperature dependence is smaller than the saturation current in thermionic emission.

2.11.3 Thermionic Emission-Diffusion Theory

Crowell and Sze developed the TED model by combining TE and Diffusion theory. This theory is based on the recombination velocity (V_r) defined at the edge of the MS interface. A voltage applied between the metal and the semiconductor interface causes an electron flow towards the metal. This situation is illustrated in Figure 2.27 [100].

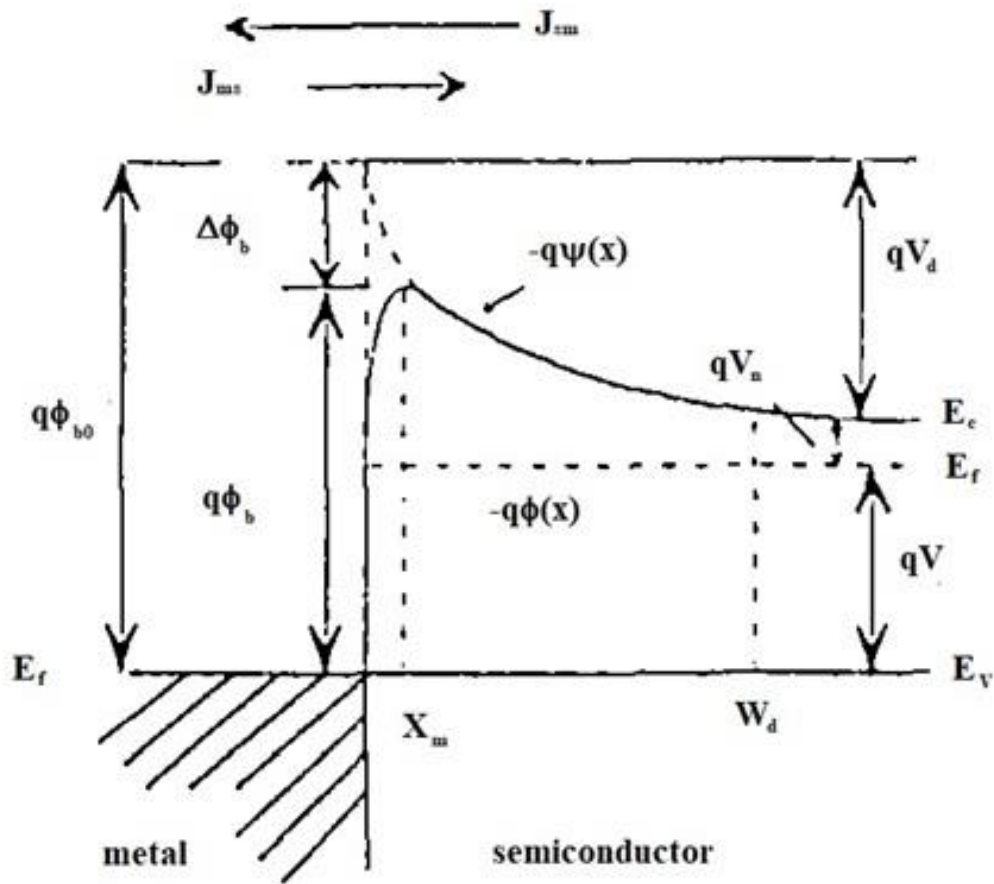


Figure 2.27 The energy band diagram [100].

Where $q\psi(x)$ is the potential energy of electron, $q\phi(x)$ is the half of the Fermi energy level. The current density throughout the region between x and W_d is given;

$$J_n = -qn\mu \left(\frac{d\phi_b}{dx} \right) \quad (2.27)$$

$$n_n = N_c \exp\left(-\frac{q(\phi_b - \psi)}{kT}\right) \quad (2.28)$$

Since some of the carriers undergo optical-phonon backscattering and some undergo quantum reflections, the value of the current decreases. Size attributed this to the decrease in recombination rate. According to this theory, when the probability of electrons oscillating from the MS interface over the potential barrier without interacting with the optical phonons and the average transmission coefficient values are considered, the Richardson constant A^* changes as A^{**} . Accordingly, J_0 is the saturation current density, and in the most general case J - V expression is;

$$J = J_0 \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) \quad (2.29)$$

Where J_0 is;

$$J_0 = A^{**} T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2.30)$$

And A^{**} is the modified efficient Richardson constant. An ideality factor n is defined in order to the deviations from an ideal diode. Accordingly, the current density expression is;

$$J = J_0 \exp\left(\frac{qV}{nkT}\right) \quad (2.31)$$

Due to the barrier reduction and the field dependence of A^{**} , n takes the values such that $1 < n < 1.2$ in Schottky diodes.

2.11.4 Field Emission (FE) and Thermionic Field Emission (TFE) Theory

Besides the TE mechanism, electrons can flow with tunneling across the barrier as quantum mechanically. This situation occurs in two types of tunneling illustrated in Figure 2.28.

Here, the semiconductor is heavily-doped and the Fermi level is below the conduction band. In low-doped semiconductors, the tunneling process also occurs in reverse bias [101]. Depletion region is quite thin due to heavily doping ratio. At low temperatures, electrons very close to the Fermi level can be tunneling from the semiconductor to the

metal. This process is called Field Emission Theory (FE). At high temperatures, a significant portion of the electrons rise above the Fermi level. These electrons can be tunneling into the metal without reaching the upper level of the barrier. The tunneling of these thermally excited electrons is known as Thermionic Field Emission (TFE). The number of electrons with energies above the Fermi level decreases rapidly. At the same time, the barrier thickness and height are also reduced. Therefore an energy is formed (E_m). The effect of TFE becomes maximum. If the temperature increases, the electrons are excited to higher energy levels and thus the probability of tunneling increases rapidly. Because the barrier to which electrons are exposed is thinner and lower. If the temperature increases further, all the electrons reach the top of the barrier, and this time the TE mechanism becomes important [102].

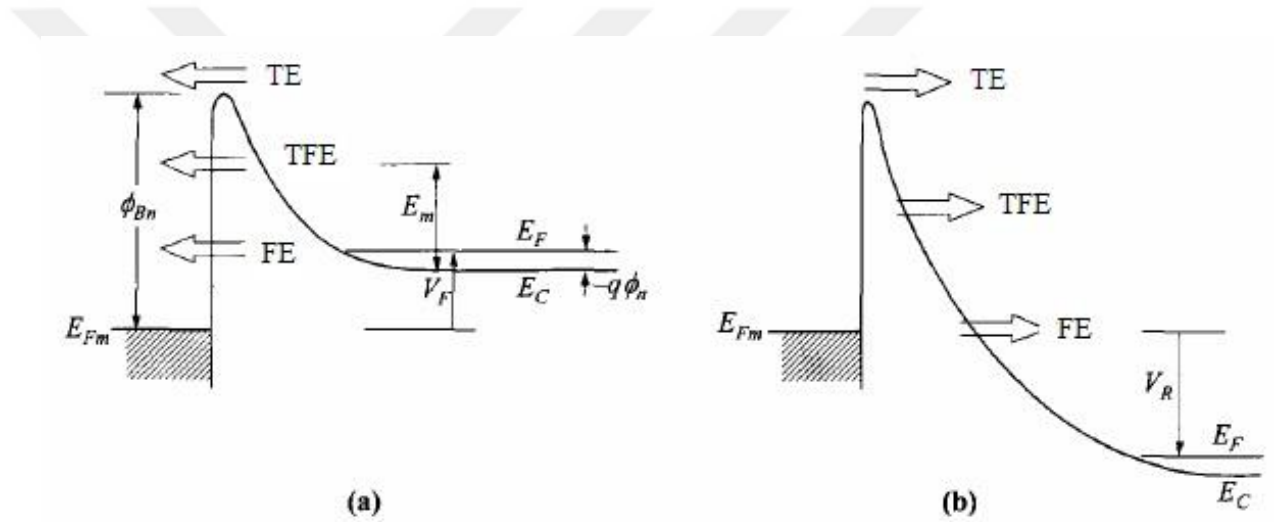


Figure 2.28 TFE and FE in Schottky barrier **a)** is forward bias, **b)** is reverse bias [95].

Padovani and Starton in 1966 and Crowell and Rideout in 1969 examined tunneling in Schottky barriers theoretically. FE occurs only in degenerate semiconductors under forward bias. I - V characteristics can be described under tunneling condition except very low forward bias as following equation.

$$I = I_s \exp\left(\frac{qV}{E_0}\right) \quad (2.32)$$

Here E_0 is;

$$E_0 = E_{00} \coth\left(\frac{E_{00}}{kT}\right) \quad (2.33)$$

And E_{00} is;

$$E_{00} = \frac{qh}{4\pi} \left(\frac{N_a}{m^* \epsilon_s} \right)^{1/2} \quad (2.34)$$

Where N_a is the acceptor concentration and m^* is the effective mass of the electron. I_s is voltage dependent as weakly and is a function of barrier height and temperature. E_{00} is an important determinant in the tunneling process and kT/E_{00} is an important parameter of tunneling emission and tunneling. At low temperatures, E_{00} takes a large value compared with kT and E_0 is nearly equal E_{00} . The slope of the $\ln I$ - V graph becomes constant and independent of T . In this case, field emission occurs. At high temperatures, that is $E_{00} \ll kT$, E_0 is equal kT . The slope of the $\ln I$ - V graph is q/kT , which corresponds to thermionic emission. For medium temperature values, we can write the slope as q/nkT .

Where;

$$n = \frac{E_{00}}{kT} \coth\left(\frac{E_{00}}{kT}\right) \quad (2.35)$$

The effect of TFE to the diode current is possible when $E_0 = kT$. When TFE has its maximum effect, the energy E_m is;

$$E_m = \frac{qV_d}{\left[\cos\left(\frac{E_{00}}{kT}\right) \right]^2} \quad (2.36)$$

Here, V_d correspond to the total band bending voltage, E_m is measured below the conduction band at the edge of the depletion region. TFE becomes important in silicon when $N_a > 10^{17} \text{ cm}^{-3}$ at $T = 300\text{K}$. At lower doping concentration, TFE can be neglected and TE becomes important.

2.12 The Band Diagram of Heterojunctions

A heterojunction is generally described as the interface between two different materials. These heterojunctions can be classified as abrupt or gradual according to the distance from one material to another near the interface. For example, for the first state,

the transition occurs at a few atomic distances and for the next state, it occurs at distances of order of several diffusion distances. Another classification is based on the type of conductivity of the material on both sides of the heterojunction. If two semiconductors have the same type of conductivity, the junction is known as isotype heterojunction, otherwise it is described as anisotype heterojunction.

The energy band profile near the interface plays an important role in understanding the current-conduction mechanism of a heterojunction. Theoretically, in the absence of interface states, the energy band profile of any heterojunction depends on the electron affinities, forbidden energy band gaps, and work functions of the two semiconductors forming the heterojunction. Among these three parameters, electron affinity and band gap are fundamental properties of a given semiconductor and are independent of doping. The work function changes depending on the doping.

Figure 2.29 shows the energy band diagram of two isolated semiconductors and an ideal abrupt heterojunction formed between these semiconductors. The electron affinity can be described as the energy required to remove an electron from the bottom of the conduction band to the vacuum level. The work function can be described as the energy required to remove an electron from Fermi level to the vacuum level. The difference between the conduction band of the semiconductors and the valance band of the semiconductors are given in equation (2.37) and (2.38), respectively [103].

$$\Delta E_c = q(\chi_2 - \chi_1) \quad (2.37)$$

$$\Delta E_v = E_{g1} + q\chi_1 - (E_{g2} + q\chi_2) = \Delta E_g - \Delta E_c \quad (2.38)$$

Here, ΔE_g is known as the energy difference between the band gaps of the semiconductors. As seen from the figure 2.29.b, it can be assumed that there is a negligible number of traps or generation-recombination centers at the interface of the semiconductors. This assumption can be valid only when the lattice constant of semiconductors are very close to each other.

The total built-in potential can be described;

$$V_{bi} = V_{b1} + V_{b2} \quad (2.39)$$

Herein V_{b1} and V_{b2} are the electrostatic potentials of the semiconductors at equilibrium and they can be expressed by following relations.

$$V_{b1} = \frac{\varepsilon_2 N_2 (V_{bi} - V)}{\varepsilon_1 N_1 + \varepsilon_2 N_2} \quad (2.40)$$

$$V_{b2} = \frac{\varepsilon_1 N_1 (V_{bi} - V)}{\varepsilon_1 N_1 + \varepsilon_2 N_2} \quad (2.41)$$

Where N_1 and N_2 are the donor concentration and the acceptor concentration, respectively. ε_1 and ε_2 are defined as the dielectric constant of the n-type and p-type semiconductors.

The depletion widths x_1 and x_2 can be obtained using following equations.

$$x_1 = \left[\frac{2N_2 \varepsilon_1 \varepsilon_2 (V_{bi} - V)}{q N_1 (\varepsilon_1 N_1 + \varepsilon_2 N_2)} \right]^{1/2} \quad (2.42)$$

$$x_2 = \left[\frac{2N_1 \varepsilon_1 \varepsilon_2 (V_{bi} - V)}{q N_2 (\varepsilon_1 N_1 + \varepsilon_2 N_2)} \right]^{1/2} \quad (2.43)$$

The equation 2.44 describe the capacitance C value of the heterojunction.

$$C = \left[\frac{q N_1 N_2 \varepsilon_1 \varepsilon_2}{2(\varepsilon_1 N_1 + \varepsilon_2 N_2)(V_{bi} - V)} \right]^{1/2} \quad (2.44)$$

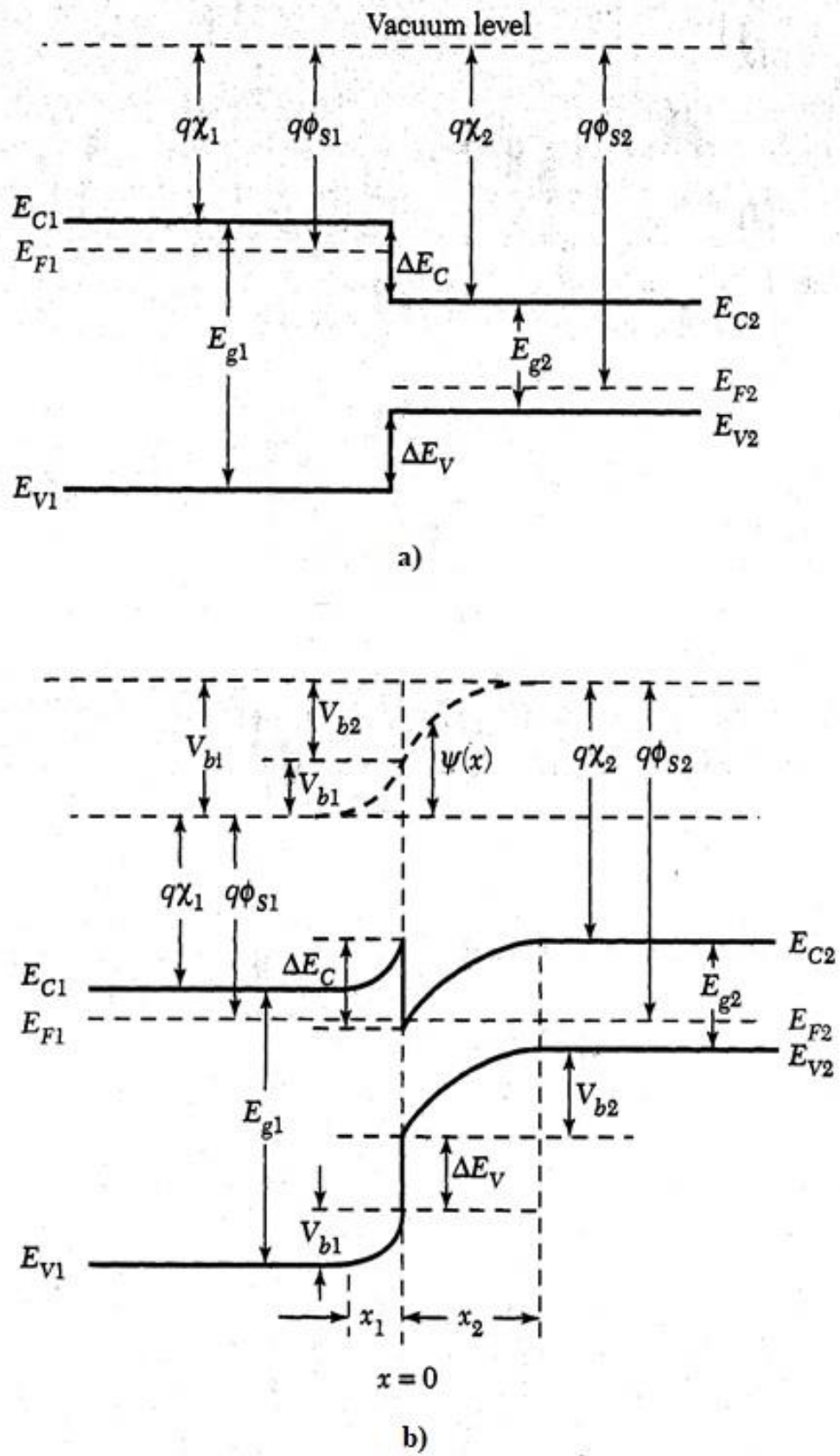


Figure 2.29 The energy band diagram of **a)** isolated semiconductors **b)** an ideal abrupt heterojunction formed these semiconductors [103].

2.13 Metal/Insulator/Semiconductor Contacts

An insulating layer is formed between the metal/semiconductor, sometimes spontaneously and sometimes intentionally. Such structures are often called metal/insulator/semiconductor (MIS) structures. These structures are very useful for studying semiconductor surfaces. MIS structures generally consist of a silicon substrate, an ohmic back contact coated on this substrate and a metal contact placed on an oxide or insulator layer. Figure 2.30 gives the schematic diagram of MIS structure and Figure 2.31 displays the energy band diagram of an ideal MIS diode at $V=0$.

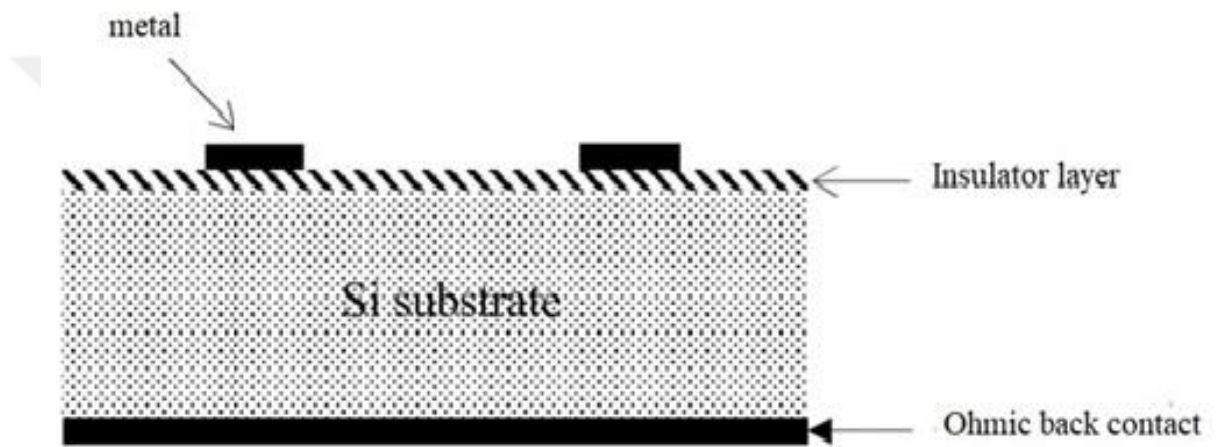


Figure 2.30 The schematic diagram of MIS structure [104].

In MIS structures, there is an interface in two separate regions. One of them is the metal/insulator interface and the other is the insulator/semiconductor interface. In an ideal case, the charges are located on the semiconductor and the metal surface close to the insulator. When dc voltage is applied, no current flows through the insulator. An ideal MIS diode has three equivalent circuits as seen in Figure 2.32. These systems are called accumulation, depletion and inversion. Figure 2.33 shows the energy band diagram of the ideal MIS structure. In fact, in MIS diodes, the settled states lie at the semiconductor/insulator interface and therefore differ from the ideal state. In some cases, current flows through the insulating layer in MIS diodes [105].

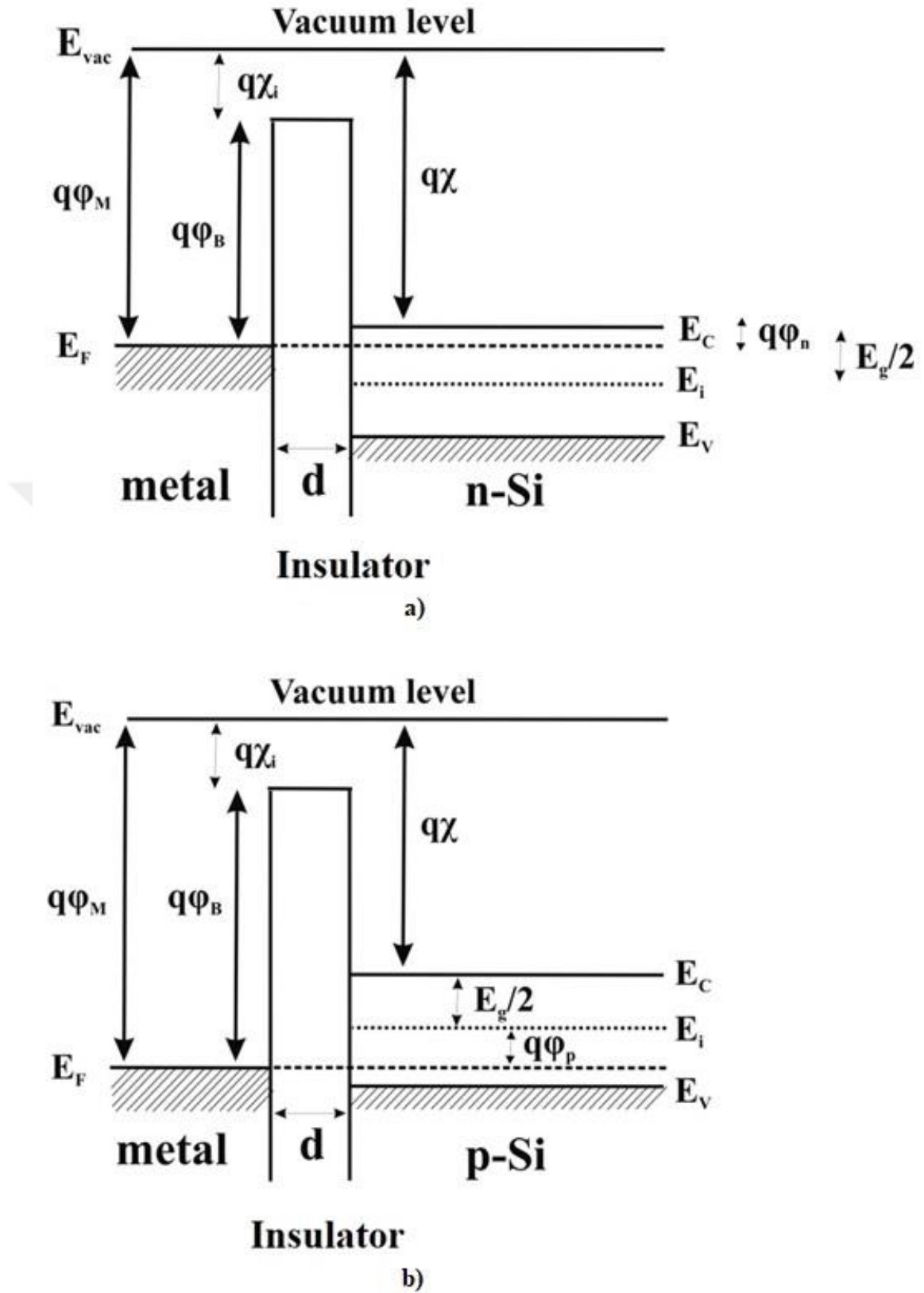


Figure 2.31 The energy band diagram of an ideal MIS diode at $V=0$ for **a)** n-type semiconductor, **b)** p-type semiconductor [106].

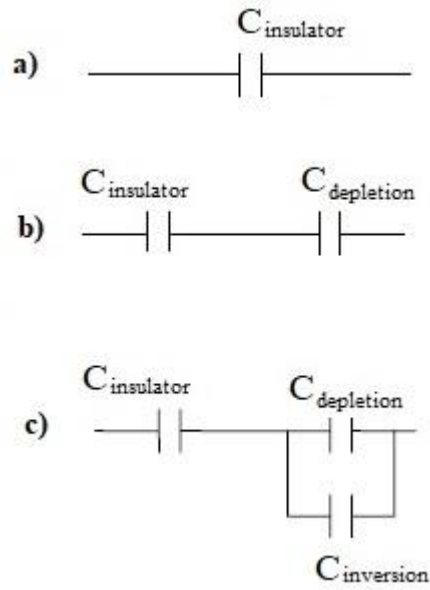


Figure 2.32 Equivalent circuits of the ideal MIS diode. **a)** accumulation, **b)** depletion and **c)** inversion region [95].

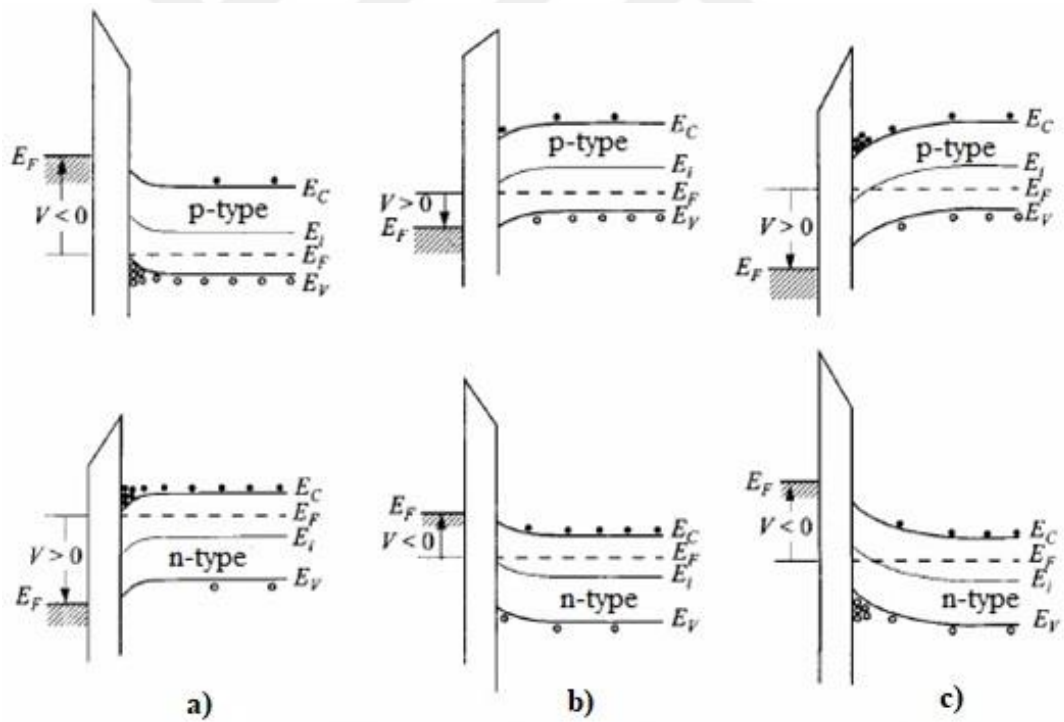


Figure 2.33 The energy band diagram of the ideal MIS structure **a)** accumulation, **b)** depletion and **c)** inversion [95].

The structure with the following features is defined as the ideal MIS structure:

- The difference between the work function of the metal and the work function of the semiconductor is zero at equilibrium ($\phi_{ms}=0$) ve it is determined following equations for n-type and p-type semiconductor, respectively.

$$\phi_{ms} = \phi_m - \left(\chi + \frac{E_g}{2q} - \phi_b \right) = 0 \quad (2.45)$$

$$\phi_{ms} = \phi_m - \left(\chi + \frac{E_g}{2q} + \phi_b \right) = 0 \quad (2.46)$$

Here, ϕ_b is the difference between the Fermi level and the Fermi level of the pure semiconductor.

- It behaves as an ideal dielectric because the band width of the insulator or oxide layer between the metal and semiconductor layers is large. There are no traps, fixed and live charges inside the insulator and at the insulator/semiconductor interface. At the same time, there are no interface states and interface charges at the insulator/semiconductor interface.
- The band gap of the insulator is so large that the charge carrier density in the conduction band of the insulator is negligibly small.
- Under DC voltage, there is no charge transfer in the insulator and it behaves like an infinite resistor.
- Under any bias voltage, the charges in the structure are adjacent to the insulator, those on the metal surface are equal to those on the semiconductor but they are oppositely charged.

2.13.1 Accumulation Process

When a negative voltage ($V < 0$) is applied to the metal electrode of the Metal/insulator/p-type semiconductor (MIS) structure, the electric field generated due to this voltage will attract the holes, which are the majority charge carriers of the semiconductor, towards the semiconductor interface like illustrated Figure 2.33.a. When there is no charge flow in an ideal diode, the Fermi energy level remains constant in the semiconductor. Since the carrier density is exponentially dependent on the energy difference, band bending causes the accumulation majority carriers near the semiconductor surface. This situation, in which the valance band approaches the Fermi level at the semiconductor interface and the conduction band bends upward

accordingly, is called accumulation due to the accumulation of the majority charge carriers at the interface. In this case, since the charge accumulated at the interface is the surface charge $C_{sc} \rightarrow \infty$, hence the equivalent capacity $C \rightarrow C_{ox}$ [95].

2.13.2 Depletion Process

When a small positive voltage ($V > 0$) is applied to the metal electrode of the metal/insulator/p-type semiconductor (MIS) structure, the electric field generated in the insulator removes the holes at the semiconductor interface from the surface. In this case, the hole density on the surface of the semiconductor begins to be smaller than the hole density in the interior of the semiconductor, and the bands bend downward. In the regions of the conduction band near the semiconductor surface, electrons begin to accumulate. On the semiconductor surface, in a region of width W that changes with the applied voltage, a depletion region is formed where the holes decrease. This region is called the depletion region and this event is known as the depletion shown in Figure 2.33.b.

2.13.3 Inversion Process

The bands bend downwards when a larger positive voltage ($V \gg 0$) is applied to the metal electrode of the metal/insulator/p-type semiconductor (MIS) structure. The intrinsic energy level (E_i) passes below the Fermi energy level. In this case, electrons, which are minority carriers, begin to increase on the surface of the semiconductor. The electron density is greater than the hole density. After this step, the p-type semiconductor surface behaves like an n-type semiconductor. This phenomenon is called inversion of the semiconductor surface. The energy-band state is shown in figure 2.33.c. In this case, the MIS capacity is determined by the ability of the electron density to follow the ac signal of the applied voltage. The electron density can follow the ac signal at small frequencies and accordingly the capacitance reaches the insulating capacitance value with increasing voltage. It can follow slower at intermediate frequencies, so intermediate frequency curves appear depending on the value of the frequency. At high frequencies, it cannot follow. The constant charge acts like a space charge and the capacitance remains at C_{min} . At high frequency, if the voltage is abruptly changed, the reversal charge accumulates later, due to the recombination rate of the minority carriers. This causes the curve to take below C_{min} [95].

2.14 Dielectric Materials

Although dielectrics are electrically insulators, they are materials that can store charge under external electric field and have high polarization capability. When the dielectric is placed in the electric field, the electric charges cannot travel through the material as in the conductive material, but they are positioned in the direction of the electric field, causing dielectric polarization. The only movement of the dielectric material placed in an electric field is small displacements of positive and negative charges in opposite directions. Due to dielectric polarization, positive charges are positioned in the direction of the field while negative charges are displaced in the opposite direction. This causes an internal electric field to be formed inside the dielectric that extends from one end to the other [107 - 109].

Figure 2.34 gives the schematic illustration of a parallel-plate capacitor with a surface area A and the distance between plates d . If a direct voltage is applied to these plates, the plates begin to accumulate. If one of the plates is assumed to be accumulated with $+Q$ and the other with $-Q$, the electric field between the plates is given by the following equation.

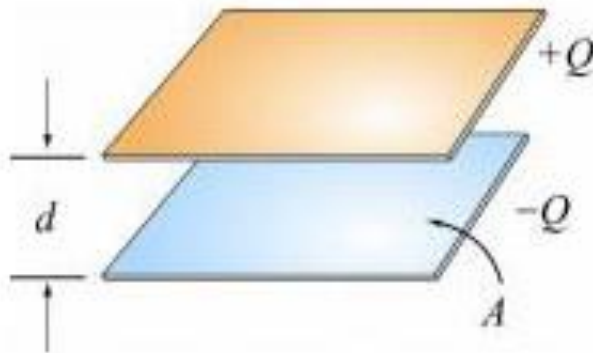


Figure 2.34 The schematic illustration of a parallel-plate capacitor [110].

$$E = \frac{\sigma_0}{\epsilon_0} \quad (2.47)$$

Where ϵ_0 is the permittivity of the free space (8.85×10^{-12} F/m) and σ_0 is called surface charge density.

The potential difference between parallel plates with a distance d between them is given equation 2.48.

$$V = Ed = \frac{\sigma_0 d}{\epsilon_0} \quad (2.48)$$

In this case, the capacity is defined by equation (2.49).

$$C = \frac{Q}{V} = \frac{A\epsilon_0}{d} \quad (2.49)$$

When dielectric material is placed between the plates, a decrease in potential difference occurs. This reduction occurs because the charges between the material and the plates neutralize each other. As a result, it continues to be accumulated a little more until the potential difference between the plates is equal to the applied potential difference. Thus, the capacitor is charged more. If the potential difference of the capacitor without dielectric material is defined by ΔV_0 , the decrease in applied potential difference is proportional to the dielectric constant of the material ϵ . Accordingly, the capacitor is accumulated with more charge.

$$\Delta V = \frac{\Delta V_0}{\epsilon} \quad (2.50)$$

$$C = \frac{A\epsilon}{d} = \epsilon C_0 \quad (2.51)$$

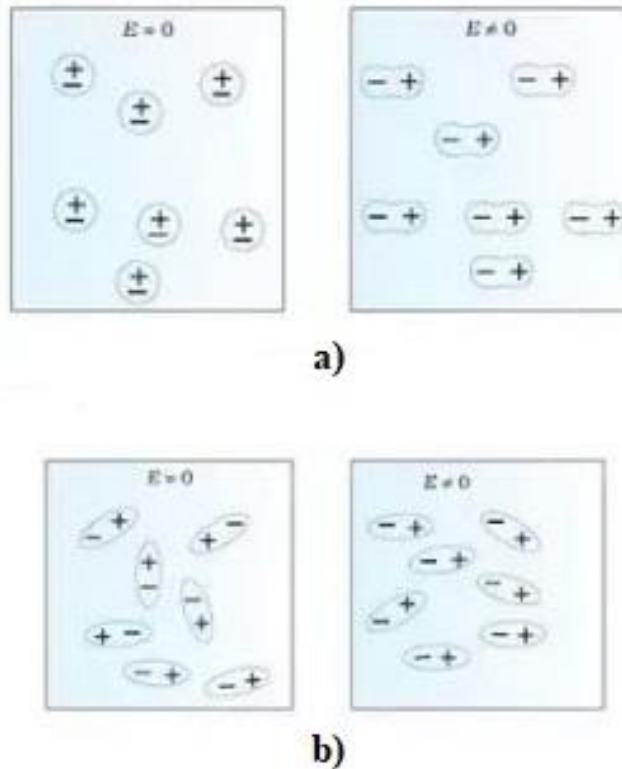


Figure 2.35 The polarization of **a)** non-polar molecules, **b)** polar molecules [111].

In the structures of some molecules, positive and negative charges do not overlap and there is an electric dipole. These are called polar molecules. They have permanent dipole moments even in the absence of an electric field. On the other hand, some molecules normally do not have dipole moments. But in an external electric field, they gain a dipole moment with the effect of opposite charges acting on positive and negative charges. These substances are called non-polar molecules [112]. The figure 2.35 shows the polarization of polar and non-polar molecules.

2.14.1 Polarization Mechanism

Polarizations in dielectric materials can be defined as electronic, ionic, dipolar and interfacial polarizations. Electronic and ionic polarizations occur faster than the others.

2.14.1.1 Electronic Polarization

It occurs in all atoms and ions with the application of the electric field and can be observed in all dielectrics even if other types of polarization are not present. A neutral atom consists of a positive nucleus at the center and electron clouds surrounding the nucleus. In this case, the charge centers in the atom are no longer coincident and induced dipole moments occur. The type of polarization that occurs in this way is called electronic polarization. Since the mass of the electron is very small, it is formed in a short time (10^{-15} s) with the applied external electric field and is almost independent of frequency.

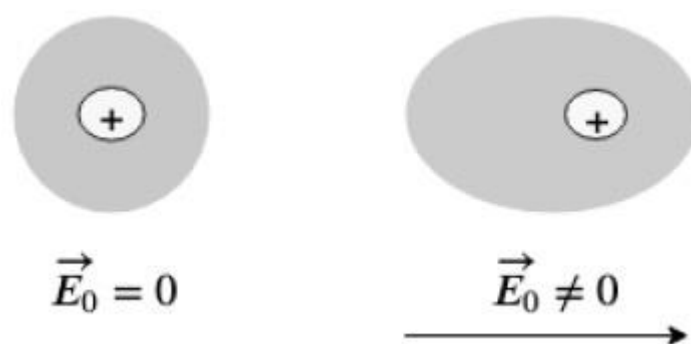


Figure 2.36 Schematic diagram of electronic polarization [108].

2.14.1.2 Ionic Polarization

It occurs by the propagation of positive and negative ions that are close to each other under an applied electric field. Since the molecules are composed of different atoms,

the shared electrons will not be homogeneously distributed. Atoms acquire charges of opposite polarity, as the scattering will be by the direction of electrons towards atoms with strong bonds. With the effect of an external electric field on these charges, the atoms orient themselves. As a result, the charged atoms will shift from their equilibrium positions by displacing each other. An interacting second dipole moment created by this displacement is the ionic polarization of the dielectric. It takes place in a short time ($10^{-12} - 10^{-13}$ s) however, it takes longer than electronic polarization.

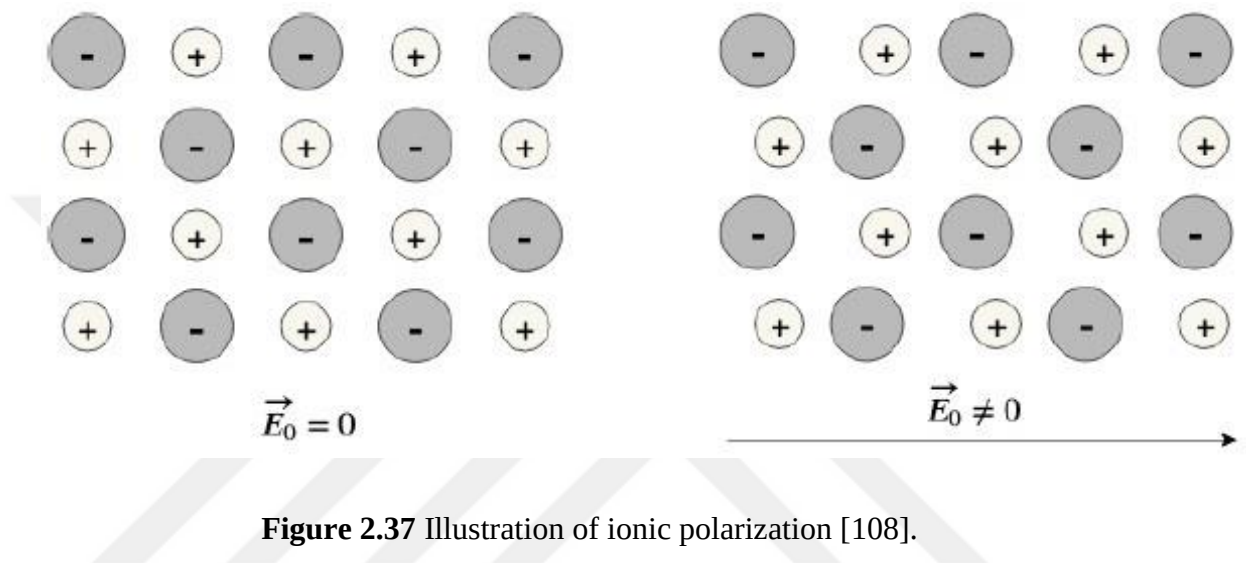


Figure 2.37 Illustration of ionic polarization [108].

2.14.1.3 Dipolar Polarization

Dipolar polarization occurs in dielectrics, called polar substances, which contain electric dipole moments even in the absence of an external electric field. Some dielectrics have quadrupole, octopole, etc. multipolar can also be found. But they contribute little to polarization. To such electric moments the external electric field will apply a torque, forcing it into the same orientation as itself, resulting in directional polarization. Temperature effects must also be considered in directional polarization. In orientation polarization, a time that is directly proportional to the size of the molecules and the viscous of the medium is needed for the molecules with dipole moments to return to their state before the field is applied. It takes places in a longer time, in the range of $10^{-3} - 10^{-9}$ s.

In this polarization, permanent dipoles are forced to rotate by external electric field effect and are not effective in rapid changes of field. It happens at low frequencies.

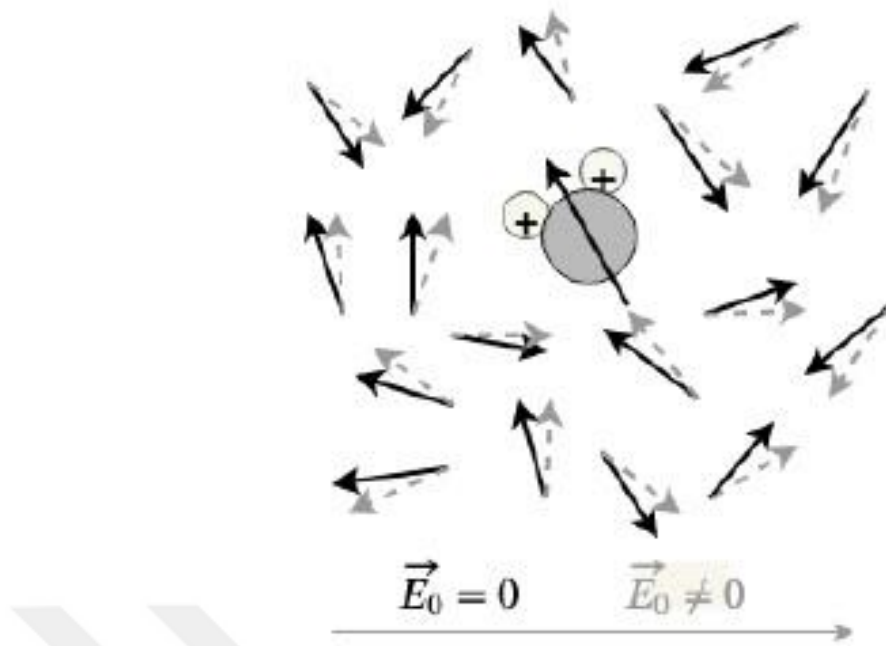


Figure 2.38 Schematic diagram of dipolar polarization [108].

2.14.1.4 Interfacial Polarization

Unlike other polarization mechanisms that occur with the displacement and orientation of the bound charges, the interface polarization consists of moving charges. Charge carriers are heterogeneously distributed due to defects in the surface charges that make up the material due to different reasons. Because of this distribution, free space charges move in part. In this way, interface-space charge polarization occurs. Since dielectrics have low conductivity, these charges move slowly. That is why it takes about 10^2 s, longer than other mechanisms.

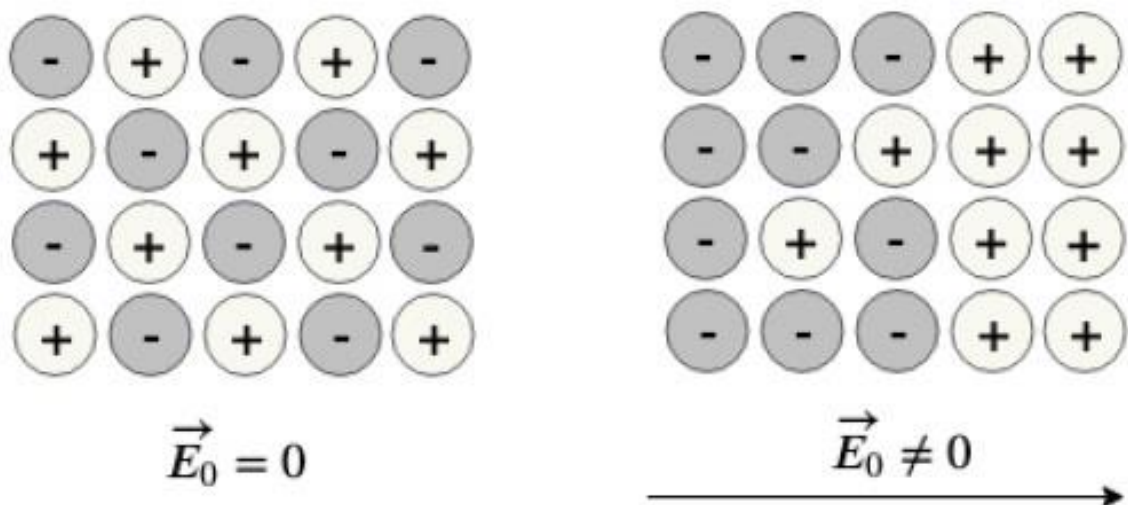


Figure 2.39 Illustration of interfacial polarization [108].

2.15 Photodiodes

A semiconductor pn junction device which converts light to electric current are called photodiodes. The current is produced by absorption of photons by the photodiode. Photodiodes may contain optical filters, built-in lenses, and have large or small surface areas. Generally, increasing the surface area of photodiodes causes slower response time. The common, conventional solar cell used to generate solar power is a large-area photodiode. The photodiode operates in reverse bias [113].

Photodiodes differ from normal semiconductor diodes in that they have a window or optical fiber connections so that light can reach the device. In many diodes specifically projected for use as a photodiode, it is preferable to use a PIN junction instead of a pn junction, as the response speed is desired to be rise. The photodiode family includes the metal-semiconductor (Schottky barrier) photodiode, heterojunction photodiode, pin photodiode and pn photodiode [114].

After a photon with enough energy arrives at the diode, thus an electron-hole pair is created. This operation is called the internal photoelectric effect. If absorption happens in the depletion region of the junction or at a diffusion length from it, these carriers are swept from the junction by the built-in energy of the depletion region. Thus, the holes move to the anode and the electrons move to the cathode and then a photocurrent is generated. The total current through the photodiode is the sum of the photocurrent and dark current produced in the absence of light. If the dark current is minimized, the sensitivity of the device is maximized [115].

2.15.1 Heterojunction Photodiode

The heterojunction formed between two semiconductors with different band gaps can exhibit photodiode properties. A heterojunction photodiode is formed from a wide-bandgap transparent material that serves as a window for the transmission of incoming optical power, so that the quantum efficiency is not seriously dependent on the junction distance from the surface. This is one of the biggest advantages of heterojunction photodiodes. Besides, heterojunction provides unique materials combination. Thus, response speed and quantum efficiency can be optimized for different wavelengths. Another advantage is a reduced dark current. If a heterojunction is obtained using two semiconductors with close lattice constants, low leakage current is observed [102].

Figure 2.34 illustrates the heterojunction photodiode with substrate and top illumination.

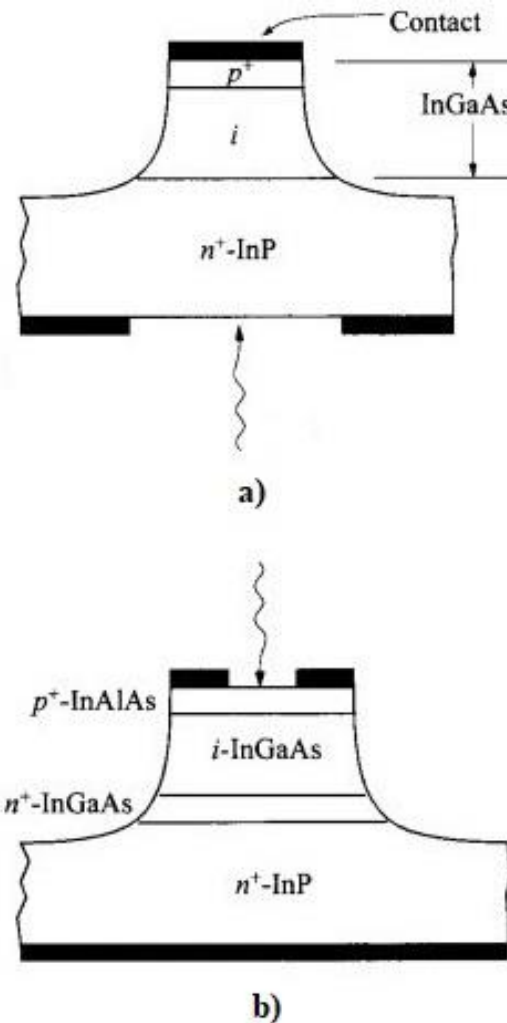


Figure 2.40 The illustration of heterojunction photodiode illuminated from **a)** substrate **b)** top [102].

2.15.2 Metal-Semiconductor Photodiode

A metal semiconductor diode can be used a high efficiency photodetector. The photodiode can be operated in two modes, depending on the photon energy. If $h\nu > E_g$, the radiation produces electron-hole pairs in the semiconductor. In this case, the basic principles of the photodiode are very parallel to those of a pin photodiode. For smaller photon energy, which means longer wavelength, the photo-excited electrons in the metal can cross the barrier and be collected by the semiconductor. This process is known as internal photoemission and is widely used to define the Schottky barrier height and to study the hot electron transport in metal films [102].

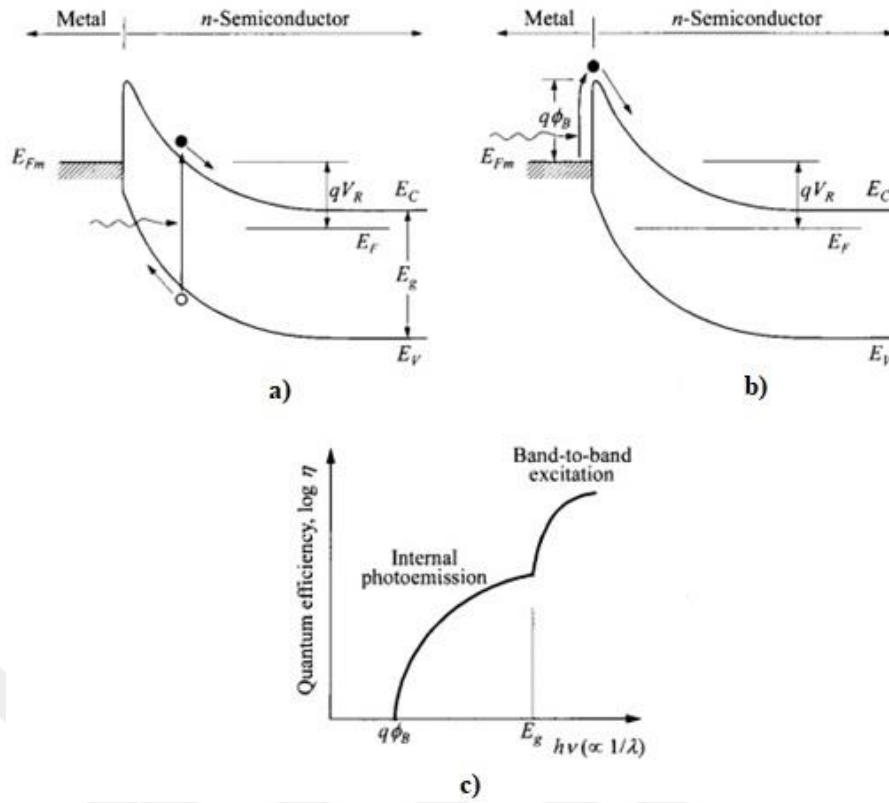


Figure 2.41 a) Band to band excitation of electron hole pair ($h\nu > E_g$) b) Internal photoemission of excited electrons from metal to semiconductor c) Quantum efficiency as a function of wavelength showing both processes [102].

2.16 The Current-Voltage (I - V) Parameters of the Contacts

For a Schottky diode with thin oxide layer of the same thickness everywhere, the relationship between the applied forward bias voltage and the current following through the structure is considered to result from the thermionic emission current and is expressed by the following equation [116].

$$I = I_0 \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (2.52)$$

Here in, I_0 is known as the saturation current, k is defined as Boltzmann constant and q is electron charge. In fact, the I - V characteristic in diodes does not satisfy the ideal situation in equation (2.52). The current expression for the real diode is;

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \left[1 - \exp\left(\frac{qV}{nkT}\right) \right] \quad (2.53)$$

Herein, n is the ideality factor and the equation can be rewritten for $V > 3kT/q$ [117];

$$I = I_0 \exp\left(\frac{qV}{nkT}\right) \quad (2.54)$$

The graph of the $\ln I$ - V is the straight line. The slope of this graph gives the ideality factor n of the diode. The saturation current value of the diode is determined using the intercept of the current axis. In the case where the current originating from the thermionic emission mechanism is effective, the saturation current can be expressed by the following equation.

$$I_0 = AA^*T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad (2.55)$$

Where, A is the effective diode area (0.052cm^2), A^* is the Richardson constant and ϕ_b is the barrier height.

There are deviations from the ideal condition when determining the electrical characteristics of MS and MIS structures. One of the reasons for these deviations is the series resistance effect. This can be happen for a variety of reasons. These are **i)** conductive wire taken from the rectifier contact for measurement, **ii)** ohmic back contact on the silicon crystal, **iii)** a dirty film layer or foreign matter placed between the body and the ohmic contact, **iv)** the body resistance between the ohmic back contact and the depletion layer on the silicon surface edge under the rectifier contact and **v)** the non-uniform doping distribution in the silicon under the rectifier contact. This effect can be reduced in various ways. The most widely used method is to precipitate the metal on the semiconductor surface by applying heat treatment to the back contact. This is known as the alloy process in semiconductor technology.

One of the methods used to define the series resistance value was developed by Norde [118]. Norde tried to obtain the series resistance and barrier height for $n=1$ with help of a defined function $F(V)$. Since this method is applied to conduction where R_s and ϕ_b do not change with temperature, only the measured I - V curve is needed for a one temperature value. After that, Sato and Yasamura [119] improved the method presented by Norde and showed that n , R_s and ϕ_b values can be calculated even when the ideality factor is greater than 1. Since this method can also be applied to situation where R_s and ϕ_b change with temperature, I - V curves at least two different temperatures are needed. The Norde function can be defined by the following equation.

$$F(V) = \frac{V}{2} - \frac{kT}{q} \ln \left(\frac{I}{AA^*T^2} \right) \quad (2.56)$$

On the other hand, Bohlin [120] rearranged the function determined by Norde, which made it possible to determine R_s , ϕ_b and n obtained from the I - V measurements of the Schottky barrier diode when the ideality factor is greater than 1 ($1 < n < \gamma$).

$$F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln \left(\frac{I}{AA^*T^2} \right) \quad (2.57)$$

Where, γ is an integer greater than the ideality factor. With the help of the Norde function, the barrier height and series resistance values is expressed with the following equations.

$$\phi_b = F(V_{min}) + \frac{V_{min}}{\gamma} - \frac{kT}{q} \quad (2.58)$$

$$R_s = \frac{kT(\gamma - n)}{qI_{min}} \quad (2.59)$$

Here in, $F(V_{min})$ is the minimum $F(V)$ value corresponding to the minimum voltage value in the graph of $F(V)$ - V .

Lien et al. [121] suggested another method to calculate R_s and n values. According to this method, $F(V_{min})$ must be found for several γ values. If β is defined as $\beta = q/kT$, the plot of I_{min} versus γ/β is a linear. The slope of this graph gives R_s and n can be calculated using intercept of this graph.

The series resistance (R_s) effect can be found with the help of the functions developed by the Cheung's also [122]. According to this method, the series resistance is effective from the exact bending point of the $\ln I$ - V graph. If the logarithm of both side of equation (2.53) is taken and rearranged according to this method;

$$V = \left(\frac{nkT}{q} \right) \ln \left(\frac{I}{AA^*T^2} \right) + n\phi_b + IR_s \quad (2.60)$$

and if the derivative of the new equation with respect to $\ln I$ is taken;

$$\frac{d(V)}{d(\ln I)} = \frac{nkT}{q} + IR_s \quad (2.61)$$

The slope of the $dV/d\ln I$ - I graph gives the ideality factor of the diode and intercept of the plot gives the series resistance value. In order to found the barrier height, a function $H(I)$ can be defined.

$$H(I) = V - \left(\frac{nkT}{q}\right) \ln\left(\frac{I}{AA^*T^2}\right) = n\phi_b + IR_s \quad (2.62)$$

The graph of the $H(I)$ - I is the linear. The slope of this graph gives the series resistance value and the barrier height is found using the intercept point of the graph.

The presence of interfacial traps and oxide charges for a MIS structure affects the measured ideal electrical characteristics of that structure [105]. Surface states N_{ss} are divided into two as slow and fast. Slow surface states are found on the metal side of the insulator. These are formed by stationary charges in the oxide structure and thermally excited ions moving in an electric field. These do not affect the capacity of the MIS structure. Fast surface states, on the other hand, are located near the insulator/semiconductor interface and have energies near the middle of the forbidden energy region of the semiconductor. Therefore, since with the change of the surface potential, in other words, the band bending, the surface states will move up and down, there is a sudden charge exchange with the conduction and valance bands.

For the MIS structure the density of interface states is described as [116];

$$N_{ss}(V) = \frac{1}{q} \left[\frac{\varepsilon_i}{\delta} (n(V) - 1) - \frac{\varepsilon_s}{W_D} \right] \quad (2.63)$$

Here, δ is the thickness of the interfacial insulator layer, W_D is the space charge region and $n(V)$ is voltage dependent ideality factor and they are described as;

$$n(V) = \frac{qV}{kT \ln(I/I_0)} \quad (2.64)$$

$$W_D = \sqrt{\frac{2\varepsilon_s V_d}{qN_A}} \quad (2.65)$$

In p-type semiconductors, the energy of the interface states E_{ss} with respect to the top of the valance band at the surface of the semiconductor can be expressed as [123];

$$E_{ss} - E_V = q(\phi_e - V) \quad (2.66)$$

Where ϕ_e is defined as the effective barrier height and is given by the following equations;

$$\phi_e = \phi_B + \left(1 - \frac{1}{n(V)}\right)(V - IR_s) \quad (2.67)$$

2.17 The Capacitance-Voltage (C-V) Characteristics of the Contacts

If the thickness of the insulator layer is δ , the capacitance value of the contact can be found with the following equation;

$$C_i = \frac{\varepsilon_i A}{\delta} \quad (2.68)$$

Where, A is effective diode area, C_i is known as the capacitance of the insulator layer, ε_i is the permittivity of the insulator layer.

In order to determine some diode parameters, $1/C^2$ - V curves of the diodes are drawn using the C - V measurements obtained at a constant frequency value. By extrapolating the linear parts of the curves, the intercept potential V_0 and acceptor density N_A values are obtained from the slopes.

$$\frac{1}{C^2} = \frac{2(V_0 + V)}{\varepsilon_s q A^2 N_A} \quad (2.69)$$

In the absence of interface states, the equation given the relationship between intercept potential and diffusion potential is [99];

$$V_0 = V_d - \frac{kT}{q} \quad (2.70)$$

If there is an insulator layer between metal and semiconductor, an expression α must be described given in following equation [124];

$$\alpha = \frac{q N_{ss} \delta}{\varepsilon_i} \quad (2.71)$$

Considering the interface states, the slope of the $1/C^2$ - V graph is expressed by the following equation.

$$\frac{d(1/C^2)}{dV} = \frac{2}{q\epsilon_s A^2 N_A} \frac{1}{(1 + \alpha)} \quad (2.72)$$

Where, ϵ_s is called the permittivity of the semiconductor (for p-Si $\epsilon_s = 11.8\epsilon_0$) and the term $\left(\frac{1}{1+\alpha}\right)$ is defined as a constant c_2 and the relation is given [125];

$$c_2 = \frac{2}{q\epsilon_s N_A (d(1/C^2)/dV)} = \frac{N_A}{N_A^*} = \frac{\epsilon_i}{\epsilon_i + qN_{ss}\delta} \quad (2.73)$$

Where, N_A and N_A^* are experimental and theoretical acceptor concentration value, respectively.

In order to calculate Fermi energy level, the following equation is used.

$$E_F = kT \ln \frac{N_V}{N_A} \quad (2.74)$$

Here, N_V is the intensity of the effective states in the valance band and it can be calculated by the following equation;

$$N_V = 2 \left(\frac{2\pi m_p^* kT}{h^2} \right)^{3/2} \quad (2.75)$$

Where, m_p^* is the effective mass of holes (for Si $m_p^* = 0.56m_0$). For Si, the value was found as $N_V = 1.04 \times 10^{19} \text{ cm}^{-3}$ [59].

The barrier height is found with the help of C-V graph also;

$$\phi_{b(C-V)} = V_d + E_F - \Delta\phi_b \quad (2.76)$$

$\Delta\phi_b$ is the Schottky barrier lowering and it is described as;

$$\Delta\phi_b = \sqrt{\frac{qE_m}{4\pi\epsilon_s}} \quad (2.77)$$

E_m is the maximum electric field and it is given as;

$$E_m = \sqrt{\frac{2qN_A V_d}{\epsilon_s}} \quad (2.78)$$

Using C-V measurement, R_s can also be determined as following equation [126].

$$R_s = \frac{G_m}{G_m^2 + (\omega C_m)^2} \quad (2.79)$$

Herein ω is the angular frequency, and it is used in order to make the units of G and C the same. R_s is an important parameter in MIS structures, as it influences the ideal behavior of C and G/ω versus voltage properties. The capacitance value of the insulating layer is expressed as follows, depending on R_s and the capacitance value in the strong accumulation region.

$$C_i = C_m \left[1 + \left(\frac{G_m}{\omega C_m} \right)^2 \right] = \frac{\epsilon_i \epsilon_0 A}{d} \quad (2.80)$$

Where ϵ_i is dielectric constant of the insulator layer (for ZnS $\epsilon_i=8.9\epsilon_0$).

2.18 Dielectric Parameters of the Contacts

To obtain the dielectric properties of the structure, complex permittivity is given equation (2.81) [127].

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (2.81)$$

Here ϵ' and ϵ'' are known as the real and imaginary parts of complex permittivity, respectively.

The dielectric constant ϵ' , the dielectric loss ϵ'' , and the loss tangent $\tan \delta$ are defined as [128, 129];

$$\epsilon' = \frac{C}{C_0} = \frac{C\delta}{\epsilon_0 A} \quad (2.82)$$

$$\epsilon'' = \frac{G}{\omega C_0} = \frac{G\delta}{\epsilon_0 \omega A} \quad (2.83)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2.84)$$

Herein C_0 is the capacitance of an empty capacitor, δ is the thickness of the insulator layer, A is the effective diode area and ϵ_0 is the dielectric permittivity of free space.

The ac electrical conductivity of the dielectric material σ_{ac} is determined as [130];

$$\sigma_{ac} = \omega C \frac{d}{A} \tan \delta = \epsilon'' \omega \epsilon_0 \quad (2.85)$$

The electrical modulus parameter M^* is expressed as;

$$M^* = \frac{1}{\epsilon^*} = M' + iM'' \quad (2.86)$$

Herein M' and M'' are known as the real and imaginary parts of the electrical modulus, respectively [131].

2.19 The Calculation of Photodiode Parameters of the Contacts

In order to determine photodiode parameters of the device, photosensitivity PS , detectivity D , photoresponsivity R and external quantum efficiency EQE values can be calculated using following equations [132-134].

$$PS = \frac{I_{ph}}{I_d} = \frac{I_{ill} - I_d}{I_d} \quad (2.87)$$

$$D = \frac{R}{\sqrt{2qI_d/A}} \quad (2.88)$$

$$R = \frac{I_{ph}}{PA} \quad (2.89)$$

$$EQE = R \frac{hc}{e\lambda} \quad (2.90)$$

Herein I_{ph} , I_{ill} and I_d are photocurrent, illuminated and dark current values. P is defined as incident light intensity and A is the active diode area. h is the Planck constant, e is known as the electron charge, c is velocity of light and lastly λ is the wavelength of the incident light.

CHAPTER III

MATERIALS AND METHODS

3.1 Sol-gel Process

Sol-gel is one of the coating methods to fabricate thin films on glass or Si substrate. Sol is the state of solid material in liquid suspension. That is, if solids remain dispersed in liquids, this system is called sol. Since the effect of intermolecular Van der Waals and electrical repulsion forces is greater than the gravitational force, the materials that make up the sol do not sink to the bottom. If this molecule expands in solution and reaches a large size, this substance is called gel. The continuity of the solid structure gives the gel an elastic property [94].

The first step in this method is to hydrolyze the precursor solution by dissolving metal organic compounds in alcohol-based solutions. Then, the solution formed as a result of polymerization is dihydrolyzed. The resulting solution is coated on the substrates used in the production of thin films by spinning, dipping and spraying techniques. The amorphous film obtained by any of these techniques is usually annealed at 500 – 800 °C, crystallized and densified. Thus, a homogeneous film is obtained [73].

The sol-gel method is generally preferred to fabricate thin films because of its advantages. It is low-cost; chemical features of the solution can be controlled; it does not cause air pollution; the thickness of the films is the same on the substrate and can be changed the number of coating; it can be applied to all kinds of materials; the low temperature is suitable. On the other hand, the high cost of materials; the high loss of material during process and the material can be harmful to health are the disadvantages of the sol-gel process [135].

3.1.1 Dip-Coating Method

The dip-coating method is based on the principle of immersing the substrate in the prepared solution with a certain velocity and removing it with the same velocity. Advantages of this method; a smooth coating can be obtained; multi-layer coating can be made; obtaining the same coating regardless of the geometry of the substrate to be coated.

The figure 3.1 gives schematic diagram of the dip-coating method [136].

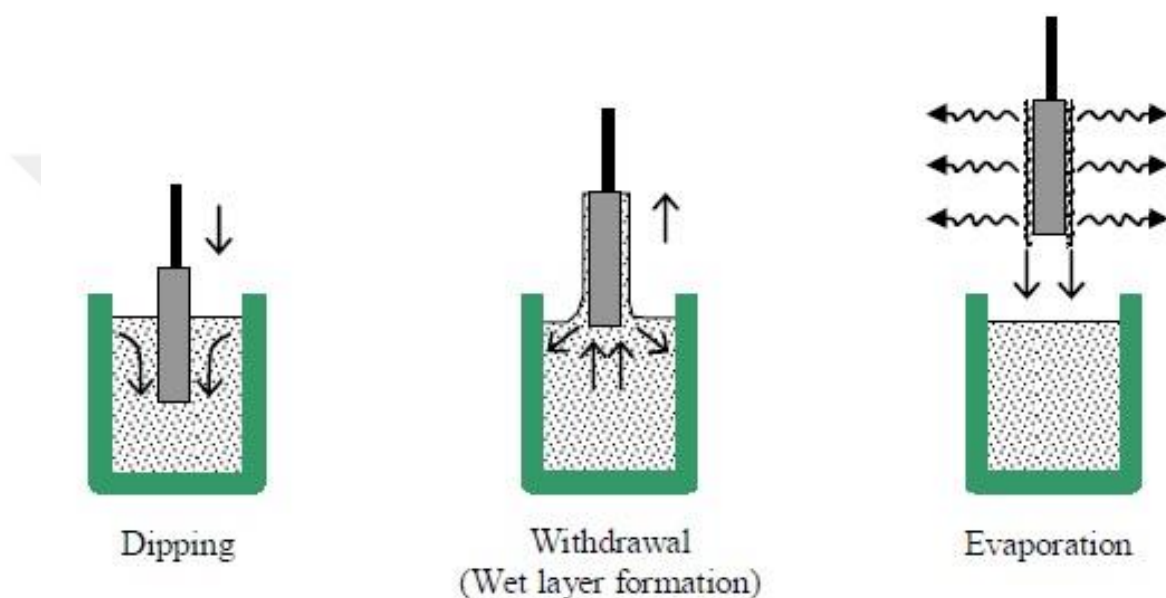


Figure 3.1 The schematic diagram of the dip-coating method [136].

3.2 The Preparation of the Solution

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$), tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), methanol (CH_4O), and ethanolamine ($\text{C}_2\text{H}_7\text{NO}$) were purchased from Merck company and used as received.

To undoped ZnS thin films, two solutions were prepared using zinc acetate and thiourea. The molar ratio was 1:3 (Zn:S). In fact, ZnS thin films were produced with the molar ratio of 1:2 and 1:4 also. However, since the optimum conditions are provided in ZnS thin films with a molar ratio of 1:3, the studies continued with this ratio. Zinc acetate and thiourea were dissolved in methanol, separately. Firstly, zinc acetate solution was prepared and then thiourea solution was added drop by drop into the solution. Ethanolamine was added to this solution to obtain a transparent solution.

After that, the obtained solution was stirred on a magnetic stirrer for 2h at room temperature. Before the coating on the substrates, the solution was allowed to age for 24h. To obtain doped ZnS thin films, tin chloride was added as the molar ratio varied 0 to 10%.

3.3 The Preparation of the Substrates

Glass and p-Si crystal were used as a substrate. Before coating, glass substrates were cleaned in ethanol and de-ionized water in an ultrasonic cleaner. Si substrates were cleaned by RCA cleaning technique. Firstly, the substrates were dipped in a 65°C solution of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:5) for 10 min. Secondly, they were cleaned in $\text{HF}:\text{H}_2\text{O}$ (1:10) solution for 30 second to remove oxide layer on the wafer. Lastly, they were dipped in a 65°C solution of $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:6) for 10 min. After all cleaning steps p-Si substrates were rinsed in de-ionized water for 30 second. Then, high-purity Al (99.999%) was evaporated from the tungsten filament onto the whole back surface of the p-Si substrates under the pressure 10^{-5} Torr as thermally. p-Si substrates were annealed at 580°C for 3 min to get a low-resistivity ohmic back contact.

3.4 The Coating Process

Both p-Si and glass substrates were dipped vertically in the solution with a velocity of 3mm/s and were removed from the solution with same velocity without waiting. After coating process, the films were dried at 300 °C for 5 min in air to evaporate solvent and remove organic residuals. The coating process was repeated 15 times for glass and 6 times for p-Si substrates to increase film thickness. Then, the films were annealed at 500 °C in vacuum for 1h to obtain highly crystalline ZnS thin films. Finally, the high-purity Al layer was evaporated on the front surface of p-Si substrates coated with solution as dots. This coating was carried out in high vacuum evaporation system under the pressure of 10^{-5} Torr.

3.5 Instrumentation

The structural analysis of undoped and doped ZnS was investigated with X-ray diffraction (XRD). XRD measurements were performed by Rigaku Miniflex 600 Table Top Powder X-Ray diffractometer using $\text{CuK}\alpha$ radiation source ($\lambda = 0.15406\text{nm}$) in the 2θ scanning range of 20-60°.

In order to detect elemental ratios in the composition, EDX analysis was carried using Hitachi SU5000 Schottky FE-SEM instrument. Film thicknesses were also found from SEM images taken using the same device.

The optical transmission (T%) measurement of material was obtained in the UV-Vis-NIR by Shimadzu 3600 spectrophotometer in the wavelength range of 300-1800 nm. Figure 3.2 presents Shimadzu 3600 spectrophotometer [137].



Figure 3.2 Shimadzu 3600 UV-Vis-NIR spectrophotometer [137].

Current-voltage (I-V) measurement of undoped and doped ZnS/p-Si structure was performed in the dark using Keithley 2420 programmable constant current source at room temperature. Figure 3.3 shows current-voltage measurement system. Illuminated current-voltage (I-V) measurement was done under $100\text{mW}/\text{cm}^2$ illumination intensity using AM 1.5 filter.

Capacitance-voltage (C-V) measurements of undoped and doped ZnS/p-Si diodes were obtained using an HP 4192 A LF impedance analyzer (5Hz to 13MHz) in the frequency range 10kHz-1.5MHz and with a test signal of 50mV at room temperature. Capacitance-voltage measurement system is given in Figure 3.4 [137].



Figure 3.3 Current-Voltage measurement system [137].

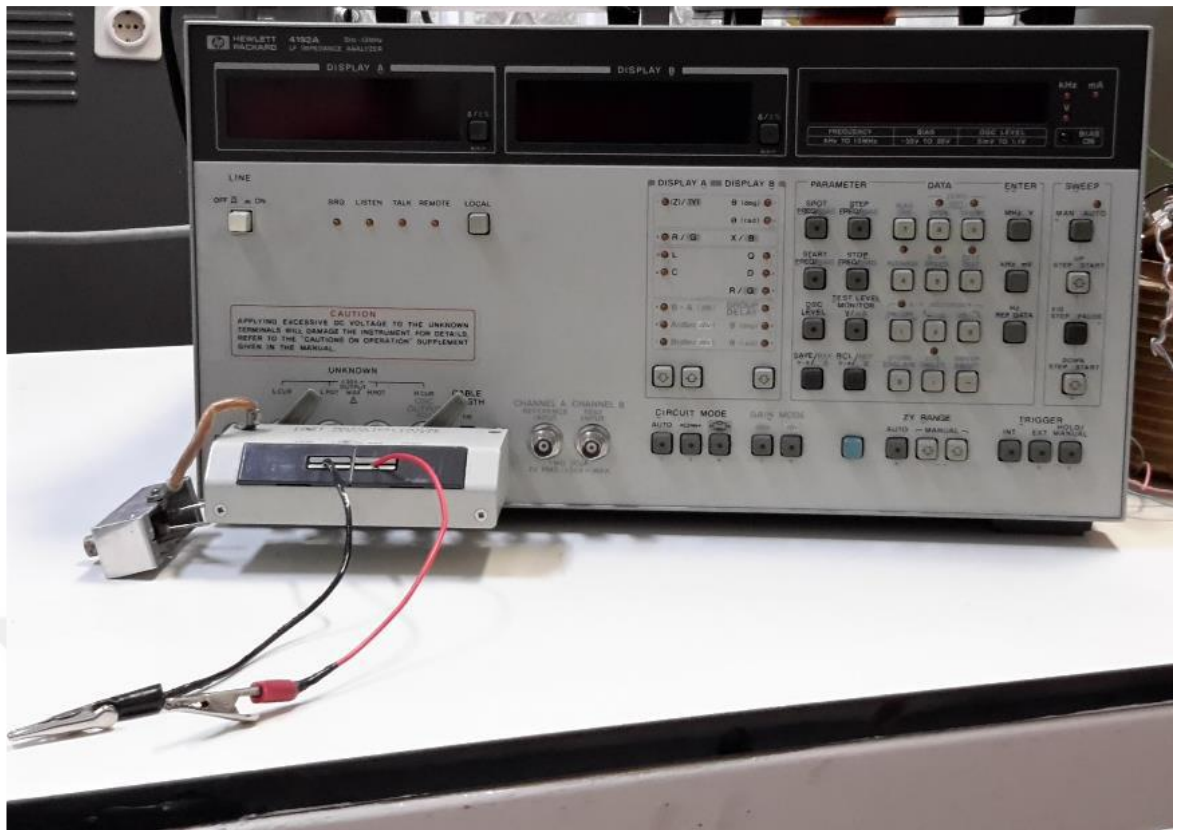


Figure 3.4 Capacitance-Voltage measurement system [137].

CHAPTER IV

RESULTS AND DISCUSSIONS

The films coated on glass and p-Si substrates are given in Table 4.1.

Table 4.1 The coating conditions of the ZnS films.

Material	Dopant Rate	Dopant Atom	Dipping	Substrate
M2	0%	ZnS	15 times	Glass
M3	0%	ZnS	6 times	p-Si
M5	1%	Sn:ZnS	15 times	Glass
M6	1%	Sn:ZnS	6 times	p-Si
M16	3%	Sn:ZnS	15 times	Glass
M17	3%	Sn:ZnS	6 times	p-Si
M34	10%	Sn:ZnS	15 times	Glass
M35	10%	Sn:ZnS	6 times	p-Si

4.1 Structural Analysis

The structural properties of the materials were determined via XRD spectrum. This measurement were performed using Rigaku Miniflex 600 Table Top Powder X-Ray diffractometer using CuK α source ($\lambda=0.15406$ nm) in the 2θ scanning range of 20-60°. Figure 4.1 and 4.2 display XRD spectra of Sn doped ZnS thin films grown on p-Si crystal and the glass substrates, respectively. It is seen from these spectra that the films grow as polycrystalline. If the FWHM value is small and the peak intensity is large, it indicates good crystallization.

According to the figures it can be say the films were grown as cubic phase. The strongest diffraction peak was observed at $2\theta = \sim 28^\circ$ corresponding to (111) plane of

the cubic ZnS structure. The intensity of the strongest peak increased with increased for 1% and 3% Sn dopant concentration. In addition, (220) and (113) planes of the cubic ZnS structure were observed with increased for that dopant concentration. On the other hand, 10% Sn doped ZnS thin film crystallized as amorphous. FWHM values increased with increasing dopant concentration and accordingly the grain size value decreased. It can be said that, undoped ZnS thin films exhibit best crystalline quality and Sn concentration caused reducing the crystalline quality.

It is clear that ZnS films grown on p-Si crystallized in the cubic structure also. Both (111) plane of Si and (111) plane of ZnS give a peak nearly same angle ($2\theta = \sim 28^\circ$) and the intensity of the cubic Si much greater than that of the ZnS reflection. The main peak position of ZnS thin film is given in figure 4.3 as enlarged in order to understand the graph clearly. According to the results, whether doped and undoped ZnS thin films were grown on glass substrate or p-Si crystal, the orientation of the strongest peak did not change. For both substrates, ZnS films crystallized in the (111) orientation.

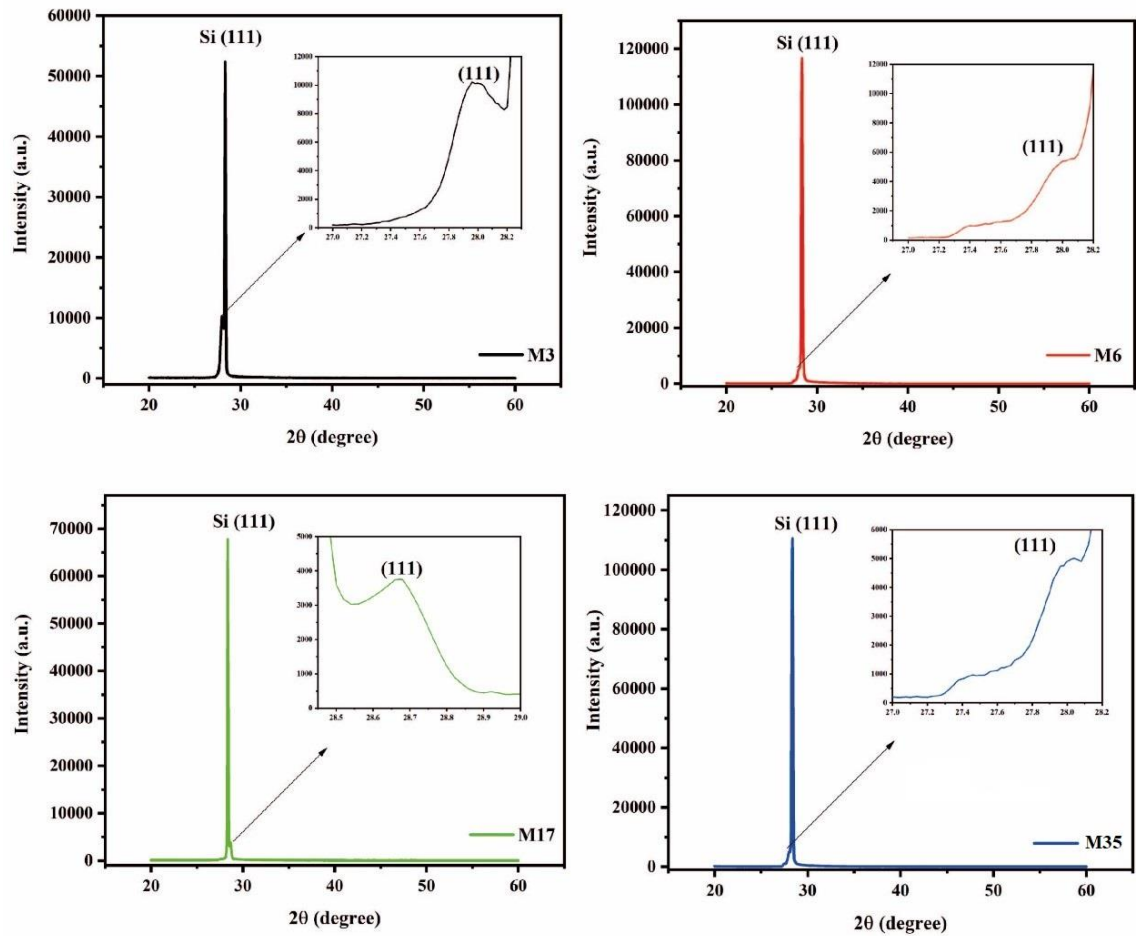


Figure 4.1 XRD spectrum of the Sn doped ZnS/p-Si.

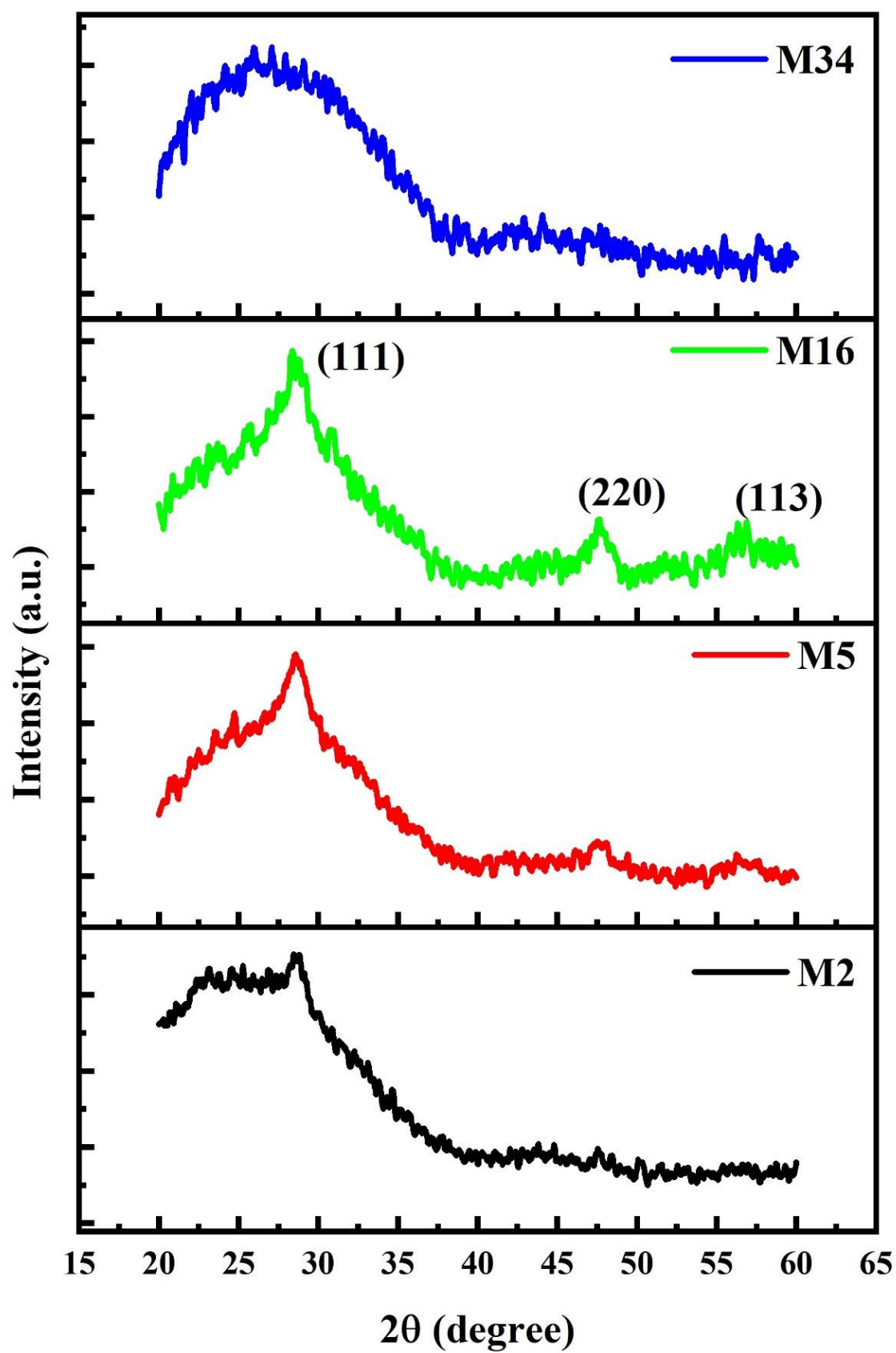


Figure 4.2 XRD spectrum of the Sn doped ZnS thin films.

The inter-planar distance values were found with the help of 2θ values obtained from the XRD spectrum and Bragg's Law given by eq. (2.1). Besides, the lattice constants of the Sn doped ZnS thin films were calculated for the cubic phase by using eq. (2.2). The crystallite size, the dislocation density, the microstrain and the lattice mismatch values were calculated using eq. (2.3), (2.4), (2.5) and (2.6), respectively. The observed and calculated values are listed in Table 4.2. The microstrain and the dislocation density values rised with increasing Sn concentration. Since the lattice mismatch value are under 1%, interface defects are decidedly minimal. Besides, undoped ZnS has the smallest lattice mismatch value. Undoped ZnS grown on glass substrate has the best crystalline quality.

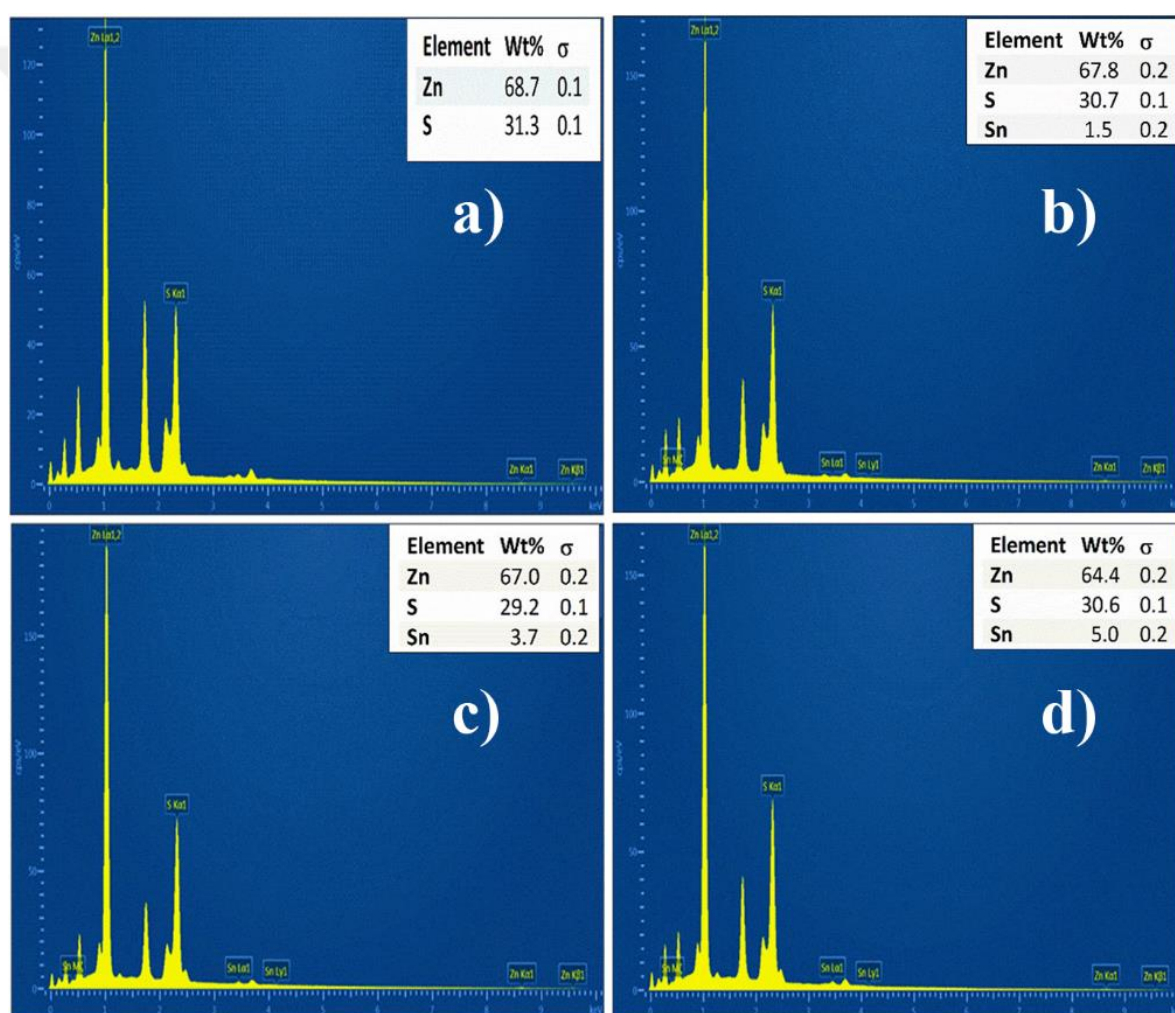


Figure 4.3 EDX spectrum of Sn doped ZnS thin films **a)** 0% **b)** 1% **c)** 3% and **d)** 10%

Figure 4.3 gives EDX spectrum of undoped and Sn doped ZnS thin films grown on the glass substrate. The spectrum shows the presence of Zn, S and Sn elements in the growth film. According to the figure, it can be said that while Sn concentration increases in the growth film, the concentration of Zn decreases.

Figure 4.4 gives the cross-sectional SEM images of undoped and Sn doped ZnS thin films. Using the cross-sectional images, the film thickness values were determined. The thickness d value were found as 276 nm, 323 nm, 292nm and 277nm for 0%, 1%, 3% and 10% Sn doped ZnS thin films.

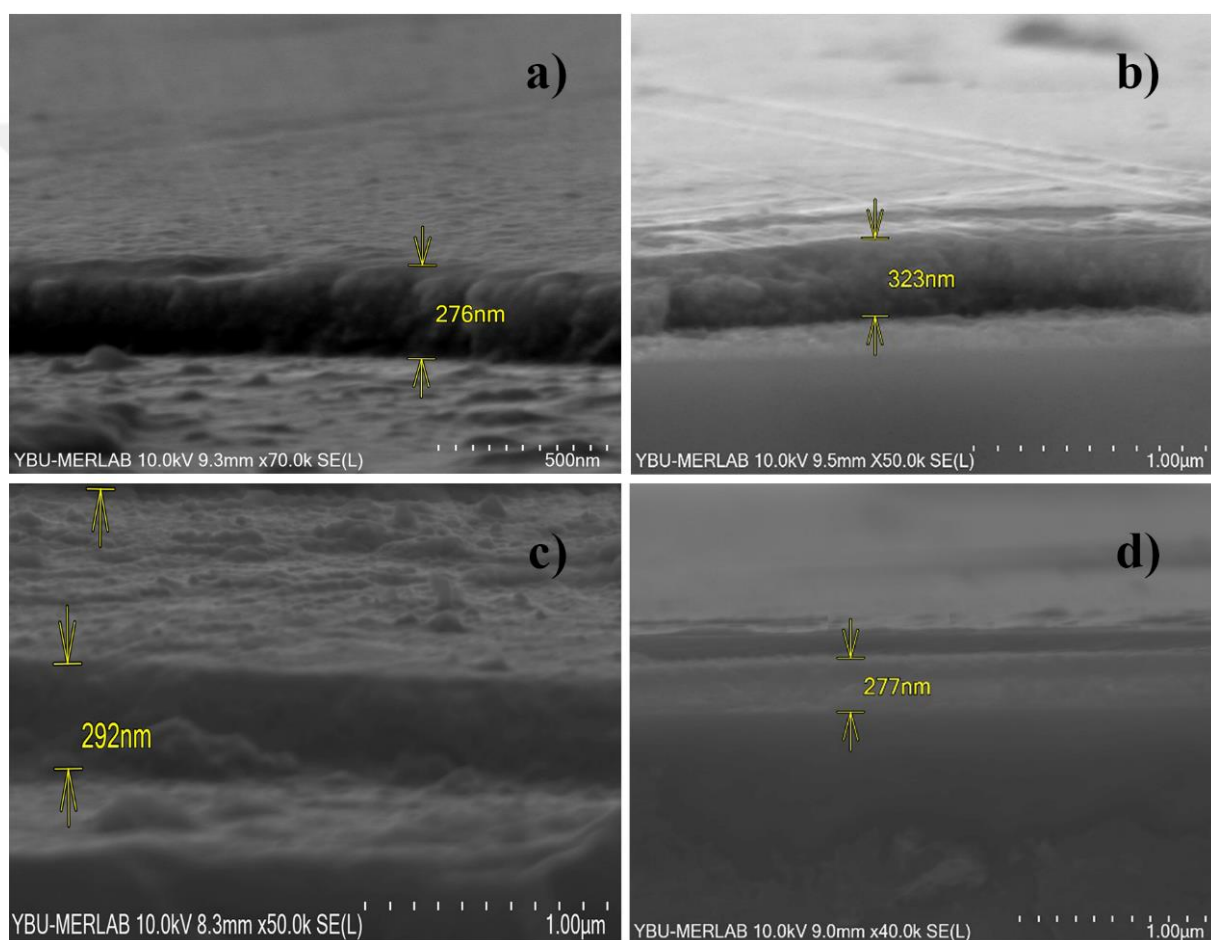


Figure 4.4 Cross-sectional SEM images of Sn doped ZnS thin films **a)** 0% **b)** 1% **c)** 3% and **d)** 10%

Table 4.2 Structural parameters of Sn doped ZnS thin films grown on glass substrate.

Material	2θ (°)	β (°)	d_{hkl} (nm)	a (nm)	$\Delta a/a$ (%)	D (nm)	δ ($\times 10^{17}$ line/m ²)	ϵ ($\times 10^{-3}$)
M2	28.46	0.8	0.314	0.543	0.017	10.71	8.7	3.38
M5	28.56	1.25	0.313	0.541	0.39	6.85	21.0	5.28
M16	28.36	1.1	0.315	0.545	0.35	7.78	16.5	4.65
M34	-	-	-	-	-	-	-	-

4.2 Optical Analysis

To obtain optical parameters of the thin films, optical transmittance (T%) and reflectance (R%) spectrum were measured using Shimadzu 3600 UV-Vis-NIR spectrophotometer in the wavelength range of 300-1600 nm. Figure 4.6 and 4.7 represent the optical transmittance and reflectance spectrum of Sn doped ZnS thin films grown on glass substrate, respectively.

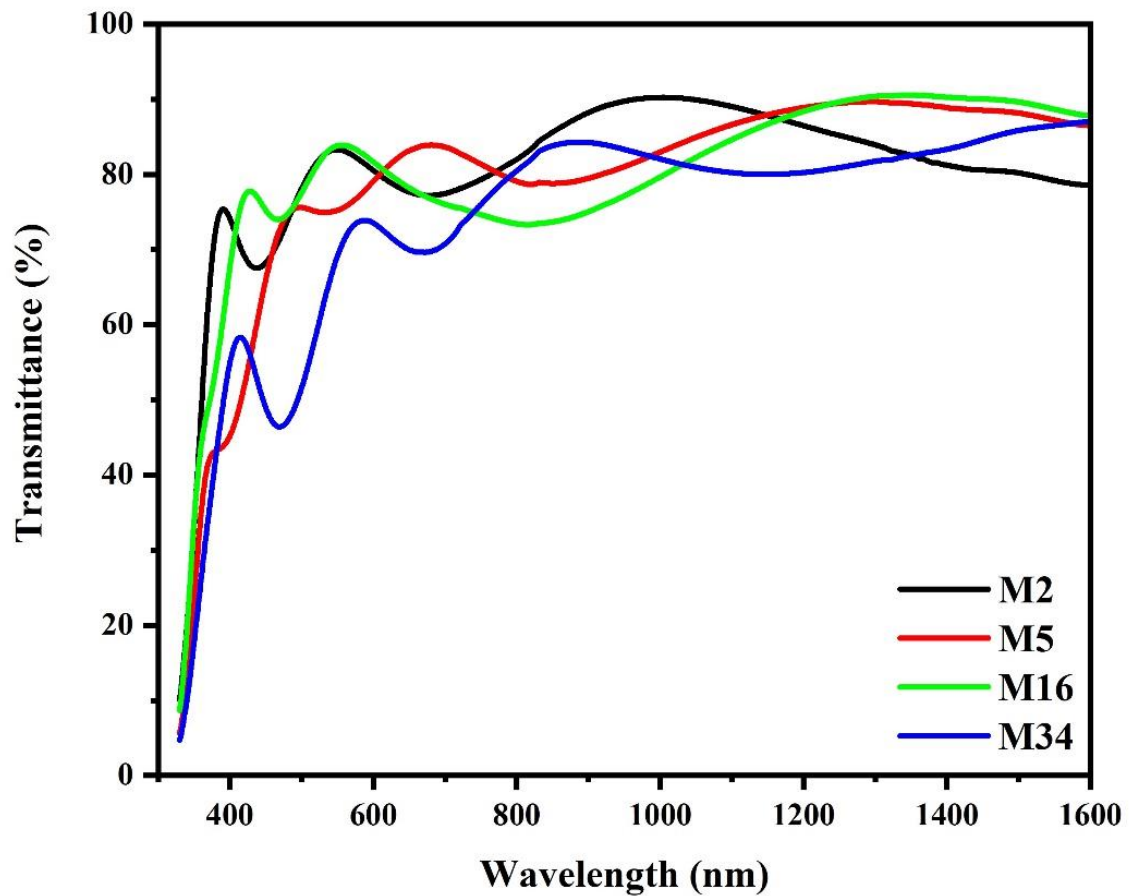


Figure 4.5 The optical transmittance graph of Sn doped ZnS thin films.

Although the films have very high transparency, the increasing in dopant concentration caused decreasing in transmittance value. The maxima transmittance value are approximately 85% in the strong absorption region.

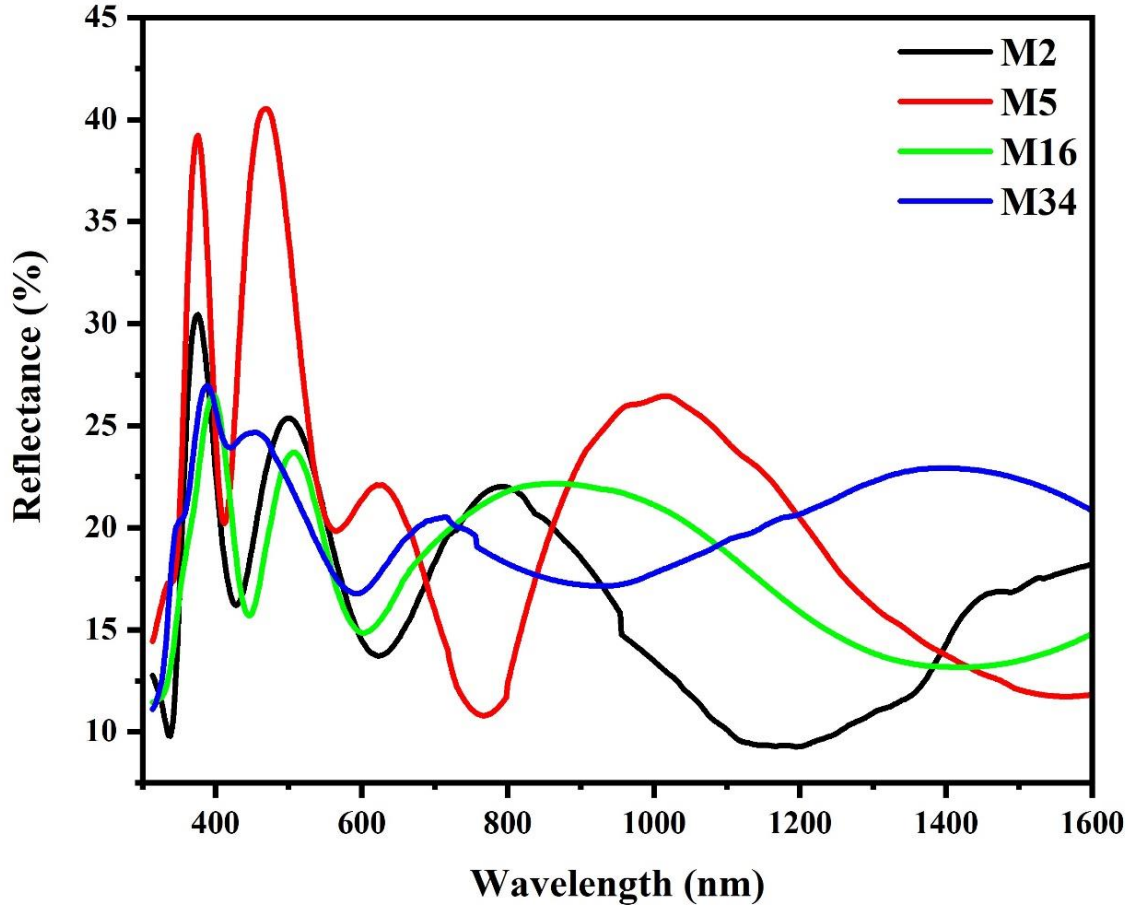


Figure 4.6 The optical reflectance graph of Sn doped ZnS thin films.

Using transmittance spectrum of the films, the optical characteristics such as film thickness, refractive index and optical band gap are obtained. Swanepoel method helps us to calculate these values.

To calculate refractive index, the maximum T_M and corresponding minimum T_m transmittance values were used and N values were obtained using equation (2.9). After that using equation (2.8) the refractive index (n) of the films were calculated. The refractive index of glass substrate is $s=1.5$. After obtaining refractive indices n_1 and n_2 for two adjacent maxima (or minima) transmittance value, the film thickness (d) was calculated using equation (2.10). Using the average thickness value, the order numbers for the extremes were obtained from equation (2.7). Taking the exact integer for the

maxima or half-integer for the minima, m values were obtained again and new thickness values and average thickness were calculated using the equations. Table 4.3 gives the optical parameters of the doped and undoped thin films.

Table 4.3 The optical parametrs of undoped, Sn doped ZnS thin films.

Material	$\lambda(\text{nm})$	% T_{max}	% T_{min}	n_1	$d_1(\text{nm})$	m_1	m_2	$d_2(\text{nm})$	n_2
M2	1005	0.903	0.8	1.86	277.08	1.05	1	270.55	1.80
	678	0.87	0.772	1.87	342.86	1.57	1.5	272.69	1.82
	549	0.833	0.73	1.91	233.37	1.98	2	287.39	1.97
	438	0.79	0.675	1.99	389.90	2.59	2.5	274.68	1.96
	391	0.754	0.64	2.03	-	2.95	3	288.91	2.10
M5	1296	0.897	0.84	1.71	287.30	1.28	1	378.07	1.72
	850	0.89	0.788	1.86	583.73	2.12	1.5	342.05	1.69
	681	0.839	0.77	1.79	581.42	2.54	2	381.54	1.80
	528	0.77	0.750	1.91	1626.6	2.95	2.5	409.71	1.75
	497	0.756	0.74	1.59	-	3.10	3	468.07	1.97
M16	1355	0.906	0.8	1.87	218.20	0.67	1	363.21	2.11
	816	0.9	0.733	2.06	265.06	1.22	1.5	297.34	1.91
	556	0.839	0.73	1.93	758.54	1.67	2	388.56	1.74
	467	0.8	0.74	1.77	1611.7	1.83	2.5	329.37	1.83
	428	0.78	0.74	1.69	-	1.91	3	379.72	2.01
M34	1152	0.81	0.80	1.55	539.17	0.60	0.5	185.70	1.19
	887	0.843	0.82	1.61	241.62	0.80	1	276.25	1.83
	672	0.79	0.697	1.91	351.44	1.26	1.5	263.66	2.08
	588	0.739	0.615	2.09	134.30	1.57	2	281.22	2.43
	469	0.64	0.464	2.54	156.03	2.39	2.5	230.73	2.42
	415	0.583	0.38	2.91	-	3.10	3	213.87	2.57

The values of the refractive index n is fitted to Cauchy dispersion relation given by equation (2.11). By extrapolating it to shorter wavelengths using this relation, a theoretical function that generalizes the spectrum is obtained. Figure 4.7 shows the variation of n relative to λ for Sn doped ZnS thin films.

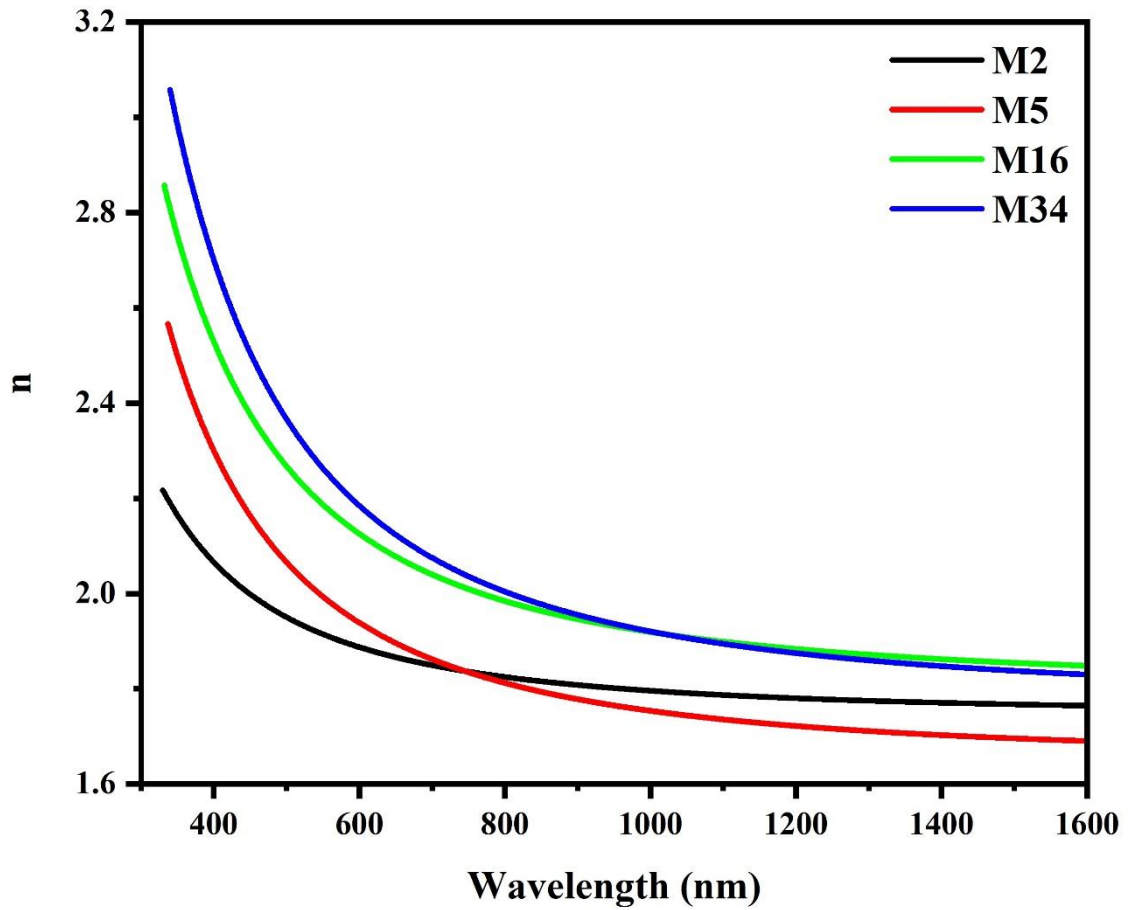


Figure 4.7 n vs λ plot of Sn doped ZnS thin films.

m and d values can also be obtained using simple graphical method. For the first extreme, suppose the order number is m_1 . Using eq.(2.12) the first order number and thickness values of the samples were determined, again.

Figure 4.8 displays $l/2$ vs n/λ plot of Sn doped ZnS thin films

Table 4.4 shows average thickness d_{avr} , the first order numbers m_1 obtained graphical and Swanepoel methods.

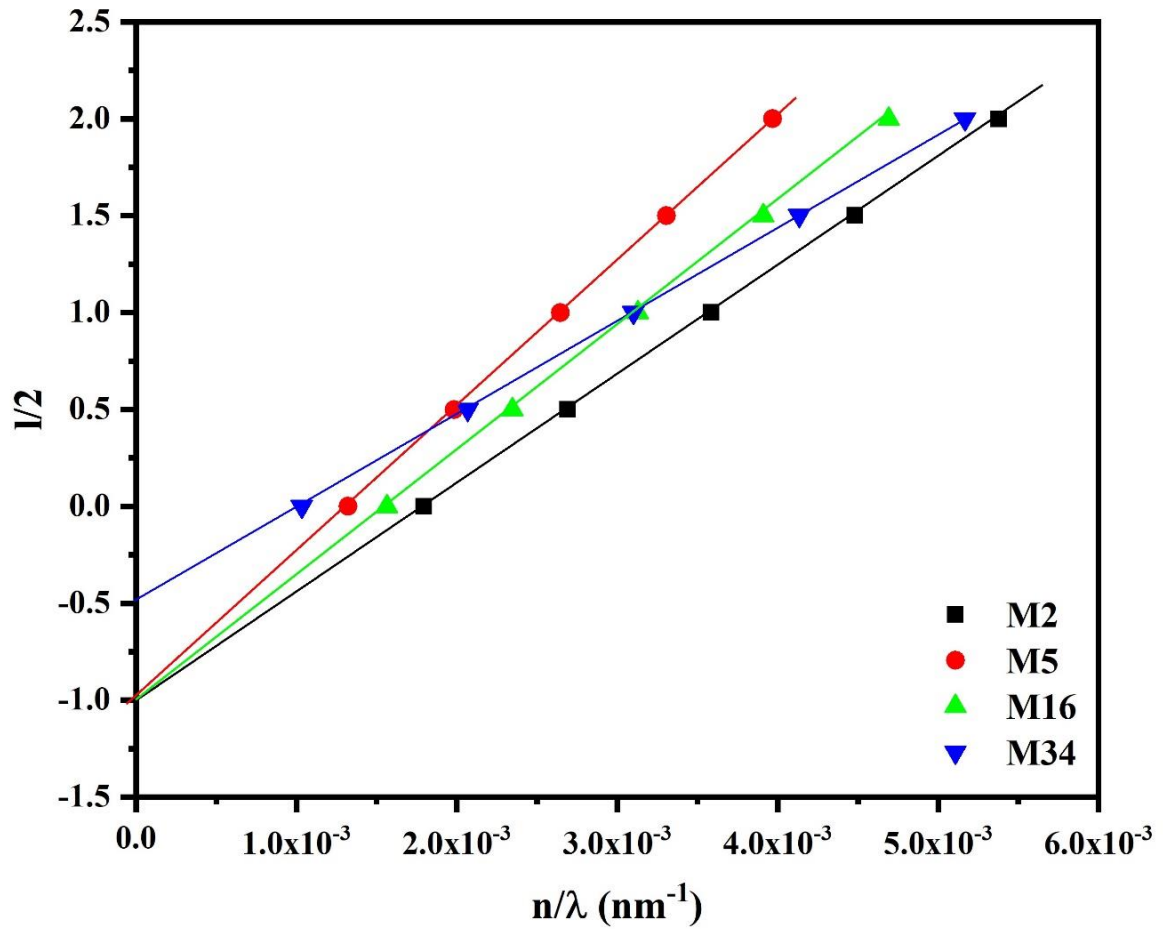


Figure 4.8 $l/2$ vs n/λ plot of Sn:ZnS thin films.

Using Tauc relation, $(ah\nu)^2$ vs $h\nu$ graph of the films were drawn. By extrapolating the graph to the $h\nu$ -axis, the optical band gap values of the films were found. Figure 4.9 shows $(ah\nu)^2$ vs $h\nu$ graph of the Sn doped ZnS thin films. According to the figure, it can be said the optical band gap value decreased with increasing Sn dopant concentration. Although the reduction in optical band gap for 1% and 3% Sn doped ZnS thin films was small, 10% Sn doping greatly reduced the optical band gap value compared to that of undoped ZnS thin film. The band gap values are given in Table 4.4.

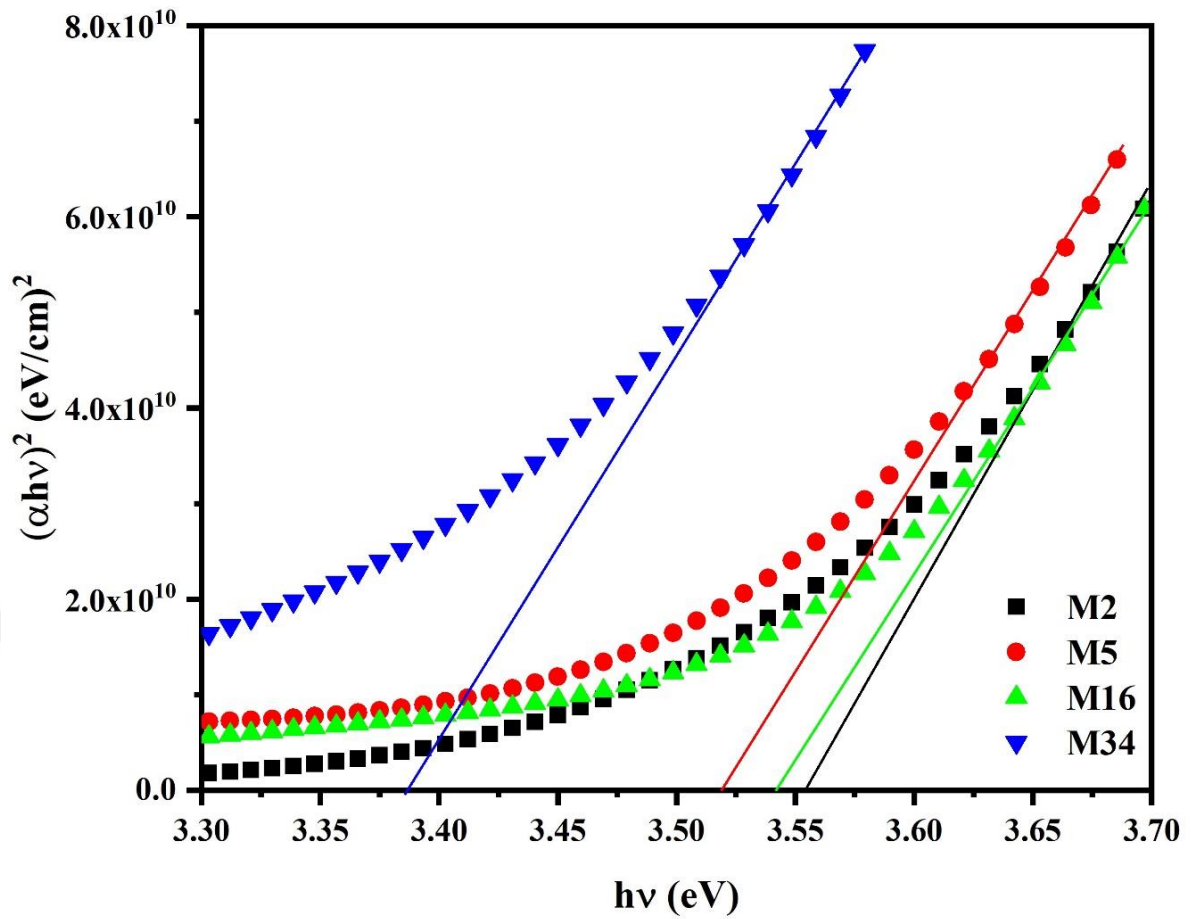


Figure 4.9 $(\alpha h\nu)^2$ vs $h\nu$ graph of Sn doped ZnS thin films.

Table 4.4 The optical parameters of ZnS thin films.

Material	Swanepoel Method			Graphical Method		E_g (eV)
	$d_{1,avr}$ (nm)	d_2 (nm)	m_1	m_1	d (nm)	
M2	284.44	278.84	1	1	278.84	3.55
M5	484.15	377.84	1	1	377.84	3.52
M16	241.63	319.62	1	1	319.62	3.54
M34	220.85	241.87	0.5	0.5	241.875	3.39

According to the table, the optical band gap value is 3.55eV for undoped ZnS thin film. The Sn concentration caused the optical band gap to decrease. Although 3% Sn doped increased the optical band gap value compared to 1% Sn doped, the band gap is still less than that of undoped ZnS.

Although there is a difference between the average thickness values $d_{1,avr}$ and the corrected thickness values d_2 found by the Swanepoel method, the thickness values calculated using the graphical method are almost the same as the corrected thickness values.

4.3 I-V Characteristics of the Al/ZnS/p-Si Diodes

To investigate diode characteristics of the undoped and Sn doped ZnS/p-Si structures, I - V measurements were performed in the dark at room temperature using Keithley 2420 programmable constant current source. Figure 4.10 displays the semi-logarithmic graph of the Sn doped ZnS/p-Si diodes in the voltage range $\pm 2V$ at the room temperature. According to the figures, it can be said that the dopant atoms increased current flowing. The rectification ratio calculated from the ratio of current values at $\pm 2V$ as 167.94, 9062.98, 18525.91 and 1876.44 for undoped, 1%Sn, 3%Sn and 10%Sn doped ZnS/p-Si structures, respectively. The rectification ratio increased with the effect of Sn concentration. The best value belongs to 3%Sn doped structure.

I - V characteristics of the structures were investigated via TE, Norde, Lien and Cheung's method.

TE can be defined using equation (2.54) for $V > 3kT/q$. According to the TE, the graph of the $\ln I$ - V is the linear. The slope of this graph gives the ideality factor n of the diode. The saturation current value of the diodes was found using the intercept of the current axis. These values are shown in table 4.5.

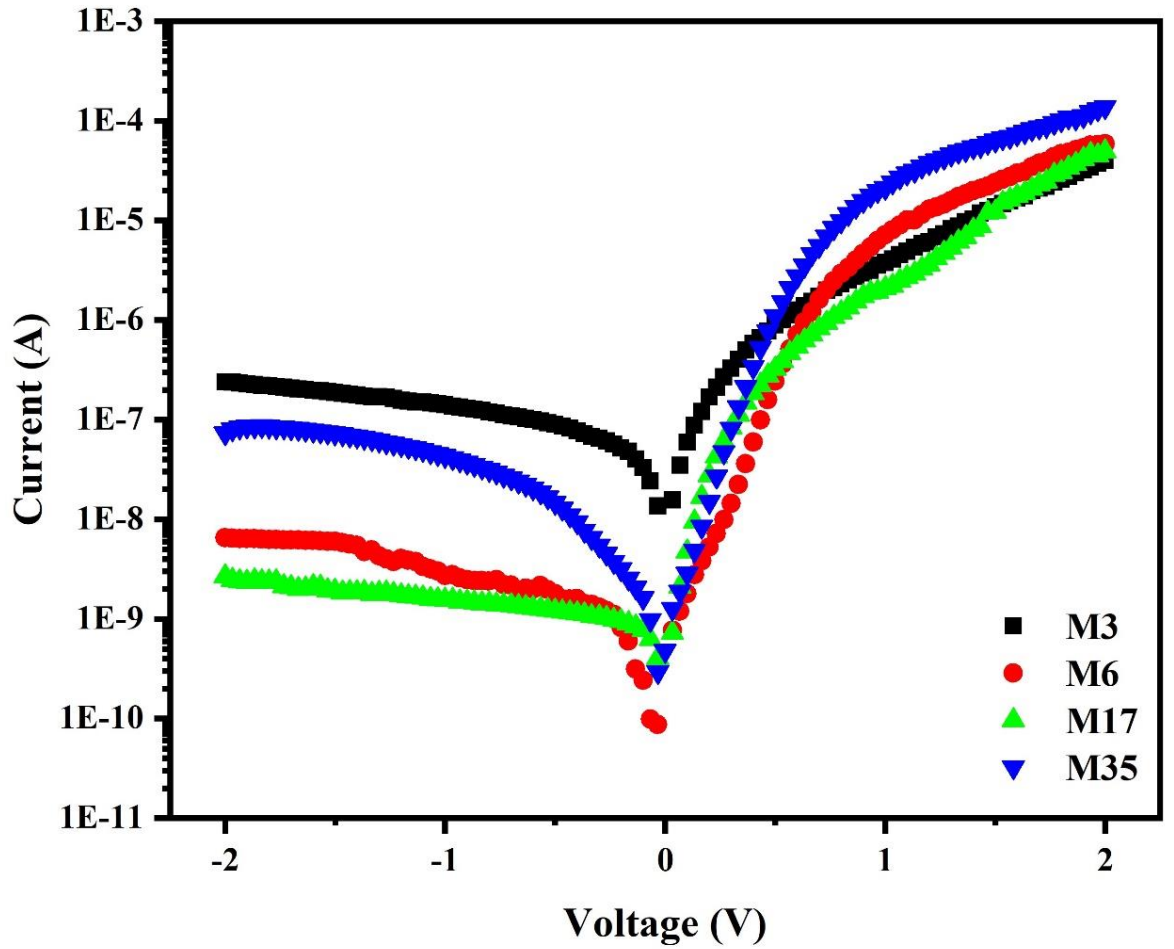


Figure 4.10 Semi-logarithmic I - V graphs of Sn doped ZnS/p-Si diodes.

In order to understand I - V properties of the diodes is Norde method. According to the Norde method, the arbitrary constant γ was selected to determine the series resistance value. Using equation (2.57), $F(V)$ values were calculated and $F(V)$ - V graphs of the structures were drawn. Figure 4.11 shows these graphs of Sn doped structures. By using the voltage corresponding to the minimum of the $F(V)$ - V graph and the current value measured at this voltage from I - V measurement, the series resistance and the barrier height were found with the help of equations (2.58) and (2.59). The calculated values are listed in table 4.5.

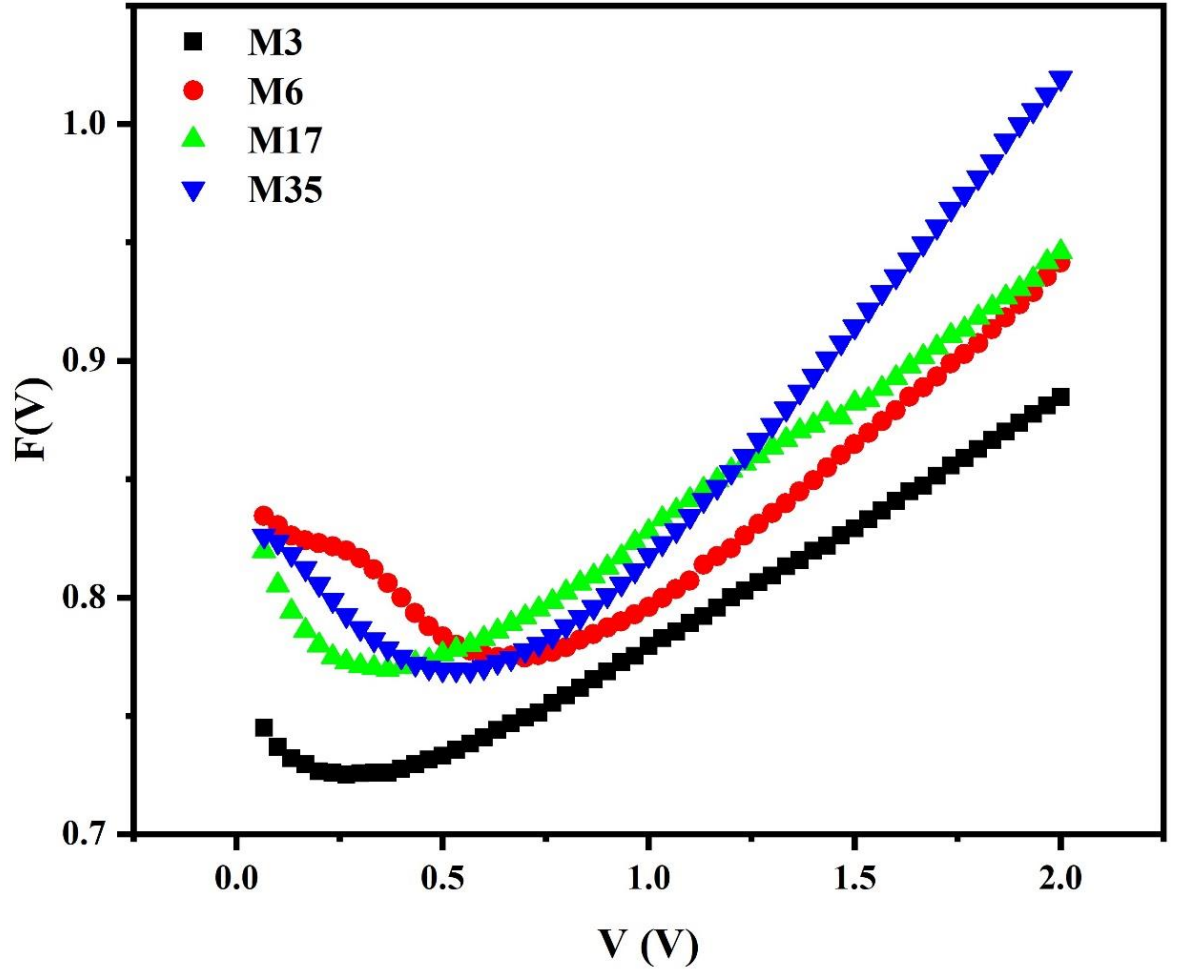


Figure 4.11 $F(V)$ - V plot of Sn doped ZnS/p-Si diodes.

The I - V characteristics of the samples continued to be examined using the Lien method. $F(V)$ - V graphs were plotted by choosing arbitrary 5 different γ values. With the help of F_{min} , I_{min} values were found and I_{min} versus γ/β graphs were plotted. Figure 4.12 shows these graphs of Sn doped ZnS/p-Si structures. The series resistance was calculated using slope of the graphs and the ideality factor was found using intercept of these graphs. Obtained values are listed in table 4.5.

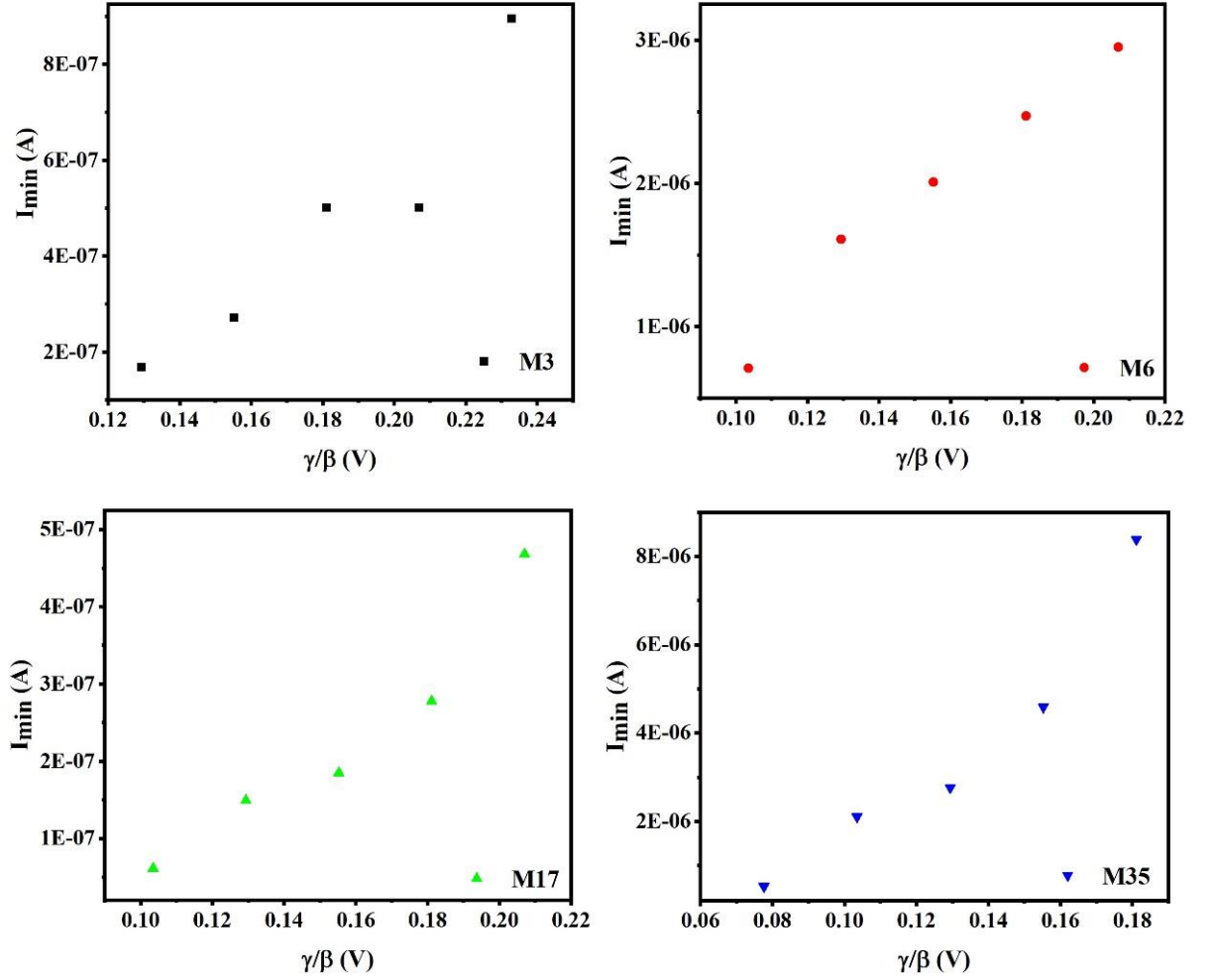


Figure 4.12 I_{min} - γ/β plots of Sn doped ZnS/p-Si diodes.

Cheung's method were also used to calculate n , ϕ_b and R_s values of the Sn doped ZnS/p-Si structures. According to this method, the series resistance is effective from the exact turning point of forward bias $\ln I$ - V graph. Using equation (2.61) and (2.62), $dV/d\ln I$ and $H(I)$ functions were determined. Figure 4.13 gives $dV/d\ln I$ - I and $H(I)$ - I graphs of Sn doped ZnS/p-Si structures. The series resistance and the ideality factor values were determined with the help of $dV/d\ln I$ - I graphs, the barrier height values were found using $H(I)$ - I graphs. Table 4.5 shows the calculated values.

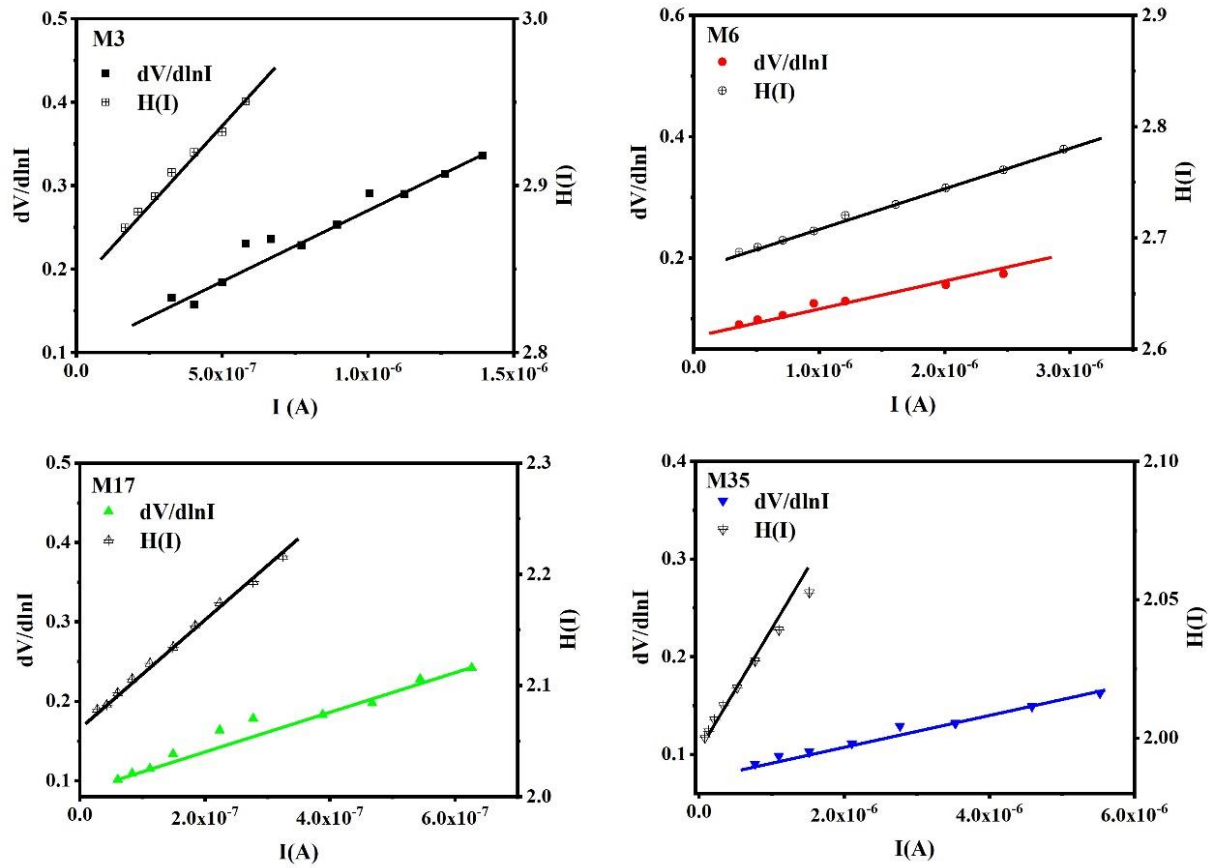


Figure 4.13 $dV/d\ln I$ - I and $H(I)$ - I graphs of Sn doped ZnS/p-Si diodes.

Table 4.5 The electrical parameters calculated from I - V measurements of undoped/doped ZnS/p-Si diodes.

Material	TE		Cheung's Method				Norde Method		Lien Method	
			dV/dlnI		H(I)					
	n	I ₀ (nA)	R _s (kΩ)	n	R _s (kΩ)	Φ _b (eV)	R _s (kΩ)	Φ _b (eV)	R _s (kΩ)	n
M3	3.86	20.95	164.0	3.85	177.7	0.74	204.9	0.74	166.7	3.87
M6	3.20	0.48	38.38	3.10	35.86	0.84	28.95	0.85	50.0	1.93
M17	2.54	1.20	239.8	3.66	470.5	0.81	427.5	0.82	250.0	2.90
M35	2.39	0.59	15.01	3.12	36.47	0.84	19.81	0.87	14.29	2.76

As seen from the table 4.5, the ideality factor value was found as 3.86 for undoped ZnS/p-Si structure using TE. It can be said that using Sn as dopant atom caused a reduction in the ideality factor value. The best ideality factor value was observed in 10% Sn doped ZnS/p-Si structure. Similarly the saturation current value decreased with the effect of Sn dopant. The series resistance value was calculated using three different methods. Although the obtained values differ, it can be said that the results are in the same order. The smallest series resistance value was obtained as 15.01k Ω for the 10%Sn doped structure, while the largest series resistance value was determined as 239.8k Ω for the 3%Sn doped structure using Cheung's method. The barrier height value of doped ZnS/p-Si structures increased with the effect of Sn dopant.

The ideality factor being $n > 1$ is the proof that the structures deviate from ideality. This results is due to the interface states. Equation (2.63) gives the expression that connects the ideality factor to the insulator layer thickness and the interface state density for the interfaces states in equilibrium with the semiconductor. With the help of equation (2.63), the density of interface states values were obtained according to the voltage dependent ideality factor values determined from equation (2.64). After calculation $E_{ss}-E_V$ using equation (2.66), N_{ss} versus $E_{ss}-E_V$ graph of the undoped and doped ZnS/p-Si structures were drawn. Figure 4.14 displays these graphs for Sn doped ZnS/p-Si diodes. According to the figure, it can be said that Sn concentration decreases the density of interface states in every amount.

The interface states were also calculated by taking the series resistance value to zero. Figure 4.15 shows these drawings. According to figures 4.14 and 4.15, the interface states increase when the series resistance is zero.

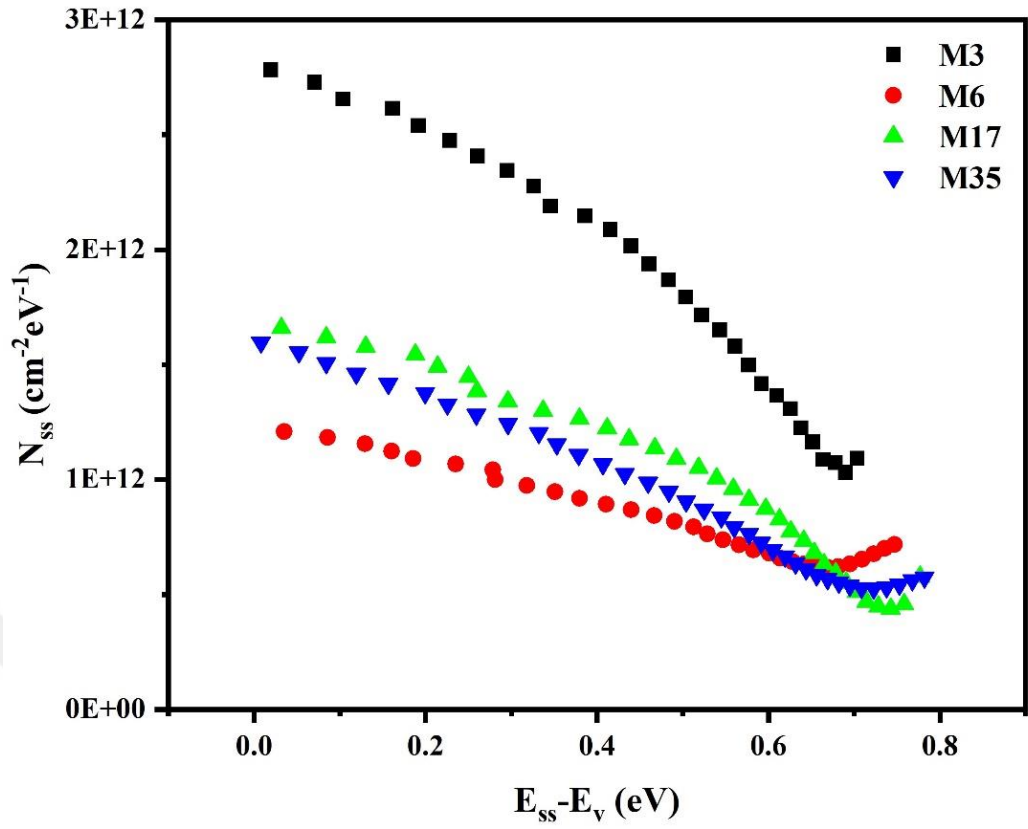


Figure 4.14 N_{ss} vs $(E_{ss} - E_v)$ graph of Sn doped ZnS/p-Si structures, $R_s \neq 0$.

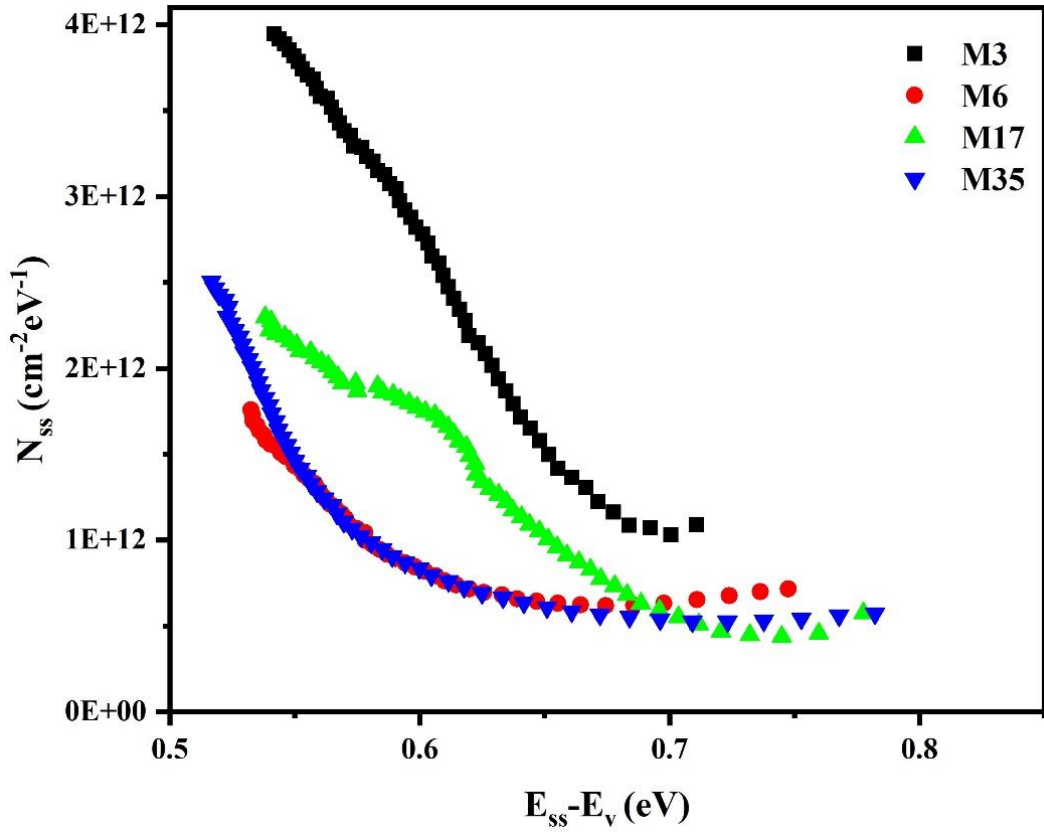


Figure 4.15 N_{ss} vs $(E_{ss} - E_v)$ graph of Sn doped ZnS/p-Si structures, $R_s = 0$.

4.4 C-V Characteristics of the Al/ZnS/p-Si Diodes

The C - V and the G/ω - V measurements of undoped and Sn doped ZnS/p-Si structures were carried out in the dark at room temperature in the frequency range 10kHz-1.5MHz using an HP 4192 A LF impedance analyzer (5Hz to 13MHz) and with a test signal of 50mV. Figure 4.16 and 4.17 display the forward and reverse bias C - V and G/ω - V characteristics of undoped and Sn doped ZnS/p-Si structures, respectively. As the figures, the capacitance values depend on the applied voltage. Moreover there are three regions on the C - V graphs; accumulation, depletion and inversion. That is, the C - V curves of the structures showed a same character with MIS structures.

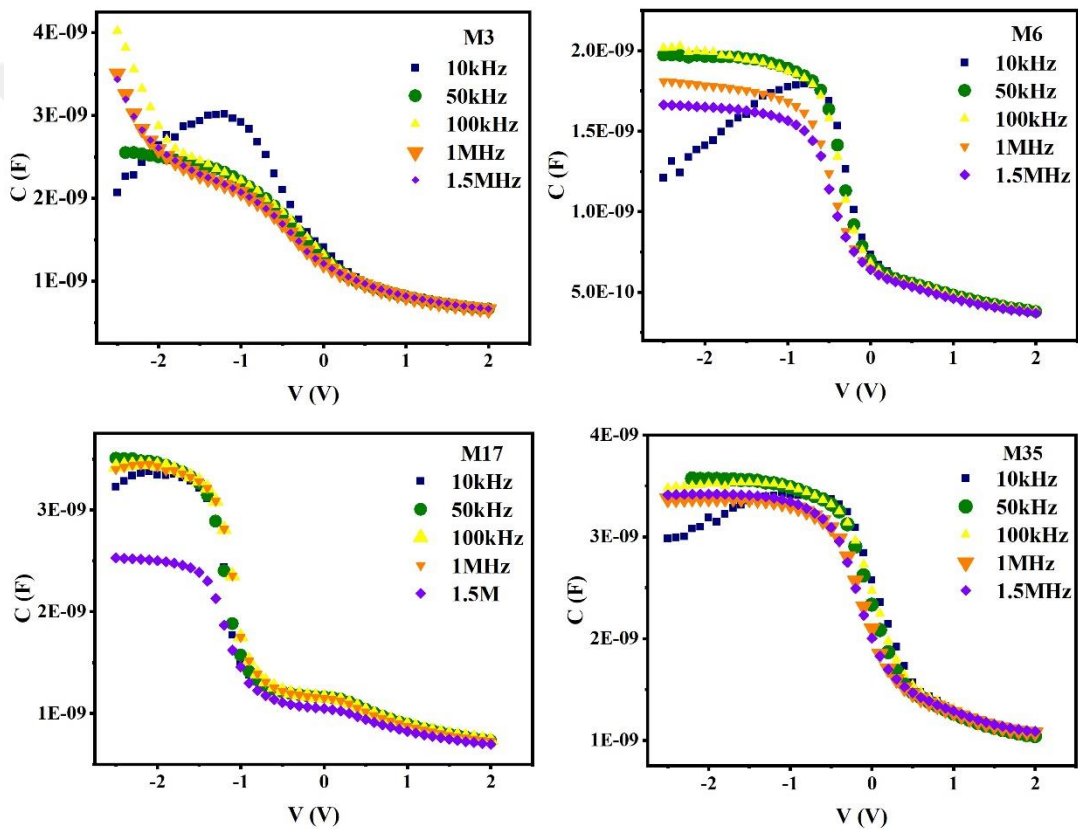


Figure 4.16 C - V graphs of Sn doped ZnS/p-Si diodes.

The C - V curves of the undoped and 1% Sn doped ZnS/p-Si structures have an abnormal second peak at low frequency values ($f=10$ kHz) and this abnormal peak cannot be observed at high frequencies and higher dopant concentration. Since the capacitance value is highly sensitive to the interface states, this abnormal peak can be observed. The conductance values changed with applied voltage and decreased frequency values. Thus, the conductance measurement exhibit voltage and frequency

dependent characteristics. According to the measurements, both C and G values decreased with increasing frequency value because of the interface states.

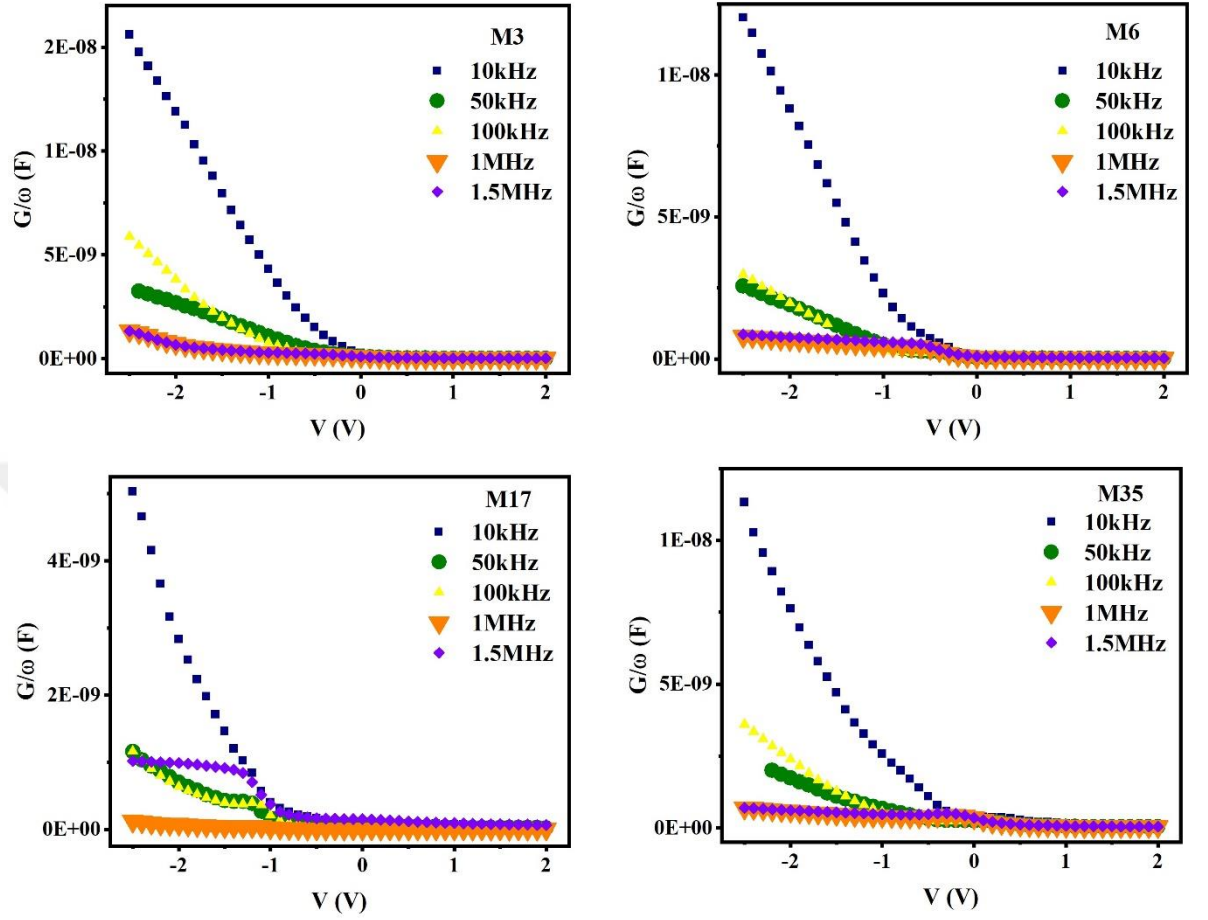


Figure 4.17 G/ω - V graphs of Sn doped ZnS/p-Si diodes.

Using equation (2.79), the R_s values were calculated as a function of applied voltage. Figure 4.18 gives the R_s values of Sn doped ZnS/p-Si. As the figure, it can be said that the R_s has a peak position and the magnitude of R_s decreased at high frequencies. When there is an insulating layer between MS contacts, the series resistance value decreases with increasing frequency. Thus, Sn doped ZnS layer behaves an insulator.

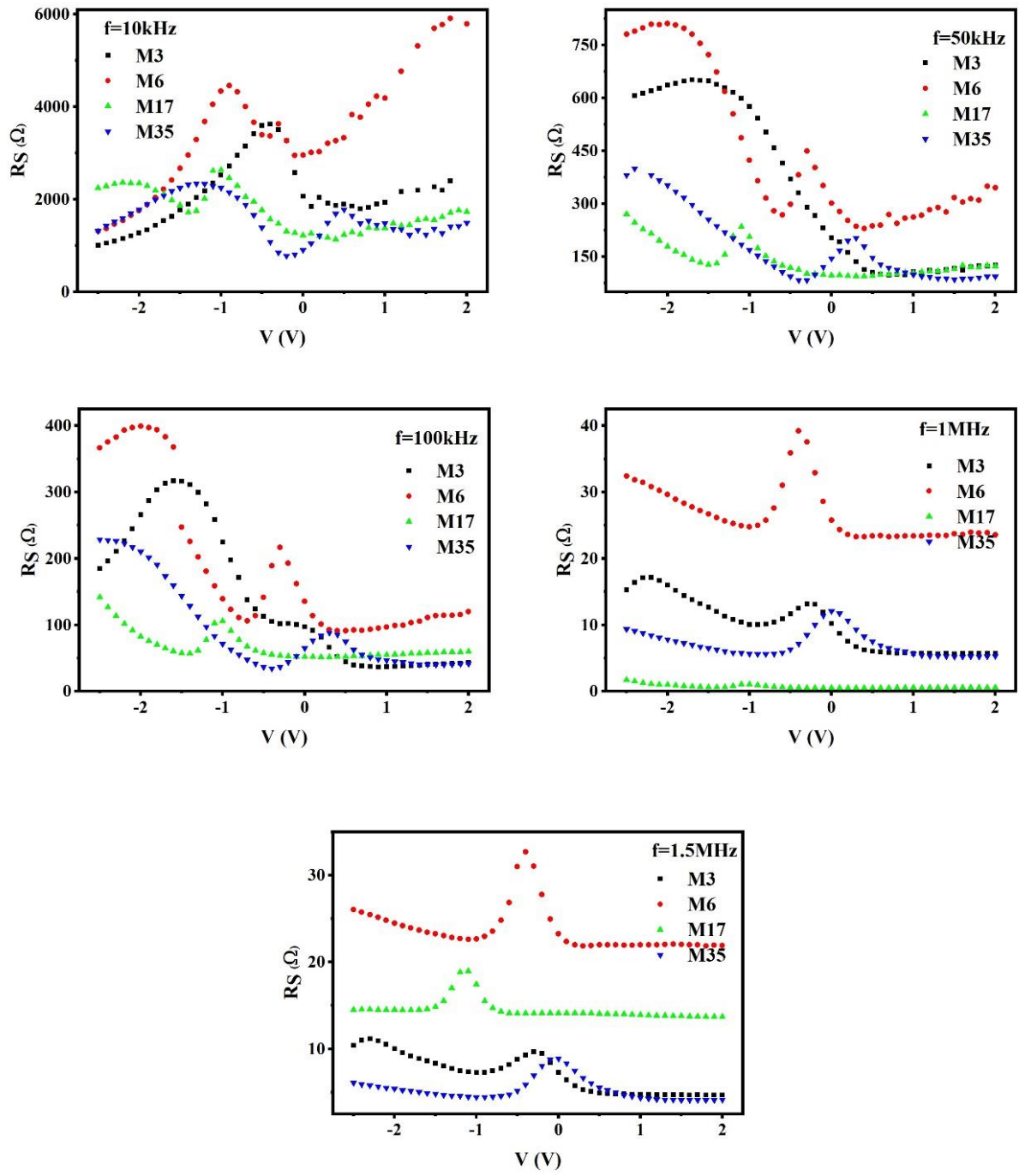


Figure 4.18 R_S - V plots of Sn doped ZnS/p-Si diodes.

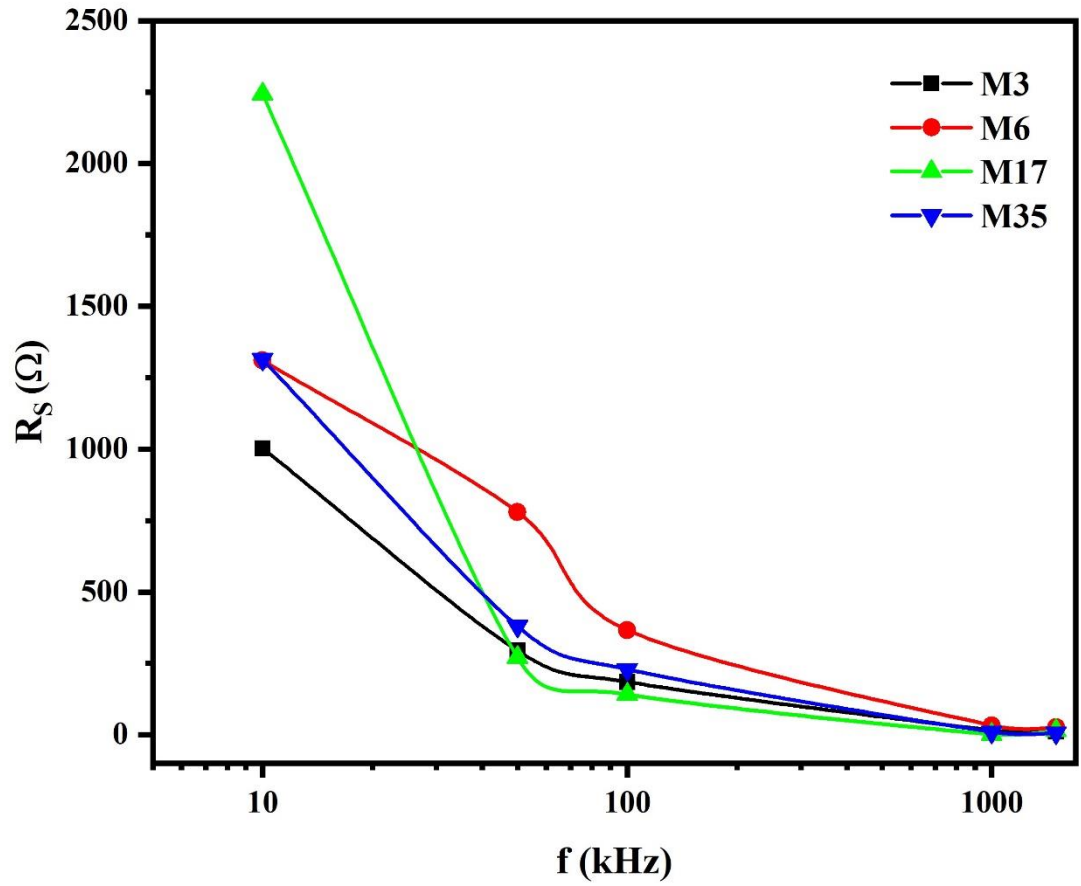


Figure 4.19 The variation of the R_s values in the strong accumulation region for Sn doped ZnS/p-Si diodes.

Figure 4.19 displays the calculated R_s values as a function of the frequency at -2.5V. The R_s values decreased with increasing frequency values and they are nearly same at the higher frequencies.

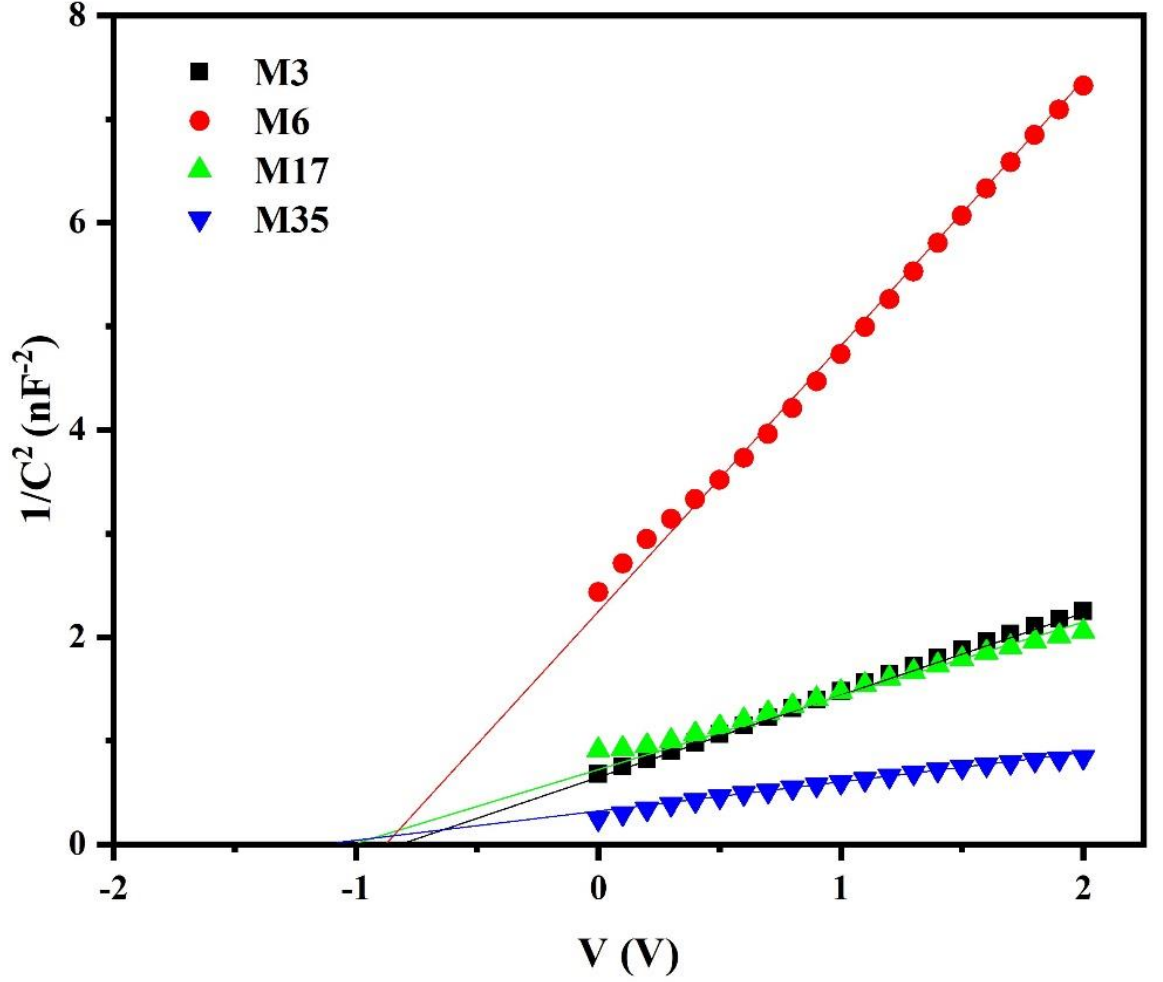


Figure 4.20 $1/C^2$ -V graphs of Sn doped ZnS/p-Si diodes.

$1/C^2$ -V graph of Sn doped ZnS/p-Si structures is given in Figure 4.20. According to the equation (2.69), the slope of the graph gives N_A and the extrapolation of the voltage axis gives V_0 values. Using equation (2.70) the diffusion potential V_d values were calculated. The depletion layer width, the barrier height values and the maximum electric field were determined using equation (2.65), (2.76) and (2.78), respectively. The calculated N_A , V_d , W_D , E_m and $\phi_B(C-V)$ values are presented in table 4.6.

Table 4.6 The diode parameters calculated from *C-V* measurements of undoped/doped ZnS/p-Si diodes.

Material	V_0 (V)	V_d (V)	$N_A \times 10^{15}$ (cm ⁻³)	$W_D \times 10^{-5}$ (cm)	E_m (kV/cm)	E_F (eV)	Φ_b (eV)	$\Delta\phi_b$ (meV)
M3	0.85	0.875	3.05	6.12	28.2	0.21	1.07	18.55
M6	0.9	0.925	1.22	9.95	18.4	0.23	1.15	14.96
M17	1.0	1.025	4.07	5.74	35.3	0.20	1.21	20.76
M35	1.05	1.075	8.14	4.15	51.2	0.19	1.24	24.99

According to the table, it is seen that increasing Sn concentration caused increasing in diffusion potential. The acceptor concentration value decreased for 1%Sn dopant while the other dopant caused increasing it. Besides, increasing carrier concentration decreased depletion region width. The barrier height values calculated from *I-V* measurements are less than those here. This difference is observed in MIS structures generally because of the inhomogenities in barrier height resulting from interface states.

4.5 Dielectric Characteristics of Al/ZnS/p-Si Diodes

The main dielectric parameters such as dielectric constant ϵ' , dielectric loss ϵ'' , loss tangent $\tan \delta$, real and imaginary part of the electric modulus (M' and M'') and ac conductivity σ_{ac} were calculated using the *C-V* and *G/ω-V* values of the undoped and Sn doped ZnS/p-Si structures.

Dielectric constant ϵ' , dielectric loss ϵ'' , and loss tangent $\tan \delta$ values of the structures were obtained using equations (2.82), (2.83) and (2.84), respectively.

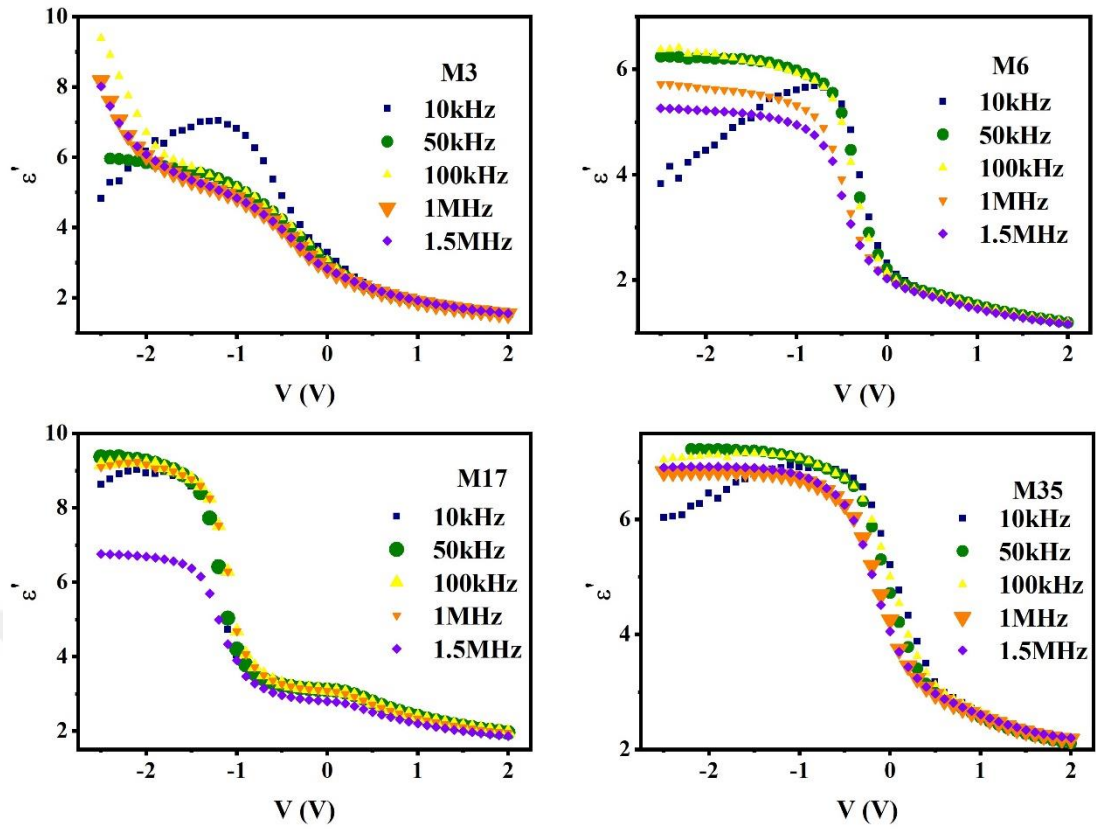


Figure 4.21 The variations of ϵ'' vs V of undoped and Sn doped ZnS/p-Si structures.

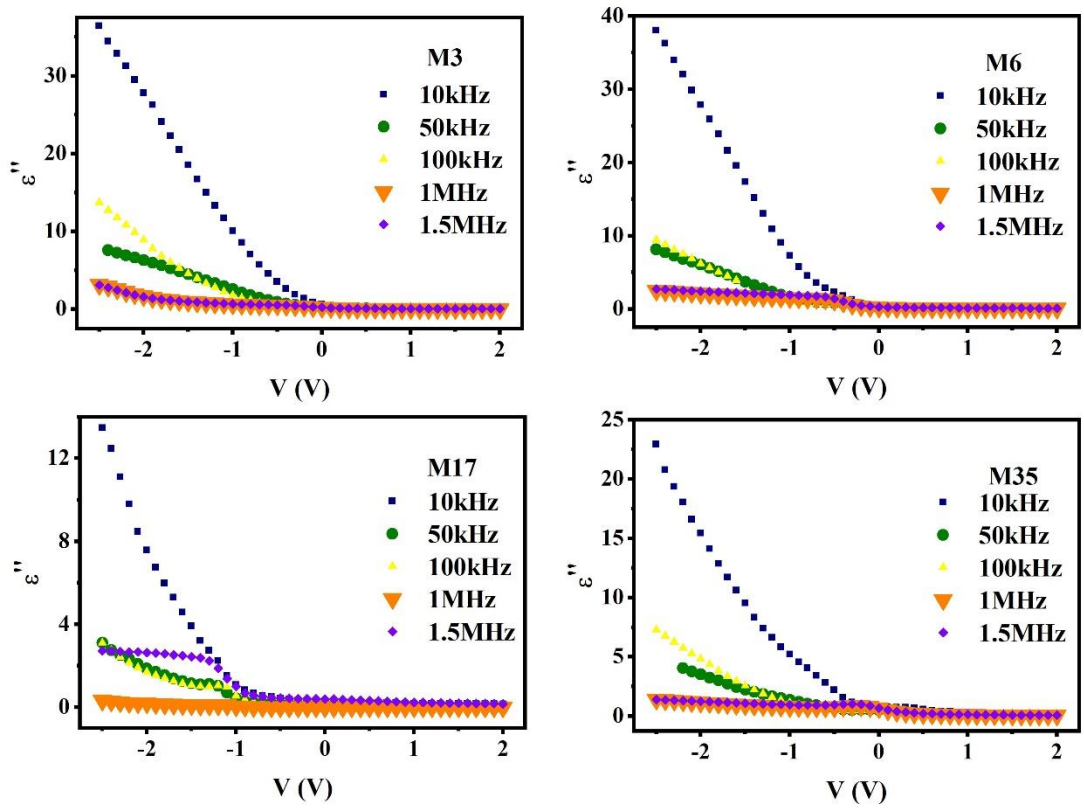


Figure 4.22 The variations of ϵ' vs V of undoped and Sn doped ZnS/p-Si structures.

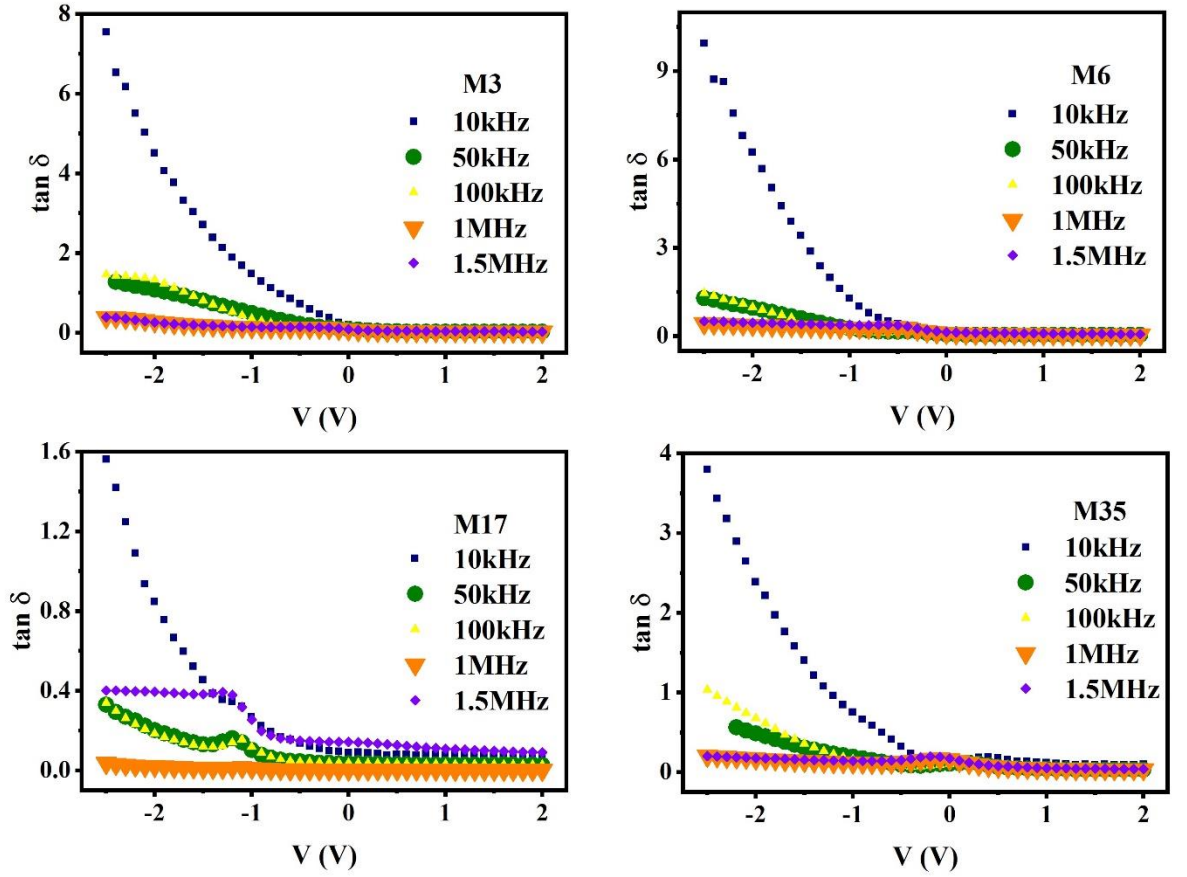


Figure 4.23 The variations of $\tan \delta$ vs V of undoped and Sn doped ZnS/p-Si structures.

As seen figures 4.21 and 4.22, ε' and ε'' values decreased with increasing frequency. The ε' and ε'' values are a strong function of voltage and frequency in the accumulation and depletion regions. In these regions, ε' and ε'' decrease with increasing frequency, while remaining almost constant in the inversion region. When these measurements are made at a sufficiently high frequency, the carrier lifetime of charges τ in traps or interfacial layer becomes much greater than the period. Thus the interface states cannot follow the ac signal at high frequencies, and it cannot contribute to the ε' and ε'' values. Accordingly, it is expected that the ε' and ε'' values will be larger at low frequencies. This means that an interface polarization mechanism exists.

The ac conductivity σ_{ac} and real and imaginary part of the electrical modulus (M' and M'') were calculated using equations (2.85) and (2.86), respectively. Figures 4.24 and 4.25 give the voltage dependent variation of the electrical modulus parameters. According to the figures, it can be clearly seen that the M' and M'' values are a strong function of frequency and voltage.

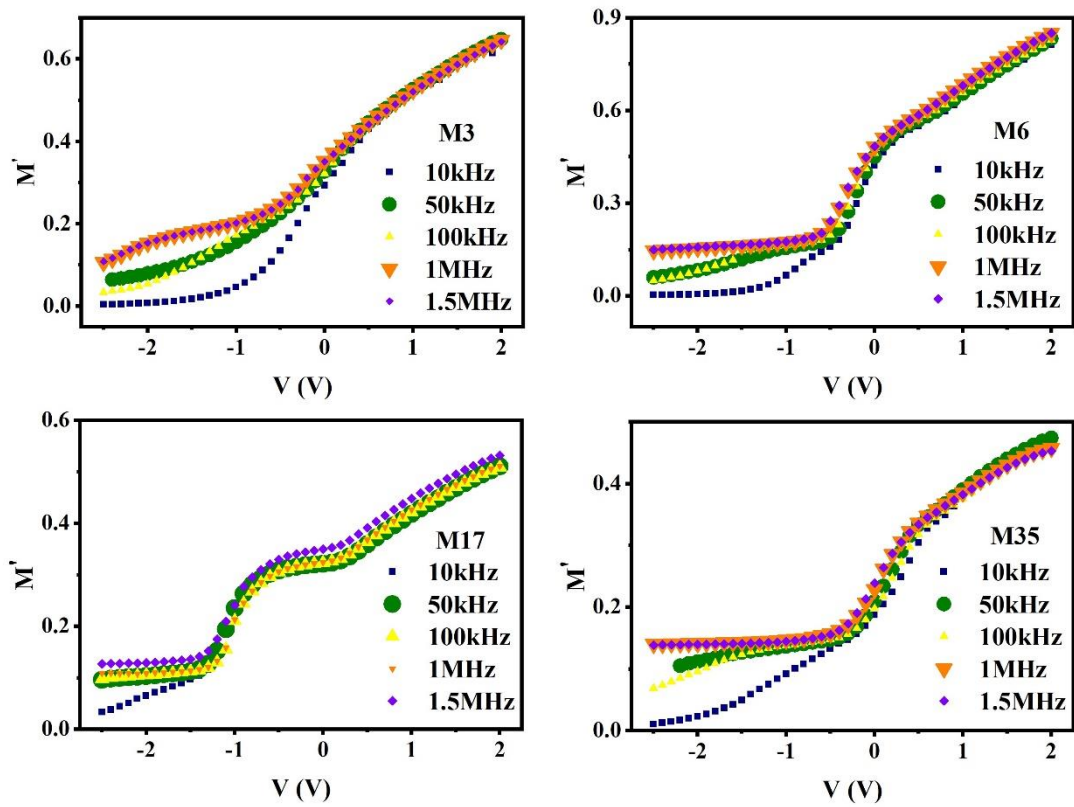


Figure 4.24 The real part of the electric modulus versus voltage plot of Sn doped ZnS/p-Si diodes.

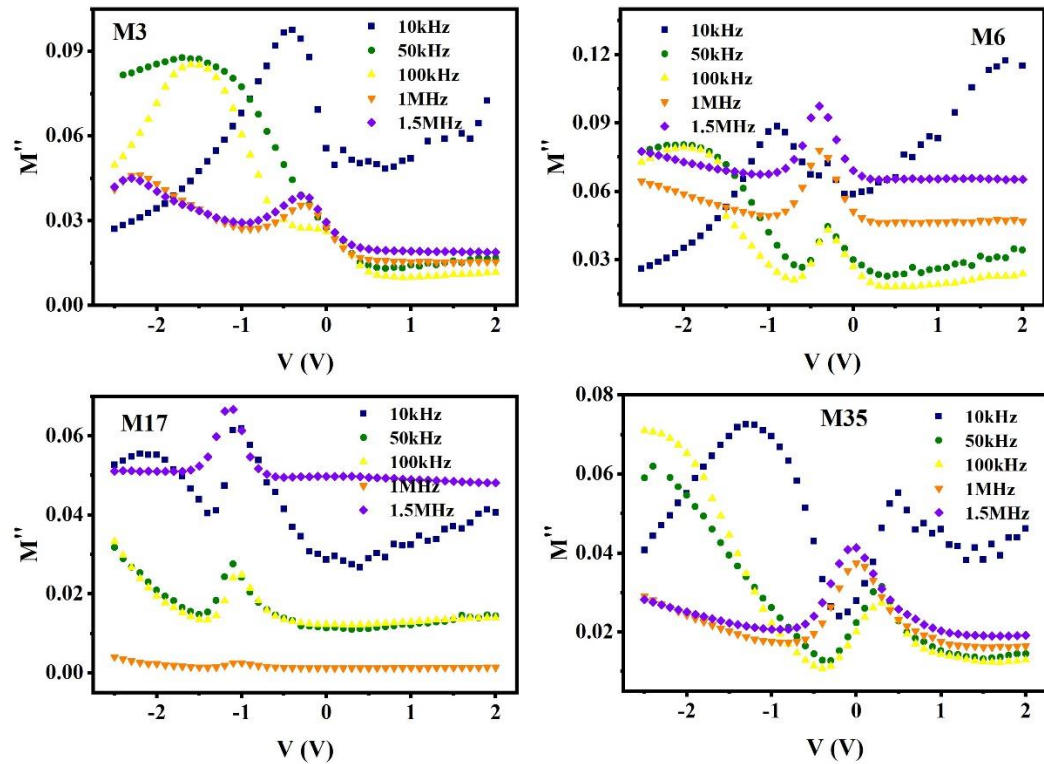


Figure 4.25 The imaginary part of the electric modulus versus voltage plot of Sn doped ZnS/p-Si diodes.

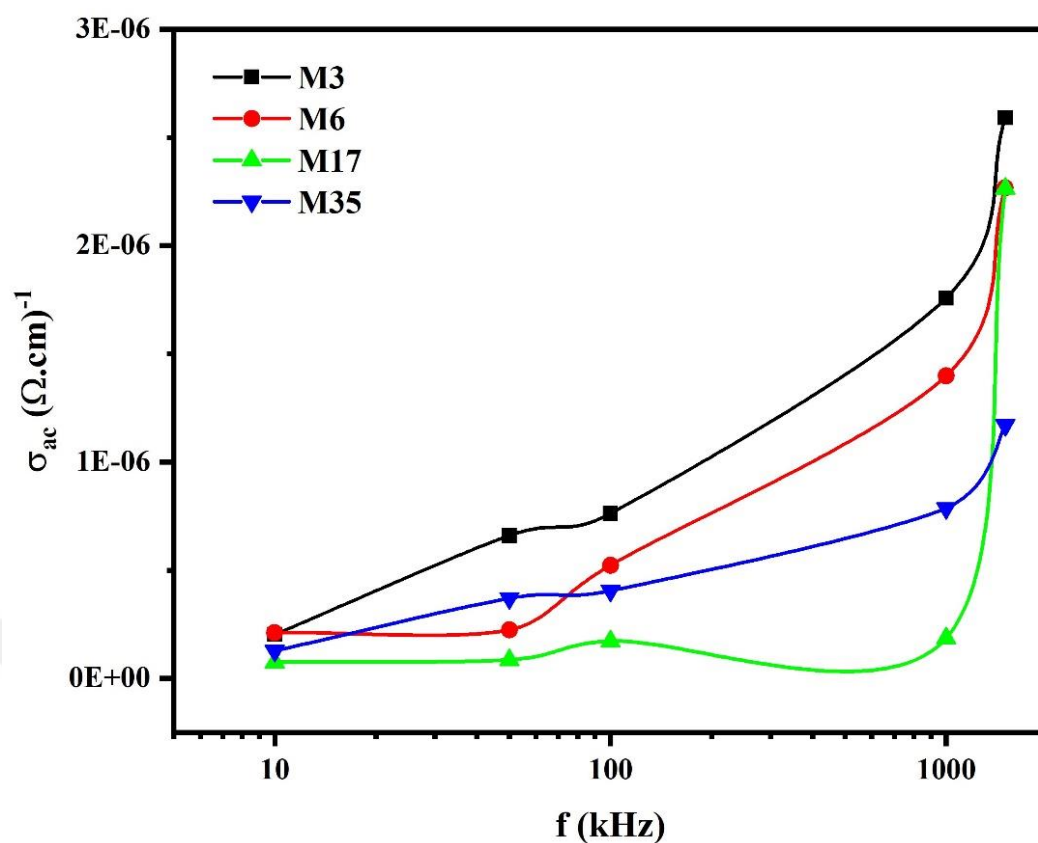


Figure 4.26 Frequency dependence of ac electric conductivity of Sn doped ZnS/p-Si structures.

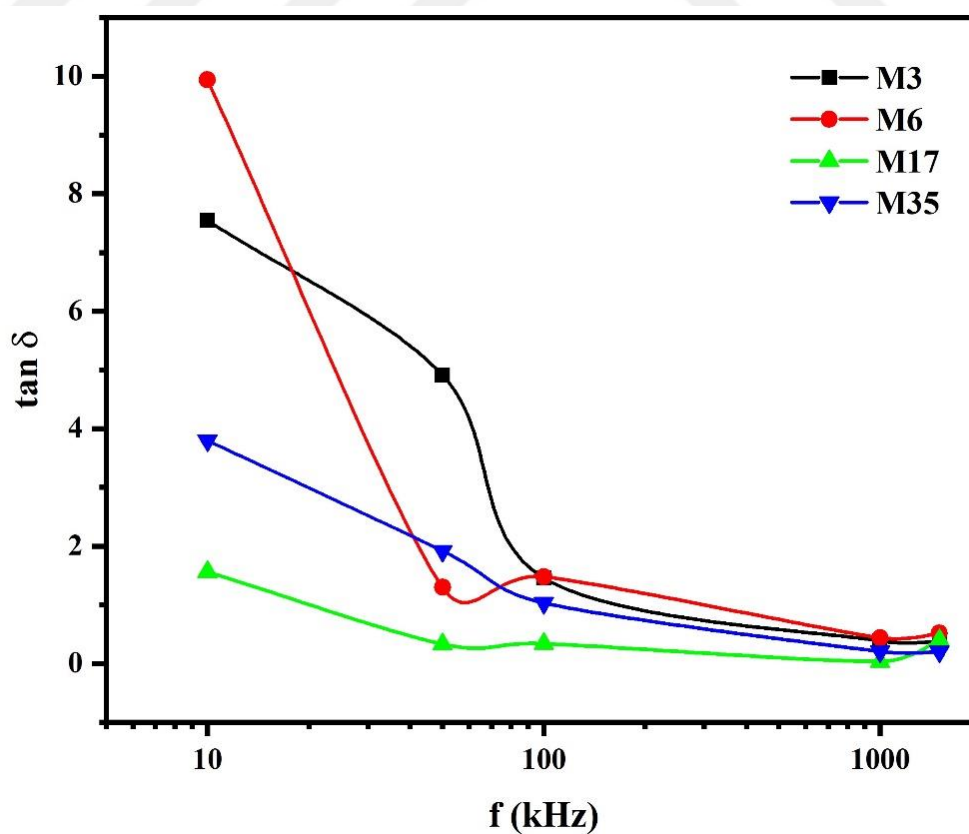


Figure 4.27 Frequency dependence of loss tangent of Sn doped ZnS/p-Si structures.

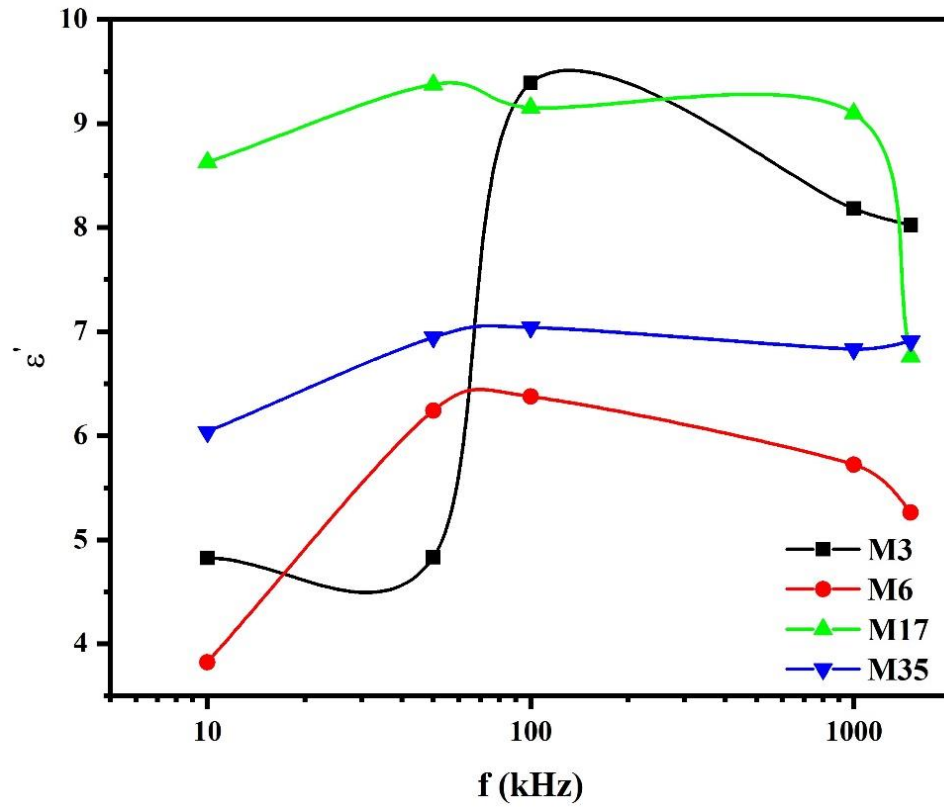


Figure 4.28 Frequency dependence of dielectric constant of Sn doped ZnS/p-Si structures.

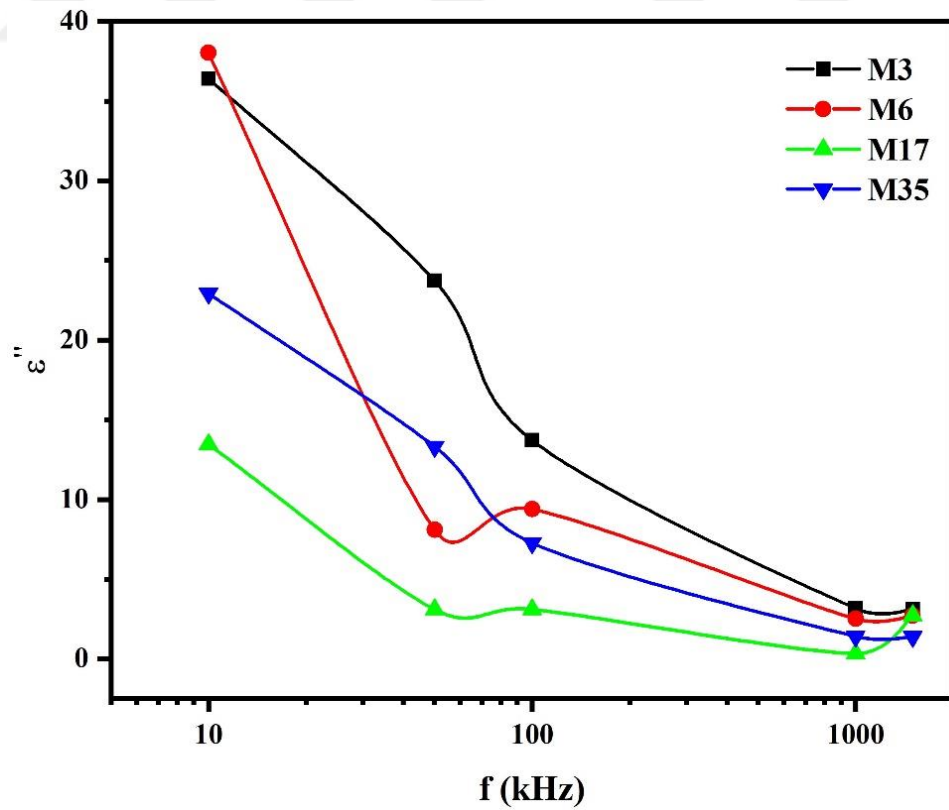


Figure 4.29 Frequency dependence of dielectric loss of Sn doped ZnS/p-Si structures.

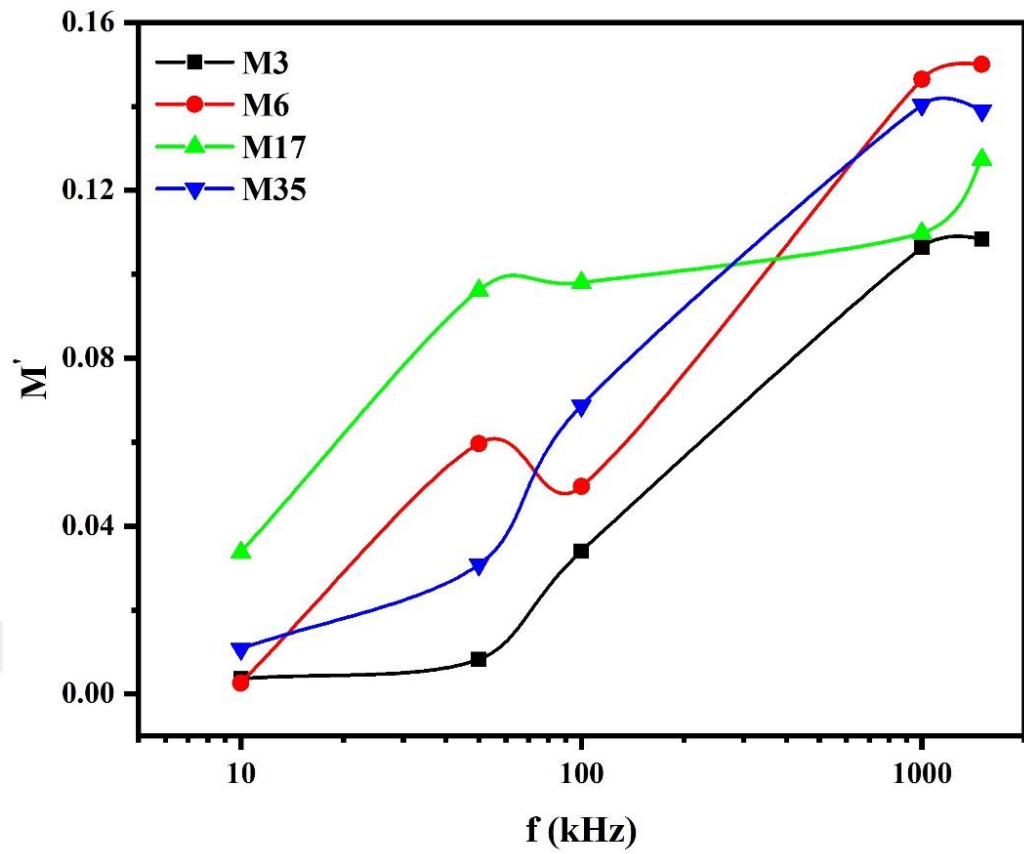


Figure 4.30 Frequency dependence of the real part of electric modulus.

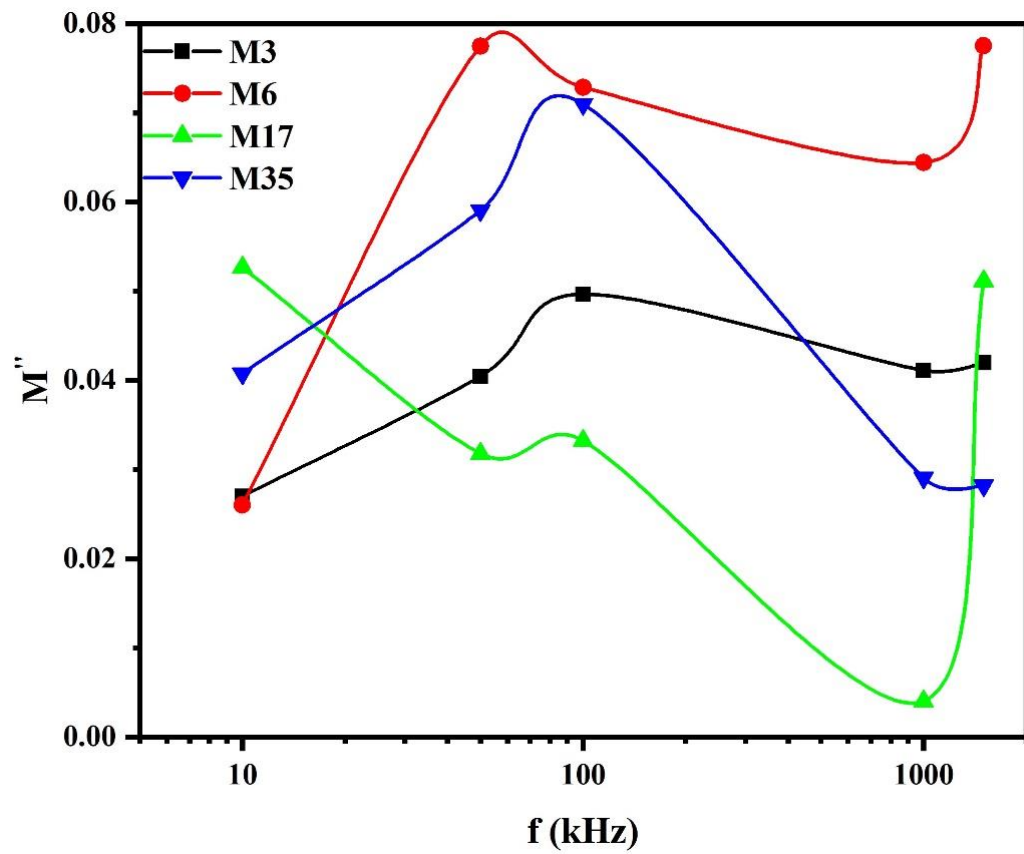


Figure 4.31 Frequency dependence of imaginary part of electric modulus.

Figure 4.26 and 4.27 display frequency dependent σ_{ac} and $\tan \delta$ plots of the undoped and Sn doped ZnS/p-Si structures in the strong accumulation region at $V=-2.5V$. According to the figures, it is seen that σ_{ac} and $\tan \delta$ values were affected by the changing frequency and Sn dopant concentration.

The frequency dependent ε' and ε'' plots of the structures are given in figure 4.28 and 4.29. It is clearly seen that ε' values firstly increased and then decreased after reaching a maximum value with increasing frequency while ε'' values decreased. According to equation (2.85), σ_{ac} value only depends on ε'' value. While ε'' decreased with increasing frequency, σ_{ac} increased.

Figure 4.30 and 4.31 show frequency dependent M' and M'' plots of the structures. As seen from the figures, M' component of the electrical modulus increased with increasing frequency, while M'' firstly increased and then decreased after reaching a maximum value. At the high frequencies, the M' goes to infinity, while at low frequencies it approaches zero. Since at high frequencies the period T is much less than the lifetime τ of the interface states, N_{ss} cannot follow an ac signal and the M' reaches a maximum value.

4.6 The Investigation of Photodiode Parameters of Al/ZnS/p-Si Diodes

In order to determine photodiode characteristics of the undoped and Sn doped ZnS/p-Si structures, they were illuminated with 100 mW/cm^2 power using AM 1.5 filter. The graph of the dark and illuminated I - V measurements in the reverse bias region is given in figure 4.32. According to the figure, it is said that the structures are sensitive to light due to increase in the current flowing. In addition, it is seen that the 3% Sn doped structure is more sensitive to light.

Using equations (2.87), (2.88) and (2.89), photosensitivity, detectivity and photoresponsivity values of the structures were calculated. The obtained values are listed in table 4. 7. Figure 4.33, 4.34 and 4.35 shows voltage dependent changes of the photodiode parameters of the structures.

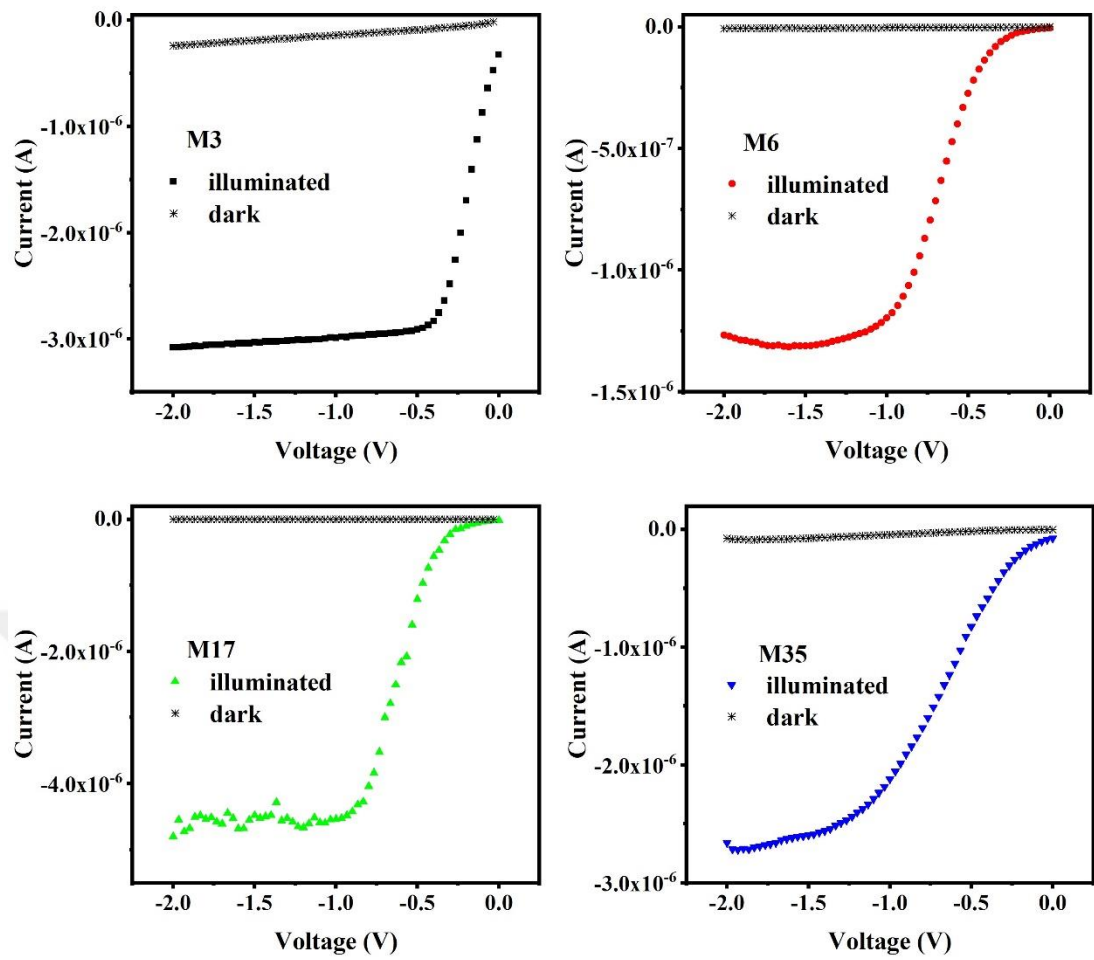


Figure 4.32 The *I-V* graph of the Sn doped ZnS/p-Si structures in the reverse bias region under illuminated and dark conditions.

Table 4.7 The photodiode parameters of the Sn doped ZnS/p-Si diodes.

Material	Photosensitivity	Detectivity ($\times 10^8$ Jones)	Photoresponsivity (mA/W)
M3	20.26	8.5	1.14
M6	439.04	25.6	0.48
M17	2900.57	128.23	1.81
M35	47.66	11.11	0.83

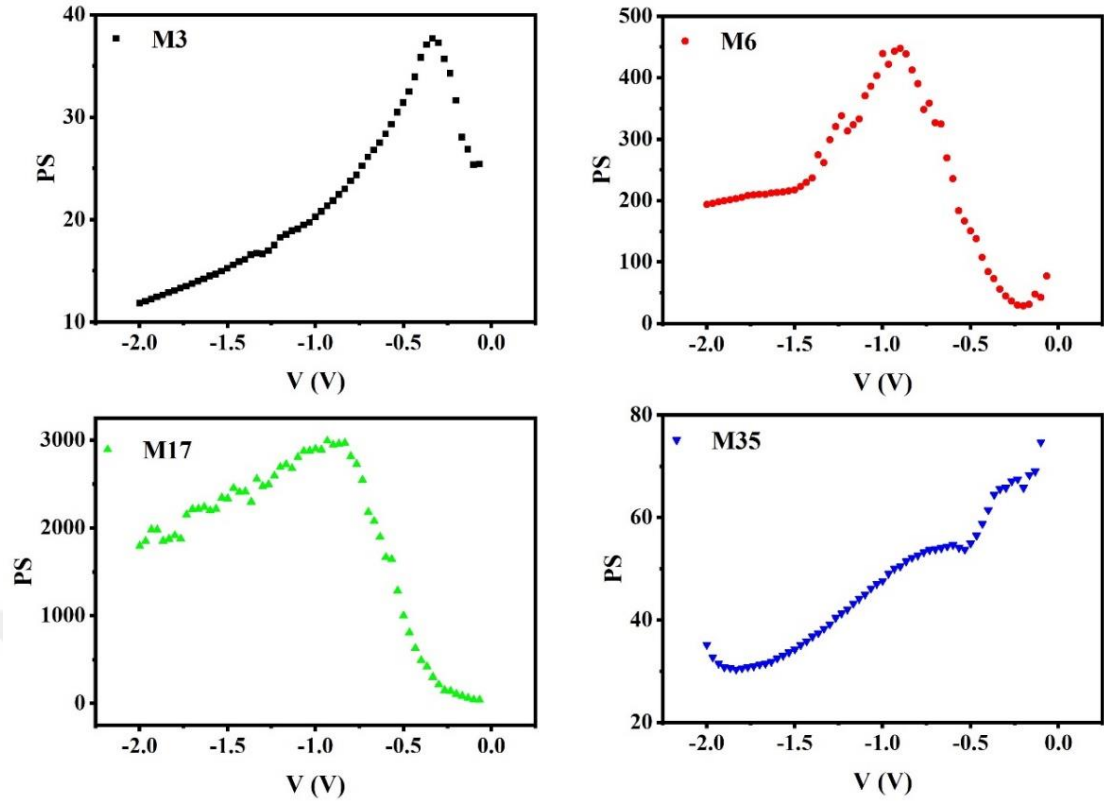


Figure 4.33 Photosensitivity versus voltage graph of the structures.

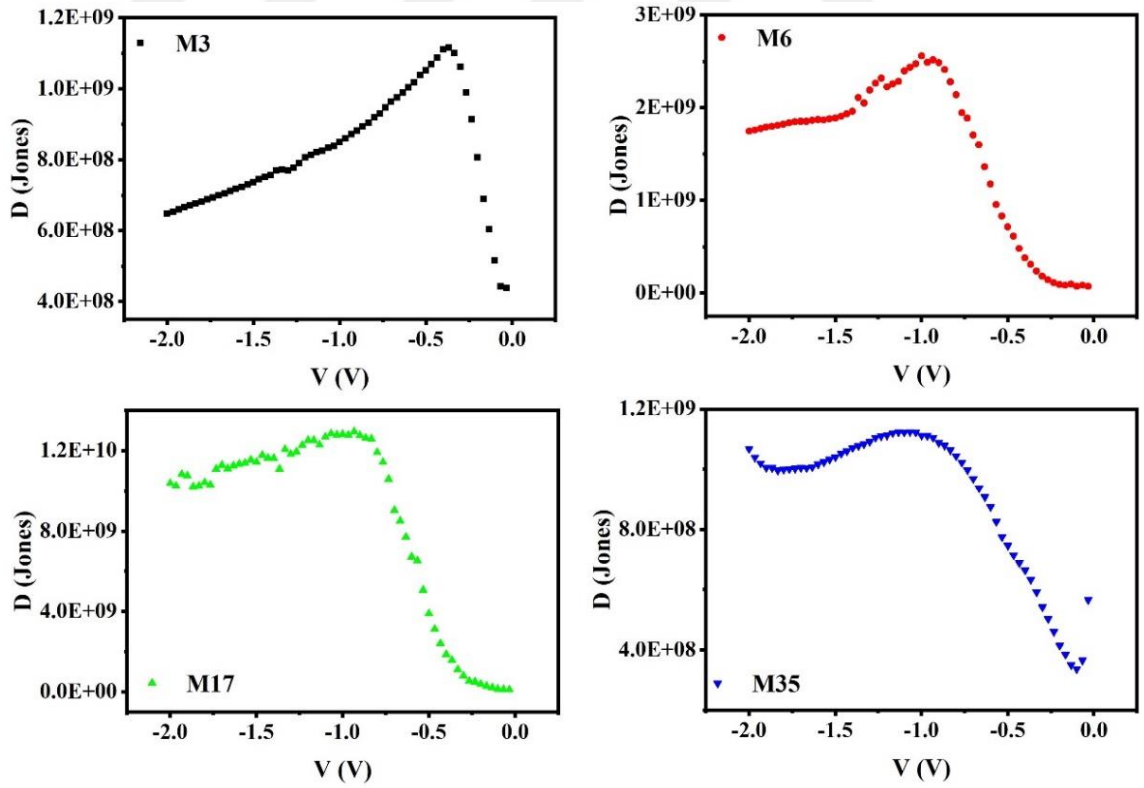


Figure 4.34 Detectivity versus voltage graph of the structures.

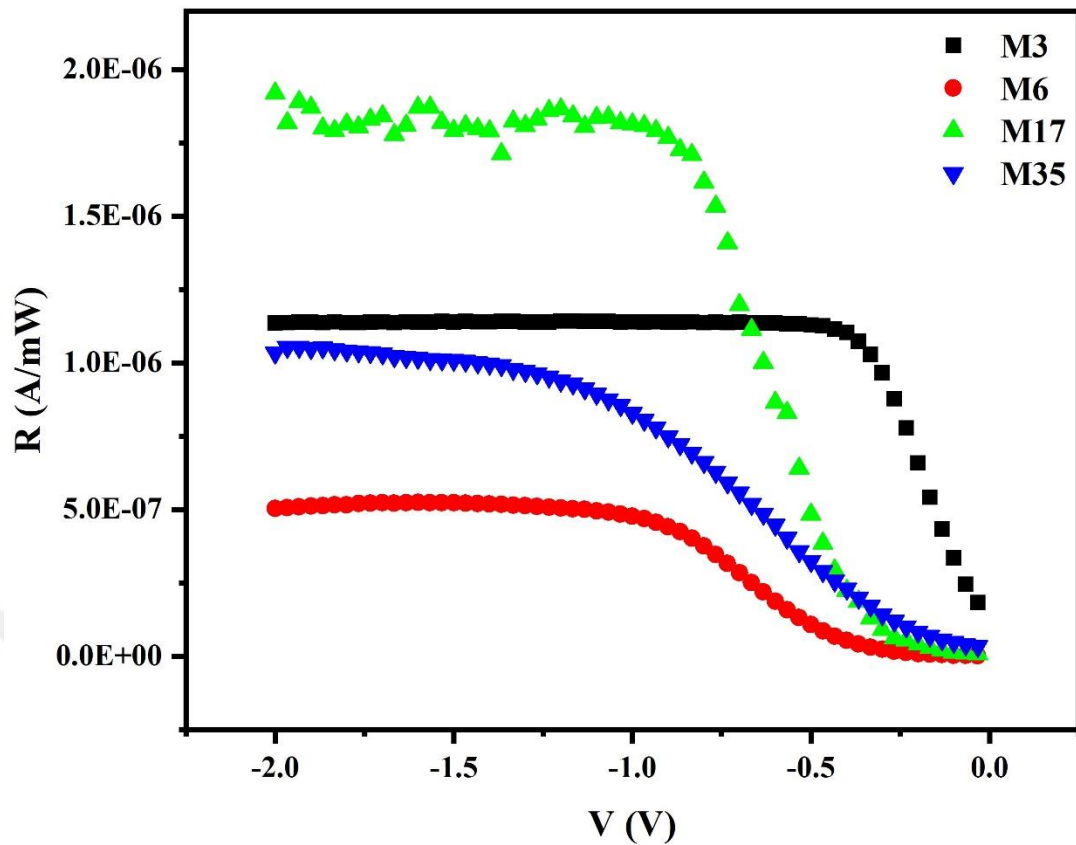


Figure 4.35 Responsivity versus voltage graph of the structures.

According to the figure 4.33 and 4.34, photosensitivity and detectivity graphs exhibit same characteristics. The values firstly increased and started to decrease after reaching a peak value. Responsivity values were almost constant in the range of -2 and -1V, but it decreased after -1V. The responsivity value for the undoped ZnS/p-Si structure started to decrease after -0.5V.

Photodiode parameters calculated at -1V are given in table 4.7. According to this, the photosensitivity and detectivity values firstly increased with increasing Sn concentration, and decreased for the 10% Sn doped structure, however it is still greater than that of the undoped ZnS/p-si structure.

CHAPTER V

CONCLUSION

ZnS is a material that has been studied by researchers for many years. Although there are many studies on doped and undoped ZnS thin films, there are not many studies on ZnS/p-Si contacts. In this study, undoped and Sn doped ZnS thin films and ZnS/p-Si heterostructures were fabricated by the sol-gel dip coating techniques and structural, optical, and especially diode characteristics were studied in detail.

Figure 4.1 and 4.2 display XRD pattern of Sn doped ZnS thin films grown on p-Si crystal and the glass substrates, respectively. According to the figures, it can be say the films were grown as cubic phase. The strongest diffraction peak was observed at $2\theta = \sim 28^\circ$ corresponding to (111) plane of the cubic ZnS structure. The intensity of the strongest peak increased with increased dopant concentration for 1%Sn and 3%Sn dopant concentration. In addition, (220) and (113) planes of the cubic ZnS structure were observed with increased Sn dopant concentration. On the other hand, 10% Sn doped ZnS thin films crystallized as amorphous. FWHM values increased with increasing dopant concentration and accordingly the grain size value decreased. It can be said that, undoped ZnS thin films exhibit best crystalline quality and Sn concentration caused reducing the crystalline quality. It is clear that ZnS films on p-Si crystallized in the cubic structure also. Both (111) plane of Si and (111) plane of ZnS give a peak nearly same angle ($2\theta = \sim 28^\circ$) and the intensity of the cubic Si much greater than that of the ZnS reflection. The main peak position of ZnS thin film is given in figure 4.1 as enlarged in order to understand the graph clearly.

The inter-planar distance values were found with the help of 2θ values obtained from the XRD spectrum and Bragg's Law. The lattice constants of the Sn doped ZnS thin films were calculated for the cubic phase. In addition, the crystallite size, the dislocation density, the microstrain and the lattice mismatch values were calculated.

The observed and obtained values are listed in Table 4.2. According to table 4.2, increasing Sn concentration caused the dislocation density and the microstrain values to rise. The lattice mismatch value are under 1%, thus interface defects are decidedly minimal. Besides, undoped ZnS has the smallest lattice mismatch value. Undoped ZnS grown on glass substrate has the best crystalline quality.

EDX spectrum of undoped and Sn doped ZnS thin films grown on the glass substrate is given in figure 4.3. The spectrum shows the presence of Zn, S and Sn elements in the growth film. According to the figure, it can be said that while Sn concentration increases in the growth film, the concentration of Zn decreases.

The cross-sectional SEM images of undoped and Sn doped ZnS thin films is given in figure 4.4. Using the cross-sectional images, the film thickness values were determined. The thickness d value were found as 276 nm, 323 nm, 292nm and 277nm for 0%, 1%, 3% and 10% Sn doped ZnS thin films.

In order to calculate the film thickness and the optical band gap value, UV-VIS-NIR spectrum of the films was measured. Although the films have very high transparency, the increasing in dopant concentration caused decreasing in transmittance value. The maxima transmittance value are approximately 85% in the strong absorption region. The film thicknesses were found as 278.84 nm, 377.84 nm, 319.62 nm and 241.87 nm for 0%, 1%, 3% and 10% Sn doped ZnS thin films, using Swanepoel method. Using Tauc relation, $(\alpha h\nu)^2$ vs $h\nu$ graph of the films were drawn. By extrapolating the graph to the $h\nu$ -axis, the optical band gap values of the films were found. The optical band gap value is 3.55eV for undoped ZnS thin film. The Sn concentration caused the optical band gap to decrease. Although 3% Sn doped increased the optical band gap value compared to 1% Sn doped, the band gap is still less than that of undoped ZnS.

In order to investigate diode characteristics of the undoped and Sn doped ZnS/p-Si structures, I - V measurements were performed in the dark at room temperature. Figure 4.10 displays the semi-logarithmic graph of the Sn doped ZnS/p-Si structures in the voltage range $\pm 2V$ at the room temperature. According to the figures, it can be said that the dopant atoms increased current flowing. The rectification ratio calculated from the ratio of current values at $\pm 2V$ as 167.94, 9062.98, 18525.91 and 1876.44 for undoped, 1%Sn, 3%Sn and 10%Sn doped ZnS/p-Si structures, respectively. The

rectification ratio increased with the effect of Sn concentration. The best value belongs to 3%Sn doped structure. *I-V* characteristics of the structures were investigated via TE, Norde, Lien and Cehung's method. The ideality factor value was found as 3.86 for undoped ZnS/p-Si structure using TE. It can be said that the contribution of Sn reduced the ideality factor value. The best ideality factor value was observed in 10% Sn doped ZnS/p-Si structure as 2.39. Similarly the saturation current value decreased with the effect of Sn dopant. The series resistance value was calculated using three different methods. Although the obtained values differ, it can be said that the results are in the same order. The smallest series resistance value was obtained as 15.01k Ω for the 10%Sn doped structure, while the largest series resistance value was determined as 239.8k Ω for the 3%Sn doped structure using Cheung's method. The barrier height value of doped ZnS/p-Si structures increased with the effect of Sn dopant.

The ideality factor being $n > 1$ is the proof that the structures deviate from ideality. This results is due to the interface states. Thus, the density of interface states values were determined according to the voltage dependent ideality factor values. N_{ss} versus $E_{ss}-E_V$ graph of the undoped and doped ZnS/p-Si structures were drawn with and without R_s . According to the figure 4.14 and 4.15, decreasing of the ideality factor value caused decreasing of the density of interface states. The interface states values with series resistance are smaller than the interface states without series resistance.

The *C-V* and the *G/ ω -V* measurements of undoped and Sn doped ZnS/p-Si structures were carried out in the dark at room temperature in the frequency range 10kHz-1.5MHz. Figure 4.16 and 4.17 give the forward and reverse bias *C-V* and *G/ ω -V* characteristics of undoped and Sn doped ZnS/p-Si structures, respectively. As the figures, the structures exhibited ideal MIS behavior. The capacitance values depend on the applied voltage and there are three regions on the *C-V* graphs; accumulation, depletion and inversion. The *C-V* curves of the undoped and 1% Sn doped ZnS/p-Si structures have an abnormal second peak at low frequency values ($f=10\text{kHz}$) and this abnormal peak cannot be observed at high frequencies and higher dopant concentration. Since the capacitance value is highly sensitive to the interface states, this abnormal peak can be observed. The conductance values changed with applied voltage and decreased frequency values. Thus, the conductance measurement exhibit voltage and frequency dependent characteristics. According to the measurements, both

C and G values decreased with increasing frequency value because of the interface states.

The R_s values were calculated as a function of applied voltage. Figure 4.18 gives the R_s values of Sn doped ZnS/p-Si. As the figure, it can be said that the R_s has a peak position and the magnitude of R_s decreased at high frequencies. When there is an insulating layer between MS contacts, the series resistance value decreases with increasing frequency. Thus, Sn doped ZnS layer behaves an insulator. Figure 4.19 displays the calculated R_s values as a function of the frequency at -2.5V. The R_s values decreased with increasing frequency values and they are nearly same at the higher frequencies.

N_A , V_d , W_D , E_m and $\phi_B(C-V)$ values were calculated using $1/C^2-V$ graph of the structures. According to the result, it is seen that increasing Sn concentration caused increasing in diffusion potential. The acceptor concentration value decreased for 1%Sn dopant while the other dopant caused increasing it. Besides, increasing carrier concentration decreased depletion region width. The barrier height values calculated from $I-V$ measurements are less than those here. This difference is observed in MIS structures generally because of the inhomogenities in barrier height resulting from interface states.

The main dielectric parameters such as dielectric constant ϵ' , dielectric loss ϵ'' , loss tangent $\tan \delta$, real and imaginary part of the electric modulus (M' and M'') and ac conductivity σ_{ac} were obtained using the $C-V$ and $G/\omega-V$ values of the undoped and Sn doped ZnS/p-Si structures. ϵ' and ϵ'' values decreased with increasing frequency. Since the interface states cannot follow the ac signal at low frequencies, it cannot contribute to the ϵ' and ϵ'' values. Accordingly, it is expected that the ϵ' and ϵ'' values will be larger at low frequencies. This means that an interface polarization mechanism exists. In addition, M' and M'' values are a strong function of frequency and voltage. The dependence of the dielectric parameters on the frequency was also investigated. According to the results, it is seen that σ_{ac} and $\tan \delta$ values were affected by the changing frequency and Sn dopant concentration. Besides, ϵ' values firstly increased and then decreased after reaching a maximum value with increasing frequency while ϵ'' values decreased. σ_{ac} value only depends on ϵ'' value. While ϵ'' decreased with increasing frequency, σ_{ac} increased. On the other hand, M' component of the electrical

modulus increased with increasing frequency, while M'' firstly increased and then decreased after reaching a maximum value. At the high frequencies, the M' goes to infinity, while at low frequencies it approaches zero. Since at high frequencies the period T is much less than the lifetime τ of the interface states, N_{ss} cannot follow an ac signal and the M' reaches a maximum value.

To investigate photodiode characteristics of the undoped and Sn doped ZnS/p-Si structures, they were illuminated with 100 mW/cm^2 power using AM 1.5 filter. The graph of the illuminated and dark I - V measurements in the reverse bias region is given in figure 4.32. According to the figure, it is said that the structures are sensitive to light due to increase in the current flowing. In addition, it is seen that the 3% Sn doped structure is more sensitive to light.

According to the figure 4.33 and 4.34, photosensitivity and detectivity graphs exhibit same characteristics. The values firstly increased and started to decrease after reaching a peak value. Responsivity values were almost constant in the range of -2 and -1V, but it decreased after -1V. The responsivity value for the undoped ZnS/p-Si structure started to decrease after -0.5V.

Photodiode parameters calculated at -1V are given in table 4.7. According to this, the photosensitivity and detectivity values firstly increased with increasing Sn concentration, and decreased for the 10% Sn doped structure, however it is still greater than that of the undoped ZnS/p-Si structure.

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2. Ş. Uzun Çam, T. Serin, A. N. Yazıcı, “Effect of Sn doping concentration on structural, optical and electrical properties of ZnS/p-si (111) diodes fabricated by sol-gel dip-coating method” *Materials Science in Semiconductor Processing*. 127 (2021) 105693. <https://doi.org/10.1016/j.mssp.2021.105693>
3. A. Yıldız, Ş. Uzun, N. Serin, T. Serin, “Influence of grain boundaries on the figure of merit of undoped and Al, In, Sn doped ZnO thin films for photovoltaic applications”. *Scripta Materialia*. 113 (2016) 23-26. <http://dx.doi.org/10.1016/j.scriptamat.2015.10.004>
4. N. Serin, A. Yıldız, E. Çam, Ş. Uzun, T. Serin, “Fluctuating in the hopping rate of CuO thin films with respect to substrate temperature”. *Superlattices and Microstructures*. 52 (2012) 759-764. <http://dx.doi.org/10.1016/j.spmi.2012.06011>
5. T. Serin, A. Yıldız, Ş. Uzun, E. Çam, N. Serin, “Electrical conduction properties of In-doped ZnO thin films” 84 (2011) 065703. <http://doi.org/10.1088/0031-8949/84/06/065703>

CONFERENCES AND CONGRESSES

1. Şirin Uzun Çam, Tülay Serin, A. Necmeddin Yazıcı. “Determination of The Optical Parameters of Ga Doped ZnS Thin Films” *Ankara International Congresses on Scientific Research-V*. (2021) (Abstract paper and Oral Presentation)
2. Şirin Uzun Çam, A. Necmeddin Yazıcı, Tülay Serin. “ZnS/p-Si Photodiodes Prepared by Sol-gel Dipping Method” *3.Uluslararası Zeugma Bilimsel Araştırmalar Kongresi*. (2019) (Full text paper and Oral presentation)
3. Abdullah Yıldız, Şirin Uzun, Sibel Gürakar, İlker Kara, Necmi Serin, Tülay Serin. “Effect of Co and Cu dopants on the structural optical and electrical properties of ZnO nanocrystals” *2nd International Nanoscience and Nanotechnology for Next Generation Conference (NaNONG)*. (2015)

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