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INVESTIGATION OF STRUCTURAL, MORPHOLOGICAL, AND OPTICAL PROPERTIES OF Cu-Sn DOPED ZnO FILMS BY SILAR METHOD

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ABJAR IBRAHIM RASHID HAFEDH

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INVESTIGATION OF STRUCTURAL, MORPHOLOGICAL, AND OPTICAL PROPERTIES OF Cu-Sn DOPED ZnO FILMS PRODUCED BY SILAR METHOD

By Abjar Ibrahim Rashid HAFEDH

February 2023

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Abjar Ibrahim Rashid HAFEDH

ABSTRACT

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January 2023

Due to its high permeability and abundance in nature, ZnO semiconductor is widely used in technological applications. ZnO nanocrystal is an alternative to other oxide materials because its structural, optical and electrical properties can be improved by adding appropriate doping. Doped and undoped ZnO thin films can be grown by different methods. In this study, FTO/ZnO, FTO/ZnO/Sn-Cu 1%, FTO/ZnO/Sn-Cu 2%, FTO/ZnO/Sn-Cu 3% doped films were obtained by using the SILAR method. The structural properties of the produced ZnO thin films were investigated depending on the additive concentration. The structural and morphological properties of the produced thin films were examined by X-Ray Diffraction Device (XRD), Scanning Electron Microscope (SEM) and UV-VIS spectrometry (UV-VIS). From the XRD anaysis, it was determined that the structure of the produced thin films changed from amorphous structure to polycrystalline structure as the Cu and Sn concentration ratio changed. From the SEM images, it was observed that the morphological properties of the produced thin films changed depending on the additive concentration. The band gaps of the produced thin films were determined by UV-VIS spectrometry. It was observed that the obtained results were compatible with the literature, and a change in the forbidden energy gaps as the doping ratio increased was observed.

2023, 56 pages

Keywords: SILAR method, Zinc oxide, Thin films

ÖZET

SILAR YÖNTEMİYLE Cu-Sn KATKILI ZnO FİLMLERİN YAPISAL, MORFOLOJİK VE OPTİK ÖZELLİKLERİNİN İNCELENMESİ

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Şubat 2023

ZnO yarıiletkeni yüksek geçirgenliği ve doğada bol bulunması gibi nedenlerle teknolojik uygulamalarda yaygın olarak kullanılmaktadır. ZnO nanokristaline uygun katkılamalar yapılarak yapısal, optiksel ve elektriksel özellikleri iyileştirilebilmesi nedeniyle diğer oksit malzemelere alternatif olarak kullanılmaktadır. Katkılı ve katkısız ZnO ince filmler farklı yöntemlerle büyütülebilmektedir. Bu çalışmada SILAR yöntemiyle kullanılarak FTO/ZnO, FTO/ZnO/Sn-Cu %1, FTO/ZnO/Sn-Cu %2 ve FTO/ZnO/Sn-Cu %3, katkılı filmler elde edilmiştir. Elde edilen ZnO ince filmlerinin yapısal özellikleri katkı konsantrasyonu bağlı değişimi incelenmiştir. Üretilen ince filmlerin yapısal ve morfolojik özellikleri X-ışını Kırınım Cihazı (XRD), Taramalı Elektron Mikroskopu (SEM) ve UV spektroskopisi (UV-VIS) yöntemleriyle incelendi. XRD analizlerinden, üretilen ince filmlerin Cu ve Sn konsantrasyon oranı değiştikçe amorf yapıdan polikristal yapısına değiştiği belirlendi. SEM görüntülerinden katkı konsantrasyonuna bağlı olarak üretilerin filmlerin morfolojik özelliklerinde değiştiği gözlendi. Üretilen ince filmlerin yasak bant aralıkları UV-VIS spektrometresi ile belirlenmiş olup elde edilen sonuçların literatürle uyumlu olmakla birlikte, katkılama oranı arttıkça yasak enerji aralıklarında değiştiği gözlendi.

2022, 56 sayfa

Anahtar Kelimeler: SILAR metodu, Çinko oksit, İnce film

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Abjar Ibrahim Rashid HAFEDH
Çankırı-2023

CONTENTS

LIST OF SYMBOLS

A	Absorbance
Å	Angstrom
°C	Centigrade degree
Cs	Crystal size
d_{hkl}	Interplaner distance
d_{XRD}	Experimental distance
d_{CARD}	Standard distance
E_g	Energy gap
E_{ph}	Phonon energy
eV	Electron volt
h	Planck's constant
I	Transmittance intensity
I_A	Absorbed intensity
I_R	Reflected intensity
I_o	Standard (Incidence) intensity
K	Shape factor
k_o	Extinction coefficient
k_B	Boltzman constant
M	Molar
$M_{(hkl)}$	Miller indices
nm	Nanometer
n_o	Refractive index
N	Complex refractive index
R	Reflectance
ν	Frequency
T	Transmittance
TCO	Transparent conductive oxides
θ	Bragg angle

LIST OF ABBREVIATIONS

EDS	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscope
UV-VIS	Ultraviolet-visible
XRD	X-ray diffraction

LIST OF FIGURES

LIST OF SYMBOLS

1. INTRODUCTION

Today, the rapid development of technology and the reduction in the size of electronic devices have increased the interest in technology. Production of electronic devices in a smaller size; it not only allowed the device to take up less space, but also increased the operating speed of the produced devices. Higher quality, useful devices have been produced using the new features gained due to reduction in the size of the materials (Akman 2020). It has enabled the development of nanotechnology with materials produced in atomic size.

The optical properties, electrical properties and crystal structures of nanomaterials obtained by the rapid development of technology and the use of modern devices in the production phase have begun to be investigated in more detail (Akhtar *et al.* 2008). With this development, thin films have found a wide execution area in the production of many technological devices. Today, because the largest application area of thin film technology is the semiconductor industry, it has become a necessity to understand the properties of semiconductors and to expand new compound semiconductors (Chang *et al.* 2012).

This technology also has been used in physical and chemical research about optic, magnetic recording devices and optical sensors, such as transistors, integrated circuits (IC), light emitting diodes (LED), LCD displays, laser applications, solar cells, night vision binoculars (Raidou *et al.* 2010). Recently, the development of thin film technology has made it possible to obtain materials which have wide usage areas more easily.

Enlarge methods of semiconductor thin films can be divided into two main topics. These are (a) gas phase and (b) liquid phase growth methods. Gas phase growth methods; these are enlarge methods such as Molecular Beam Epitaxy (MBE), Metal Organic Chemical Vapor Deposition (MOCVD), Reactive Sputtering (RF). Growth methods in liquid phase are growth techniques such as Chemical Bath Deposition (CBD), Liquid Phase Epitaxy (LPE), Chemical Spraying (SP), SILAR (Succesive Ionic Layer Adsorption And Reaction) (Vanmaekelbergh and Vugt 2011). Gas phase growth techniques are less preferred because they involve quite expensive systems compared to others. On the other

hand, liquid phase growth techniques are preferred because of their important advantages such as large-area thin film production and low cost of producing thin fims (Zhang *et al*. 2010).

ZnO (Zinc Oxide) based semiconductor, which has a great potential in the development of devices based on nanotechnology, is the most studied material today. In addition, thanks to its wide band gap, ZnO has the potential to be used in the construction of devices such as laser diodes, which operating in the UV region, and Light Emitting Diodes (LED) (Kokubun *et al.* 2003).

The film studies, which are transparent and highly conductive, have a wide range of uses in both industry and research studies. This has triggered the investigation of semiconductor thin films. This result has attracted attention in research on the structural properties of films and producing films containing ZnO and ZnO in order to reduce the cost and alternative materials (Liang and Yoffe 2002).

These semiconductor transparent films are produced; they have been used in a wide range of applications, such as solar cells, heat reflectors, gas sensors, light transparent electrodes, biosensors, display devices, photocathodes in photoelectrochemical batteries, coating in the control of surface temperature in satellites and surface layer in electroluminescence applications (Sutton *et al.* 2007).

Thin films can be produced by lower cost methods. The thin films produced are widely used in many application areas, such as solar cells, semiconductor photodetectors and lasers, because of their electrical and optical properties. For this reason, thin films are also extensively investigated in academic research (Taflove and Hagness 1995). Looking at the literature, the relevant research is on additives and nonadditives thin films. Multilayer and singlelayer films, first produced by Nicolau with the SILAR method, continue to be developed for use in various devices.

Thin film technology, which has advantages, to the other production techniques such as more pure material is obtained, film specific material properties can be obtained due to atomic growth and these properties can be controlled, it allows sequential processes, so that multi layered and very different films can be ontained, also it is an industrial and economical technique that can be used quickly and easily (Willander *et al.* 2009).

ZnO has been the material used in device production for the last 50 years due to its wide band gap, abundance in nature, low cost, high optical transmittance, and being a rigid hard semiconductor material with good heat, light and electrical conductivity. ZnO has a hexagonal wurtzite structure. Because of that, its electrical and optical properties can be changed by heat treatment or additives. Due to these properties, ZnO thin films are preferred instead of Indium Tin Oxide (ITO) films in recent studies. There are many application areas where Cu, Sn, Na, Al, In, Ga, Li and F atoms are used as additive atoms (Yıldırım 2010). Doped and undoped ZnO thin films are widely used in areas such as gas sensors, biosensors, solar cells, heat mirrors, acoustic wave devices and photoelectric devices.

ZnO, which is II-VI group compound in the periodic table, is an n-type semiconductors. ZnO, an inorganic compound found in abundance in nature, has a white powder appearance and can be dissolved in water (Zhongwei *et al.* 2021). ZnO compound, low cost due to its abundance in nature, is widely used in the production of many devices owing to its high transparency, direct transition wide band gap and fast electron mobility. It is a preferred compound for biosensor, gas sensor and solar cell applications. ZnO, which is the most interesting and popular material of recent years, has a broad band gap of approximately 3.3 eV with a direct transition energy gap, its resistance is changed in the range of 10^{-3} to 10^{5} Ωcm. It is transparent in the visible region (about 80 % - 90 % optical transmittance) also it is not poisonous and has many features desired for electro optical devices, because of all, it has been used in many academic researches.

SILAR method, sol-gel method, chemical vapour deposition method (CVD), radio frequency magnetron sputtering, thermal evaporation, ultrasonic sputtering (SP), stepwise ionic layer adsorption reaction methods were used to obtain ZnO thin films (Kim *et al.* 2004).

In this study, SILAR method was used because of the easy layer control in the films produced, low cost, easy to apply and etc. UV-VIS, XRD and SEM/EDS methods were used to examine the structural, optical and structural characterization properties of the prepared films.

In the literature, electrical, optical and various structural properties of nonadditive ZnO thin films have been investigated while producing nonadditive and additives ZnO thin films (such as Cu, Sn, Al, Ni, and In) (Gao *et al.* 2004). Some of the most important of these studies are:

In the examinations made by XRD method of ZnO thin films formed by doping different ratios of Copper (Cu) and Tin (Sn) produced using the sol-gel method, it was observed that the samples were in polycrystalline structure and only crystallization of the ZnO structure was observed (Hernandez *et al.* 2008). As a result of the study, it was determined that the surface roughness and grain sizes of the thin films produced increased depending on the additive ratio.

Sn-doped ZnO thin films grown by spray pyrolysis method were investigated in a similar study (Natsume *et al.* 2000). End of the study, they observed that the surface morphology of the samples changed depending on the rate of additive in the examinations made with the XRD method. It was concluded that there is crystallization of the ZnO structure depending on the additive ratio, and this situation has a direct effect on the surface roughness. It has been stated that increasing surface roughness depending on the amount of Sn additive is important, especially in gas sensor applications as it increases the sensitivity (Taner *et al.* 2011).

In another study, the structural, morphological and optical properties of Sn-Cu doped ZnO thin films, grown by SILAR method, were investigated by using UV-VIS, XRD, SEM methods (Vu *et al.* 2019). The forbidden band gaps of the produced films were found as 3.37 - 3.48 eV. Results of the study showed that the Sn-Cu additives significantly affected the characteristic properties, including the structural and optical data.

In a similar study, optical and structural properties of Cu doped ZnO thin films grown by SILAR method were investigated by UV-VIS, XRD and SEM methods (Abdel-Wahab *2021*). It has been determined that the forbidden band gap of the thin films varies between 3.37 eV and 3.48 eV according to the amount of additives. As a result of the study, they claimed that Cu doped ZnO heterojunctions that can be used in various applications can be made.

In this thesis, FTO/ZnO and FTO/ZnO/Cu-Sn %1, FTO/ZnO/Cu-Sn %2, FTO/ZnO/Cu-Sn %3 doped films were obtained using the SILAR method. The structural, morphological and optical properties of the produced thin films were investigated by using UV-VIS, XRD, SEM/EDS methods. As a result of the analysis, the band gap of the produced thin films was observed as 3.56 - 3.98 eV. Depending on the additive ratio, effects on optical properties and morphological properties were investigated.

This thesis work is organized as given below. In the first chapter, the introduction of the study is given. In the second part, band structure and material parameters of ZnO semiconductor are given. In the third chapter, electron conduction theory and conduction mechanisms of semiconductor materials are reviewed. In the fourth chapter, informations about the measurement techniques, analysis techniques and experiment sets are given. In the fifth chapter, the experimental results obtained from UV-VIS, XRD, SEM/EDS measurements are discussed, its application and results are given. The results of the study conducted in the sixth section are discussed.

2. GENERAL THEORETICAL INFORMATION

From a technological point of view, one of the innovations that brought the most innovations to our lives in the last century is the production of semiconductor materials. Transistors produced by using semiconductor technology are used in many devices that we use in our daily lives (Xiangdong *et al*. 2005).

With the invention of the semiconductor transistor, semiconductor systems started to replace the tube circuits used in previous years. Semiconductor systems are more advantageous than tube circuits (Yıldırım 2010). These advantages are that they are small and light compared to tube circuits, there is no need for heaters or losses due to heaters, they are more rigid and more efficient, and they do not need warm-up time.

There are basically two classes of semiconductors. These; i) elemental ones in group IV in the periodic table and ii) compound semiconductors formed by the combination of III-V group or II-VI group elements in a certain ratio. Elemental semiconductors consist of a single atom. Examples are Silicium (Si) and Germanium (Ge). For binary compound semiconductors, ZnO and InAs are the most widely used (Zhang *et al.* 2010). In addition to these, there are also ternary semiconductors such as InGaAs.

Elements in group IV, such as Si and Ge, form covalent bonds between them; each element has four valence electrons, and each atom forms covalent bonds with its four neighbors. Electrons in the outermost orbit with respect to the atomic nucleus are called valence electrons (Leong and Yu 2006). The electrical characteristics of substances can be described by looking at the number of valence electrons;

- Substances with a small number of valence electrons, such as one, act as conductive materials because they can donate electrons easily.
- Elements with three to five valence electrons behave as semiconductors.
- Elements with eight valence electrons do not tend to gain or lose electrons because they are stable. Because of that, they act as insulators.

Elements in group IV, Si and Ge are similar to each other in characteristic structure. The resistance per cm^3 of the element Si is approximately 1.6 Ω/cm^3 (Güney and Duman 2016). Silicium and germanium, which are group IV elements, can be affected by heat and light. Because of this feature, some changes occur when electric current is applied to these materials. These changes have led to the establishment and development of the semiconductor concept (Figure 2.1).

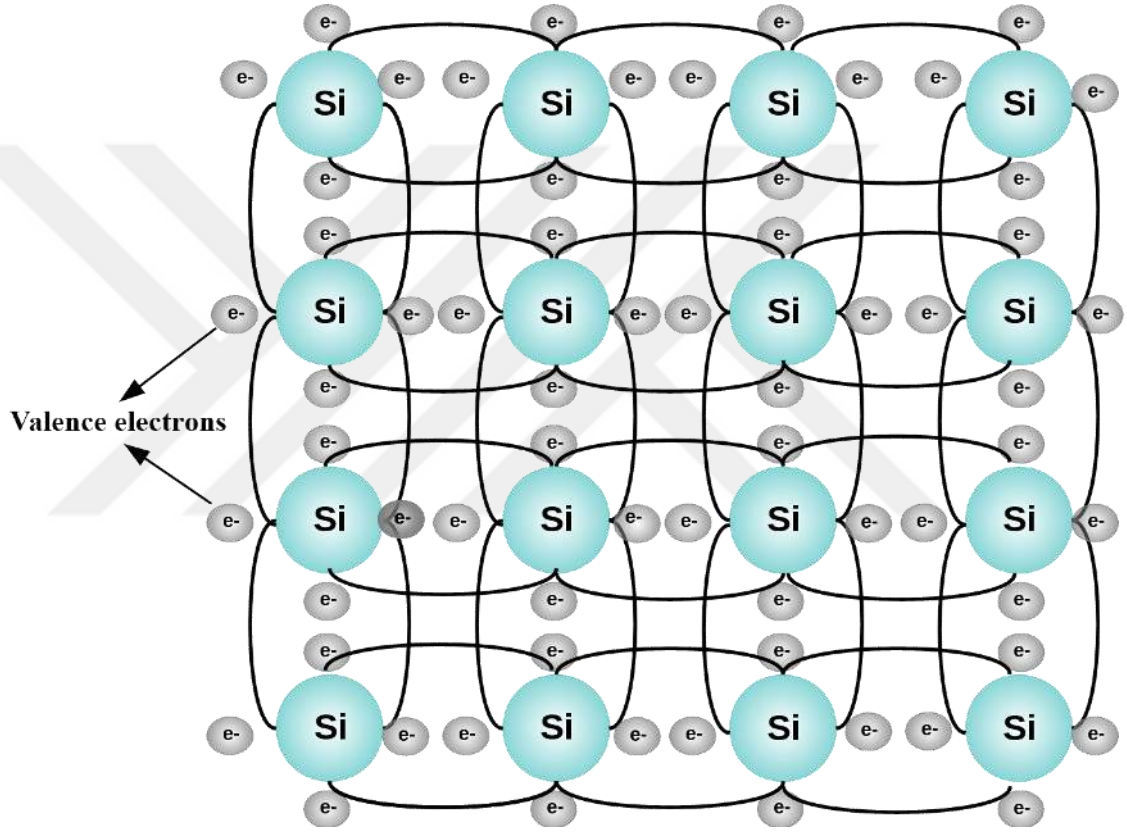

Figure 2.1 Two-dimensional representation of the covalent bond structure of the silicium atom (Chen *et al.* 2000)

When the atomic structure of the Silicium is examined, it is seen that it has a crystalline structure (Ilıcan *et al.* 2008). As a result of the analysis, it has been observed that the atomic structure of the Silicium is periodic. This structure of atoms is called crystal structure, and its periodic arrangement is called lattice structure. Such substances, which consist of the same type of crystal structures that are repeated over and over, are called

monocrystalline structures. Silicium and Germanium elements are suitable for use in the field of electronics due to these properties.

Figure 2.1 shows the covalent bond structure of the silicium atom. The four electrons in the last outer orbital of each silicium atom make bonds with the electrons in the last outer orbital of the other atom. Bonds formed by sharing of electrons are called covalent bonds. As can be seen in the Figure 2.1, the silicium atom forms a crystalline structure by establishing a covalent bond with another silicium atom. This bond in the outer orbit repeats itself constantly. Even if an atom is neutral to the external environment, it is possible to change the electron balance in the final orbital by applying a sufficient amount of kinetic energy. There must be some effects to break away the electrons in the covalent bond. After that broken bond electrons can be in a free state. Some of these effects are magnetic field effect, natural causes, light energy in the form of photons, heat energy of the environment. At room temperature conditions, semiconductors have a certain number of free electrons.

As the ambient temperature increases, the free electrons that form the covalent bonds become free by collecting thermal energy. Therefore, an increase in the number of electrons is observed. This increase in the number of free electrons also causes an increase in the conductivity of the material. On the contrary, the electrical resistance of the material decreases. This is the opposite when compared to conductors. When the temperature increases in the material, the resistance of the conductors also increases. This is the most important feature that distinguishes semiconductors from conductors (Kurt 2009).

2.1 Defects in Semiconductors and Additive Atom in Semiconductors

Doping atoms can be found in a semiconductor for natural reasons or as a result of deliberate doping. Doping atoms can be found in the place (lattice points) of one of the atoms in the crystal structure of the semiconductor material (Farooq and Kamran 2012). These are actually lattice defects. If these atoms are not desired in the semiconductor material, they are called impurity atoms. In some cases, if they are added to change the structure of the semiconductor material, they are defined as doping atoms (Bamiduro *et*

al. 2014). Doping atoms are used to change the semiconductor material properties. This is especially used to improve the electrical conductivity of semiconductor materials.

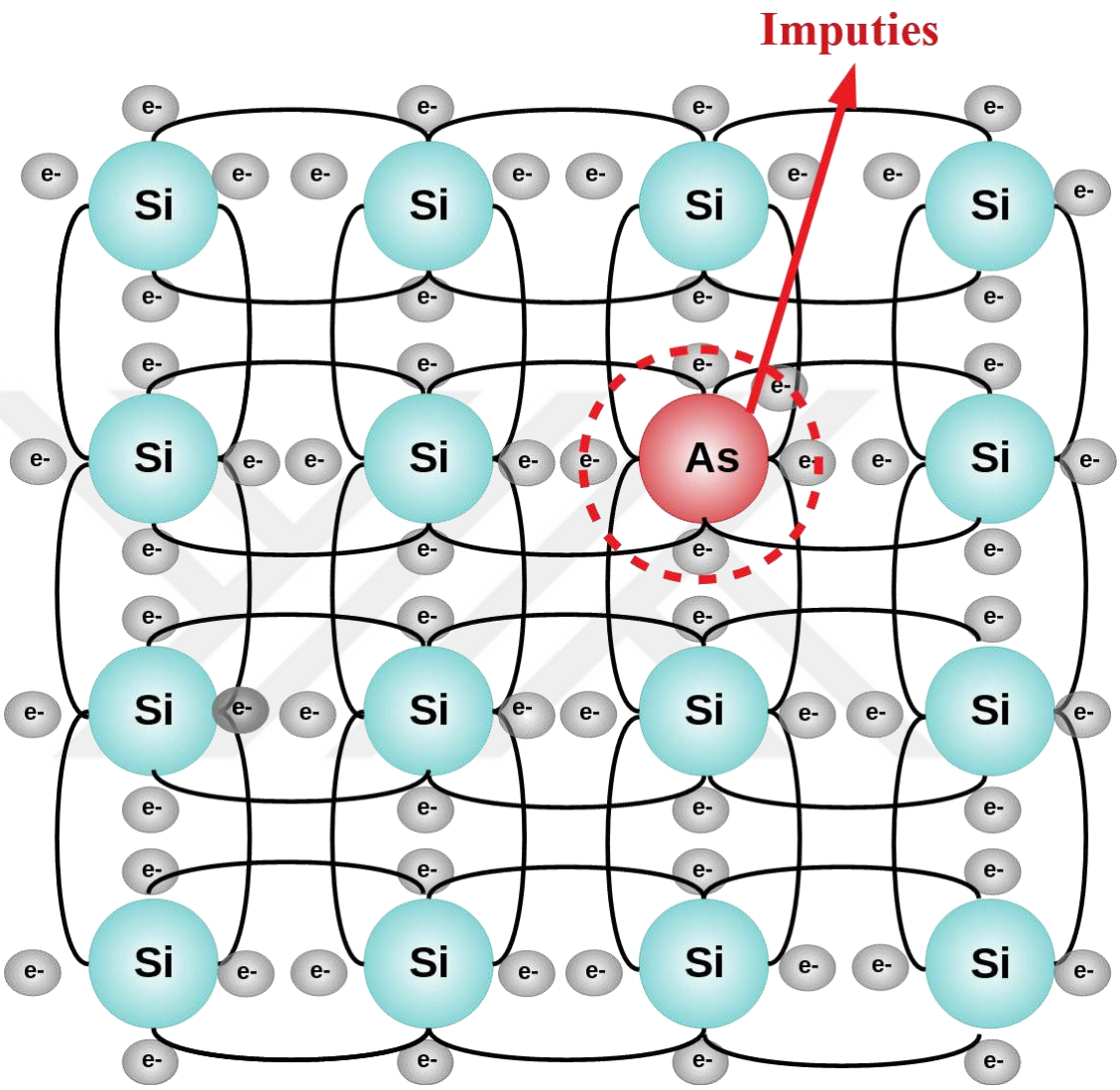

Figure 2.2 Interstitial impurity atom of silicon atom (Chen *et al.* 2000)

A set of complex and chemical methods are required to create semiconductors that can be used for applications in the field of electronics (Figure 2.2). Therefore, a pure silicium cannot be used directly in the field of electronics (Barbe *et al.* 1997). For example, it is necessary to increase the conductivity of the semiconductor material before it can be used in electrical applications. For this reason, it is necessary to add external additives to the silicium material. Elements with a valence electron number of five, such as antimony,

gallium, arsenic, are preferred for these additives, depending on the properties of the application (Ashoka *et al*. 2010).

These additives are made in very small quantities.

By adding semiconductor materials, 2 types of materials are obtained. These are:

(1) n-type semiconductor,
(2) p-type semiconductors.

2.1.1 n-type semiconductor

An n-type semiconductor is formed by adding a certain amount of dopant material to the silicium base (Al-Gaashani *et al.* 2013). The atoms of the elements silicium and germanium are in an interaction called a covalent bond, which is based on the shared use of electrons in the last orbital under normal conditions. For this reason, there are no free electrons in the environment. Additives are made to increase its conductivity so that it can be used in the electronic field. Doping atoms with five valence electrons, such as Antimony, are added to the Silicium structure to form an n-type semiconductor (Avcı *et al*. 2019). In this case, the four electrons of the added Antimony make a covalent bond with the other silicium atoms. But the five electron remains free and suspended in the crystal structure. The free electron can be easily separated from the material. This increases the conductivity of silicium (Figure 2.3).

In this case, silicium goes from a neutral to a charged state because it has more electrons. Since it has excess electrons, it is negatively charged against the external environment. As a result of this situation, an n-type semiconductors are produced (Bougrine *et al*. 2003). The n-type semiconductor formation is given in Figure 2.3. The antimony atom added to the silicium is called the donor. This is because antimony donates its excess electrons to silicium.

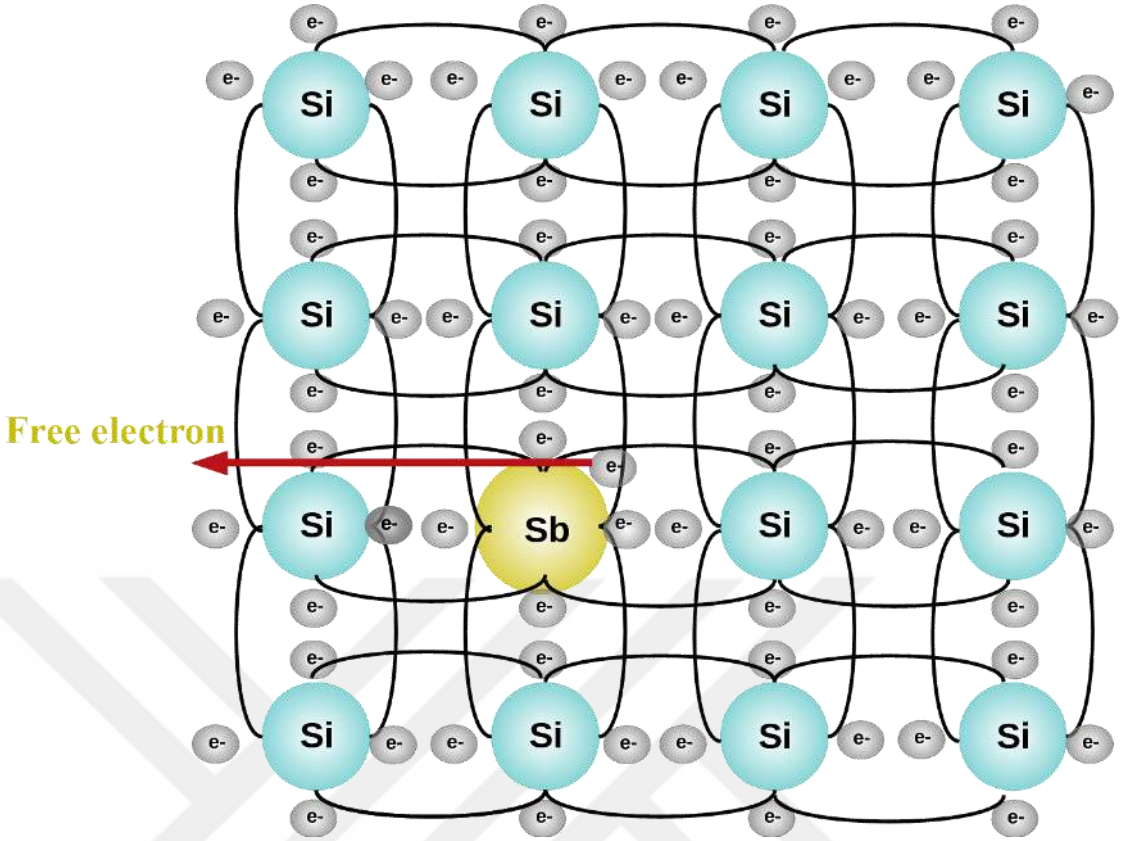

Figure 2.3 Formation of the n-type semiconductor (Araki *et al.* 2004)

2.1.2 p-type semiconductor

Doping atoms with three valence electrons, such as Boron, are added to the Silicium structure to form a p-type semiconductor (Chen *et al*. 2010). The most commonly used elements for this purpose are boron, gallium and indium. The effect of boron, one of these elements, on the silicium base is shown in Figure 2.4.

As can be seen in Figure 2.4, it will be seen that there are not enough electrons to complete the covalent bond in the newly formed structure. The reason for this is that one electron is missing in the covalent bond made between the three valence electrons of the boron atom and the four valence electrons of the silicium atom. Since this point needs to receive electrons, it remains empty and is represented by the + symbol. These gaps formed in p-type material are called cavities (holes). The resulting structure is positively charged due to the lack of electrons.

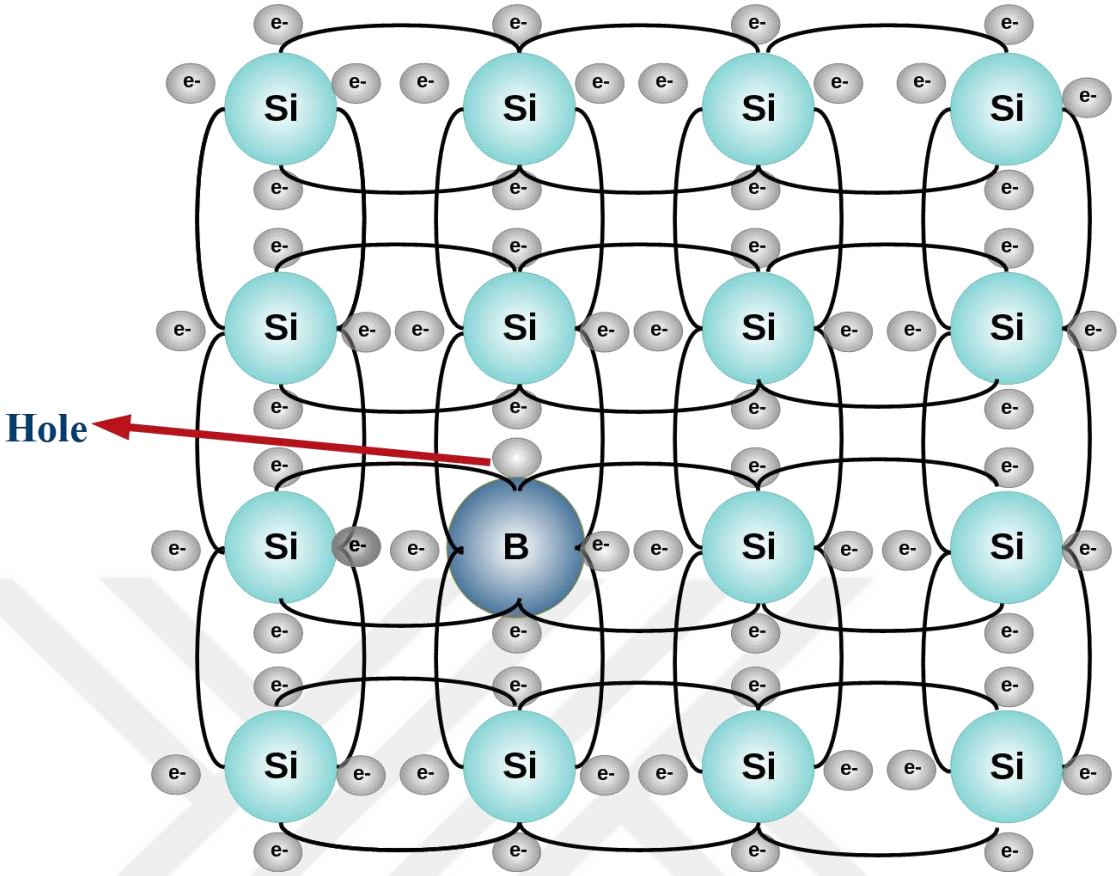

Figure 2.4 Formation of p-type semiconductor (Klein *et al.* 2020)

The newly consisted silicium structure tends to receive electrons from the external environment due to the lack of electrons. This type of structure is called an acceptor. This new structure formed is called a p-type semiconductor.

For technological applications, n-type and p-type semiconductor materials can be made by using the right doping atom. In the n-type substance, excess electrons are released in the crystal structure, and in the p-type substance, cavities that are released in the crystal structure are formed (Mondal *et al.* 2013). In other words, in the n-type semiconductor, the majority current of carriers are electrons. In the p-type semiconductor, the majority of current carriers are cavities. These majority of current carriers are materials that allow controlled current to flow through the semiconductor.

On the other hand, in the doping process, while increasing the conductivity of both n-type and p-type semiconductors, very few cavities occur in the n-type semiconductor, and a very small amount of electrons in the p-type semiconductor due to the unbalance of the energy distribution in the valence levels. These are called minority current carriers. However, it should not be forgotten that the ratio of minority current carriers to majority current carriers is at a negligible level.

2.1.3 Energy bands in semiconductors

The forbidden band gap determines the characteristics of any substance, especially in terms of electrical conductivity (Taner *et al.* 2011). The energy bands of semiconductors give very important information about the material. Energy bands are evaluated in two groups as allowed and forbidden energy bands. When a hydrogen atom with a single electron is investigated to understand the energy band concept, it is seen that the energy of this bound electron is quantized; that is, only certain values of the electron energy are allowed, and thus the electron can only be found at certain energy levels. According to the radian density function for the electron, there is the probability of finding an electron at a certain distance from the nucleus.

This result indicates that the electron is not localized at a certain radius. Applying the result of this single atom to a crystal and applying the quantum mechanics and Schrödinger wave equation, it is concluded that the electronic energy levels are in the form of levels separated by bands of forbidden energy (Wang and Liu 2005). These allowed energy levels are actually discrete due to the Pauli exclusion principle, but the difference between them is very small.

The conductivity of materials is best described by their band energy, as described below. For this reason, in order to understand the band structure, first of all, it is necessary to talk about the concepts of valence band and conduction band (Yoon *et al.* 2015).

As seen in Figure 2.5, every substance has a certain energy level of valence electrons. This is called the valence band energy. There is an energy that must be given in order to separate the valence electron from the atom. This energy is defined as conduction band energy (Zheng *et al.* 2011).

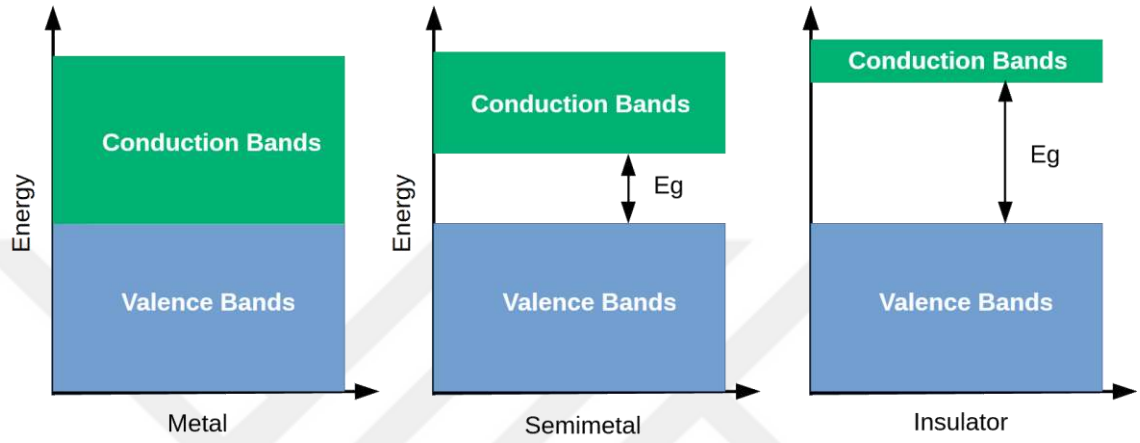

Figure 2.5 Band energies varying according to the degree of conductivity (a) conductor, (b) semiconductor, (c) insulator (Anta *et al.* 2012)

In metal elements, the valence band energy level and the conduction band energy level are adjacent (Ahn *et al.* 2007). Therefore, with a given small energy, many valence electrons become free. In semiconductors, there is a certain gap band (Figure 2.5).

In order to make the semiconductor a conductor, it is necessary to give an extra energy as much as a gap band to the valence electrons. Isolators have a very wide gap band. In other words, a large amount of energy must be given to transfer electrons from the valence band to the conduction band.

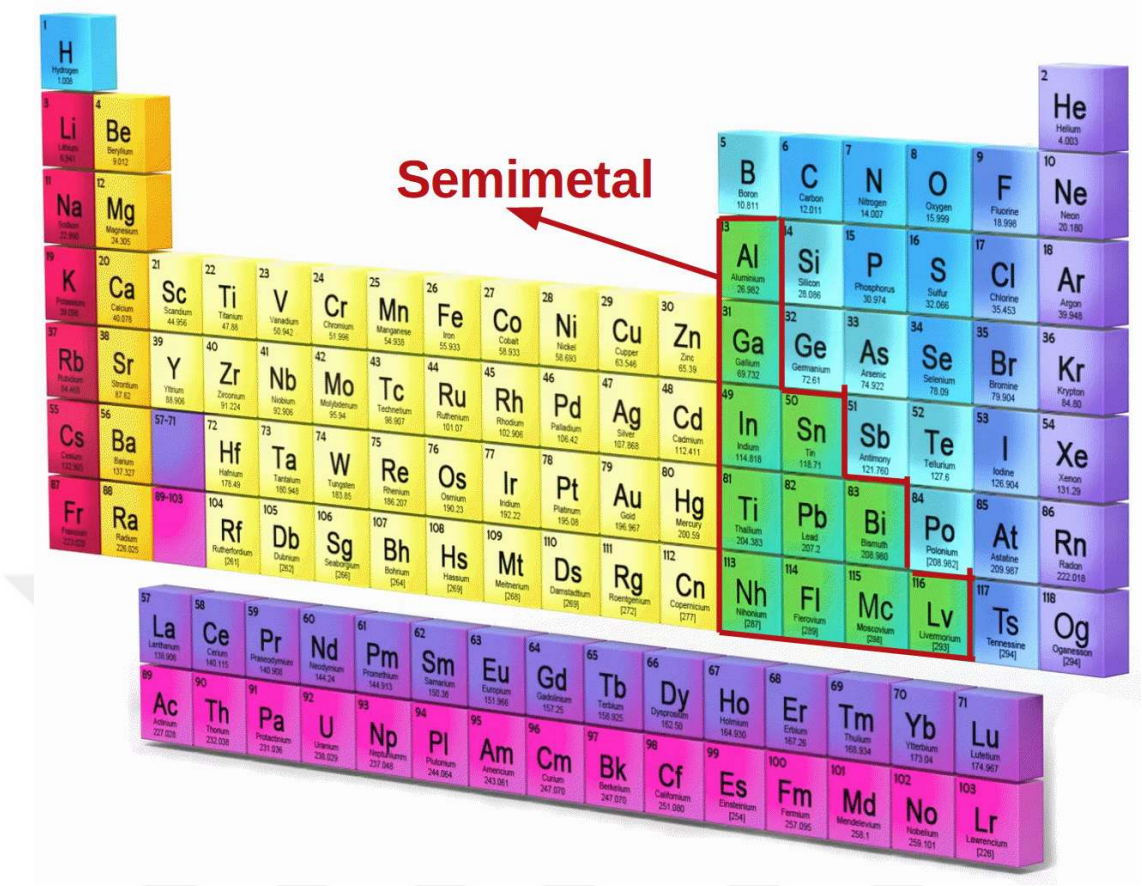

Figure 2.6 Representation of semiconductor elements in the element table (Taylor 1964).

A semiconductor is a material whose conductivity level lies between the boundaries of an insulator and a highly conductive conductor such as copper (Figure 2.6). The resistance of a substance to charge flow or current is inversely proportional to its conductivity (Aksoy *et al.* 2019). The resistance levels of solid materials are indicated by the symbol ρ. The resistivity of a material can be examined by considering the resistance of a material sample which has 1 cm length and $1cm^2$ cross section area. In other words, the resistance of the $1cm^3$ sample is determined by the resistivity in Equation (2.1).

$$R = \frac{\rho l}{A} \tag{2.1}$$

As can be seen from Equation (2.1), the greater the resistivity of a material means, the greater its resistance. Here ℓ represents the length of the material and A represents its cross section. Equation (2.2):

Unit of ρ;

$$R = \frac{\rho l}{A} = \Omega cm \qquad (2.2)$$

is obtained as above.

For example; It can be given as $\rho = 10^{-6}$ Ωcm (copper) for conductive materials, ρ = 50 Ωcm (germanium), $\rho = 50 \times 10^{3}$ Ωcm (silicium) for semiconductor materials, and $\rho = 10^{12}$ Ωcm (mica) for insulating materials.

2.1.4 Factors affecting to the forbidden energy gap of semiconductor

Semiconductors have many advantages and practical application areas. A good conductor or a good insulator can be made from the same material if desired by adjusting the conductivity of the semiconductors (Alferov *et al.* 1971). In addition, since the mobility is very high in semiconductors, it is used in the construction of fast circuit elements. This feature is due to a change in the forbidden energy gap of semiconductor materials.

The factors that change the forbidden energy gap of semiconductors are generally as follows:

1) Temperature

As the temperature increases, the vibration of the crystal lattice increases and the crystal lattice expands. In most semiconductors, the band gap becomes smaller. This causes the absorption to shift to the longer wavelength region. In addition, with the increase in temperature, the electron-phonon interaction in the crystal increases (Anta *et al.* 2012).

2- Pressure

Pressure; Since it reduces the distance between atoms, it can cause the narrowing of the forbidden energy gap. The reason for the decrease in the forbidden energy gap may be due to the decrease of the lattice parameters (a, b, c) and the change of $(k = \frac{\pi}{a})$.

3- Magnetic field

The absorption curve of a semiconductor under the influence of a magnetic field changes according to the situation in the absence of a magnetic field. The growth of the band of forbidden energy under the influence of the magnetic field causes the main absorption edge of the absorption spectrum to shift to the short wavelength region.

4- Electric field

In semiconductors placed in an externally applied electric field, bending of energy bands can be observed. In this case, electrons pass from the valence band to the conduction band by tunneling. The height of the tunnel barrier is calculated as follows in Equation (2.3).

$$d = \frac{E_g}{e\delta} \tag{2.3}$$

Here, the height energy of the tunneling barrier is *Eg*, the tunnel barrier height is *d*, and the potential of the external electric field is δ. As δ increases, the barrier height decreases and the passage of electrons through tunneling becomes easier.

5- Defect atoms

One of the primary conditions for producing an ideal semiconductor is chemical purity. So even the slightest flaw can have a devastating effect on how the material behaves. A high level of crystal perfection is also important, as defects in the crystal structure (linear,

planar defects and twin crystals) can affect the semiconducting properties of the material. Crystal defects are one of the main causes of defects in semiconductor materials. The presence of defect atoms is among the most important factors affecting the forbidden energy gap of the semiconductor.

2.1.5 Conductivity in semiconductors

In order to understand electrical conductivity in semiconductors, it is necessary to know how electrons behave (Zhuang *et al.* 2019). For this, the most known Silicium crystal structure can be looked at. Silicium has a structure with four valence electrons, and these valence electrons make covalent bonds with the valence electrons of neighboring Silicium atoms. At T = 0 Kelvin, there are six electrons around each Si atom, and all of these electrons are at the lowest energy levels and all are in the valence band, so in this case, the electrons are in the top full band. The conduction band, which is an upper energy band, is completely empty.

As the temperature begins to rise, some electrons begin to gain enough energy to break the covalent bond and move to the next higher level, the conduction band. As the temperature increases, more electrons move into the conduction band. There are enough empty levels to allow the movement of electrons, and thus Silicium gains semiconductivity.

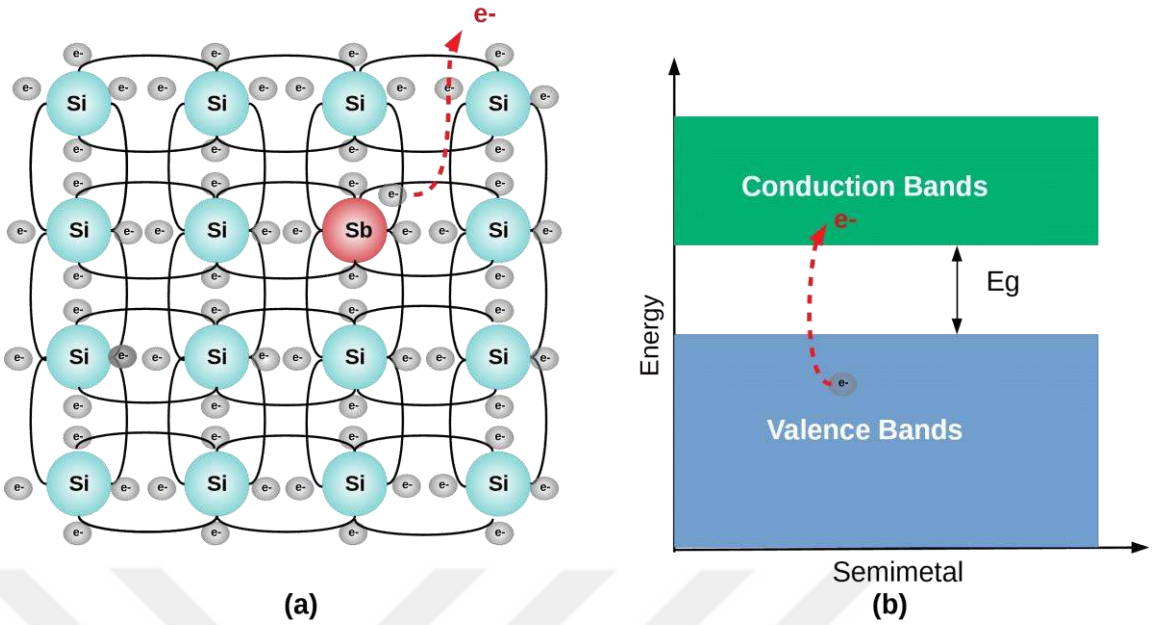

Figure 2.7 (a) Two-dimensional representation of the breaking of a covalent bond and (b) the formation of a negative and positive charge by breaking a covalent bond (Grandbois *et al.* 1999)

As the electrons move into the conduction band, the spaces they left empty in the valence band remain as positively charged holes, which can contribute to the electric current. When an external electric field is applied, electrons can now move because there are enough empty levels that electrons in the conduction band and holes in the valence band can move in the bands. While electrons move in contrast to the applied electric current, the holes move in the direction of this electric field so this creates a net electric current. Thus, at a certain temperature, which can be room temperature, semiconductors gain conductivity.

Materials whose energy bands are completely filled or completely empty can be said to be insulators (Figure 2.4). In insulators, E_g is around 3.5 - 6 eV. In this case, because this E_g cannot be broken at room temperature and electrons cannot pass to the conduction band, conductivity is almost absent in insulators, but their resistance is quite high.

When looking at the energy bands of metals, in the first case, the conduction band is partially electron-filled, which provides a high conductivity. In the second case, the allowed and forbidden bands are intertwined, and in this case, a high conductivity is

ensured because there are both a large number of electrons and a large number of levels where these electrons can move (Grandbois *et al.* 1999).

2.2 Structure and Properties of ZnO Compound

ZnO compound is preferred in many technological applications due to its superior properties, such as being abundant in nature, high exciton binding energy, high ionicity, and direct transition wide band gap. Thin films prepared with ZnO compounds are the most preferred materials among metal oxide semiconductors due to their high electrical conductivity, optical transmittance and reflection in the visible region.

ZnO compound, which is a semiconductor of group II-VI in the periodic table, is an odorless powder, soluble in acid and alkaline solutions, insoluble in water and alcohol. It is widely used as an additive in products such as plastic, ceramic, glass, rubber, paint material, adhesive, and batteries. In addition, the ZnO compound is a chemical that shows base properties against acids and acid properties against bases. In other words, ZnO shows both acidic and basic properties.

2.2.1 Crystal structure

Most of the II-VI group compound semiconductors crystallize in either a cubic zinc-blended or hexagonal wurtzite close-packed structure (hcp). In the hexagonal wurtzite close-packed structure, each anion is surrounded by four cations located at the corners of a tetrahedron. Although this tetrahedral coordination is a general feature of sp3 covalent bonding, the ionic character of these structures allows the forbidden energy gap values to exceed those expected from covalent bonding.

In the ZnO compound, the presence of Zn atoms in the middle of the molecule causes the formation of donor levels in the oxygen vacancies and band gaps. ZnO is one of the covalent and ionic semiconductors in terms of ionicity in the wurtzite crystal structure under normal conditions. In the hexagonal structure of the ZnO unit cell, each Zn atom is

surrounded by four O atoms in the first shell and twelve Zn atoms in the second shell (Figure 2.8).

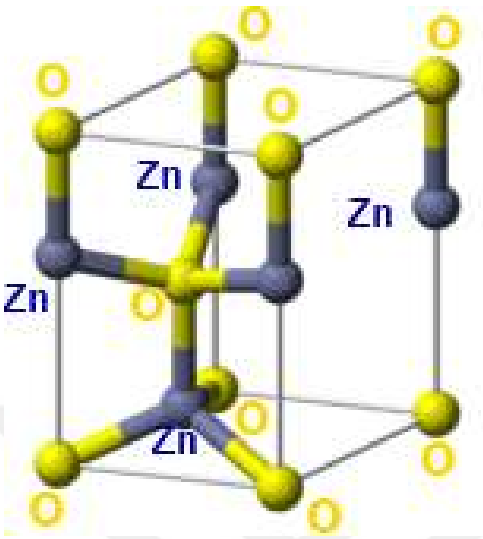

Figure 2.8 Hexagonal wurtzite crystal structure of ZnO (Xu and Sun 2003)

2.2.2 Physical characteristics

In nanotechnology and biomedicine, ZnO compound has a wide usage area in semiconductor based multilayer devices, photothermal conversion systems, bio sensors, gas sensors and optical vision sensors and many more because of its own properties. Today, with the increasing interest in optical communication systems, ZnO compounds and doped ZnO compounds are of great interest in infrared photoelectric and light emitting devices.

In addition, ZnO based thin films (films doped with Sn, Cu, Ni, Co, Al, In etc.) can also be used as a transparent and conductive electrode for light emitting devices. The physical properties of the ZnO compound are given in Table 2.1.

Table 2.1 Physical properties of ZnO

Features	**Value**
Lattice Structure	Hegzagonal Wurtzite
Lattice parameters (a)	0,32495 nm
Lattice parameters: (c)	0,52069 nm
Lattice parameters: u (c/a)	1,602
Melting Point	1975 ºC
Density	5,606 g/cm^3
Thermal Conductance	25,2 W m^{-1} K^{-1}
Optical Transmittance	Approximate % 80 - % 90
Electrical Resistance	Approximate 10^{-3}-10^{+5} Ωcm

2.3 What is Thin Film?

Thin film, which is widely used in technological applications, can be defined as coatings on substrates with thicknesses ranging from 100 A° to a few μm. The thin film is prepared by arranging the atoms or molecules selected as the target one by one on the surface to be coated. Thin films, when coated on the surface of bulky materials, provide many properties that they cannot provide and cannot have on their own. In this way, they are widely used as high-tech materials in industries that concern optical, electrical, magnetic, chemical and mechanical fields.

The most common optical application areas where thin films are used are Reflective / non-reflective layer, Interference (light) filters, decoration (color, brightness, etc.), compact disc (CDs), Solar cell applications. Electrical application areas are insulator and conductive materials, semiconductor devices, dielectric materials.

Thin film is used in several chemical application areas, such as alloys or diffusion prevention, protection against oxidation or corrosion, gas/liquid sensors, paints, rubber, plastic, cosmetics, soap production, the pharmaceutical industry.

Thin films are also used at mechanical application areas such as friction-related coatings, hardness, adhesive, micro-mechanics, zinc plate making, roofing materials, and the tire industry.

Thin film can grow on the target surface in 3 different ways; the first is to grow into islands (Volmer and Weber 1926), the second and most ideal growth is layered growth (Frank and Van der Merwe 1949) and the third growth is a mixed growth with both island and layer growths (Figure 2.9).

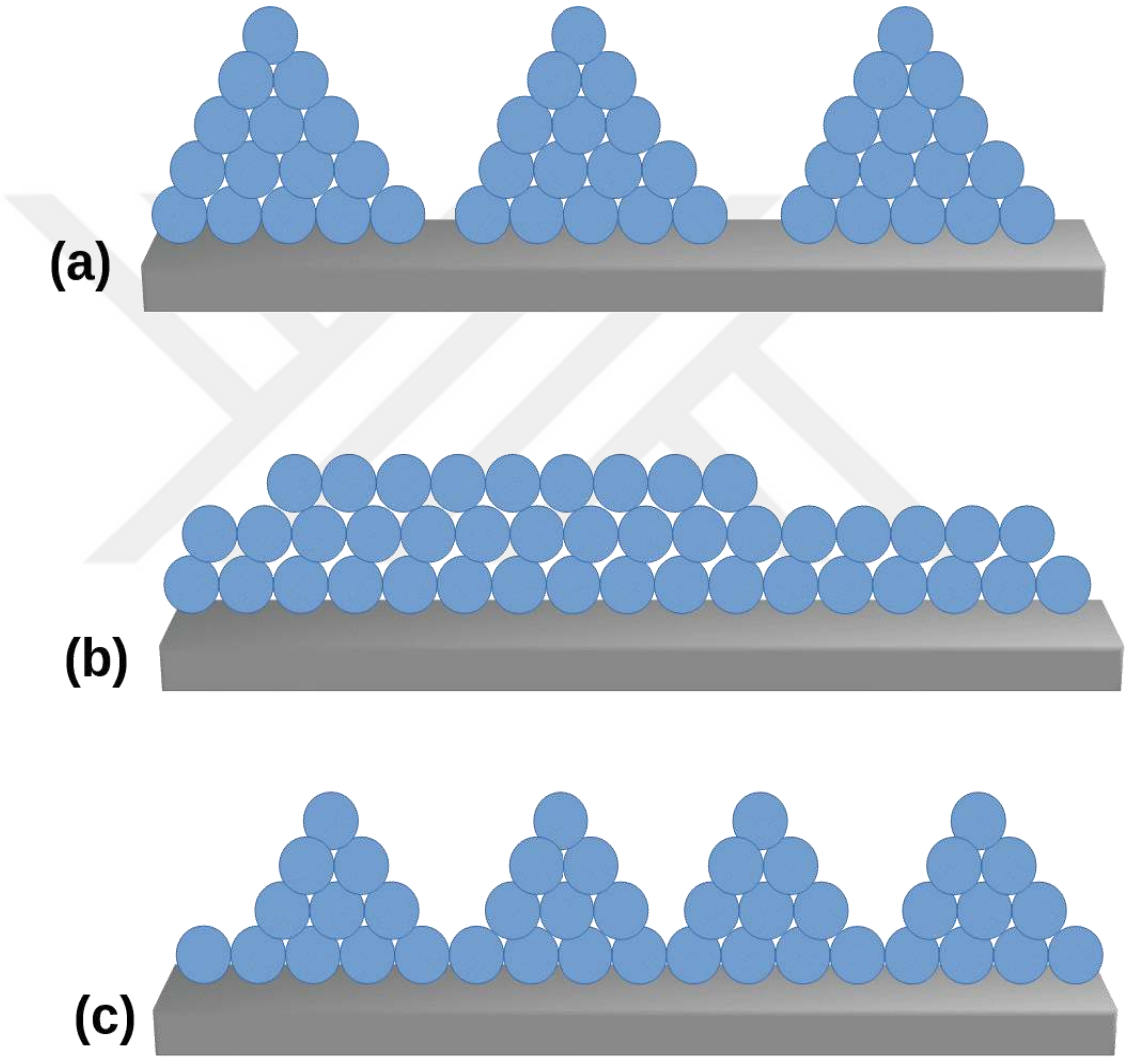

Figure 2.9 (a) Growing in islands, (b) growth in layers, (c) growth in both layer and island

2.4 Production Methods for Nanomaterials

Nanotechnology is the production of structures with improved or completely new physical, chemical and biological properties by working at the level of atoms and molecules (sizes greater than 100 nm) in units per billion.

With materials produced by nanotechnology, more robust and high quality, long-lasting, cheaper, lighter and smaller devices are being developed. In addition, with the development of nano technology, microscopes that can measure and examine at nanoscale and the methods created to make operations in these dimensions have been significantly affected.

The most important of these methods are:

i. Scanning Electron Microscope (SEM)
ii. Atomic Force Microscope (AFM)
iii. Transmission Electron Microscope
iv. Near Field Scanning Optical Microscope

Nanoparticles show superior properties because they are very small in size. In addition, the bond structure between atoms at nano size can also be changed; while the material is mechanically strengthened or weakened, its electronic conductivity can completely change. The shapes and morphologies that can be controlled during production also have an effect on the superior properties of materials produced in the nanoscale.

By using chemical surfactants, surface and interfacial properties can be improved. In this way, the surface of the particles is charged with additive additions and allows a balance to be formed between the particles against aggregation and conglomeration.

Production methods of nanomaterials can be grouped under two main headings. These: (a) Top down methods, (b) Bottom-up methods in Figure 2.10.

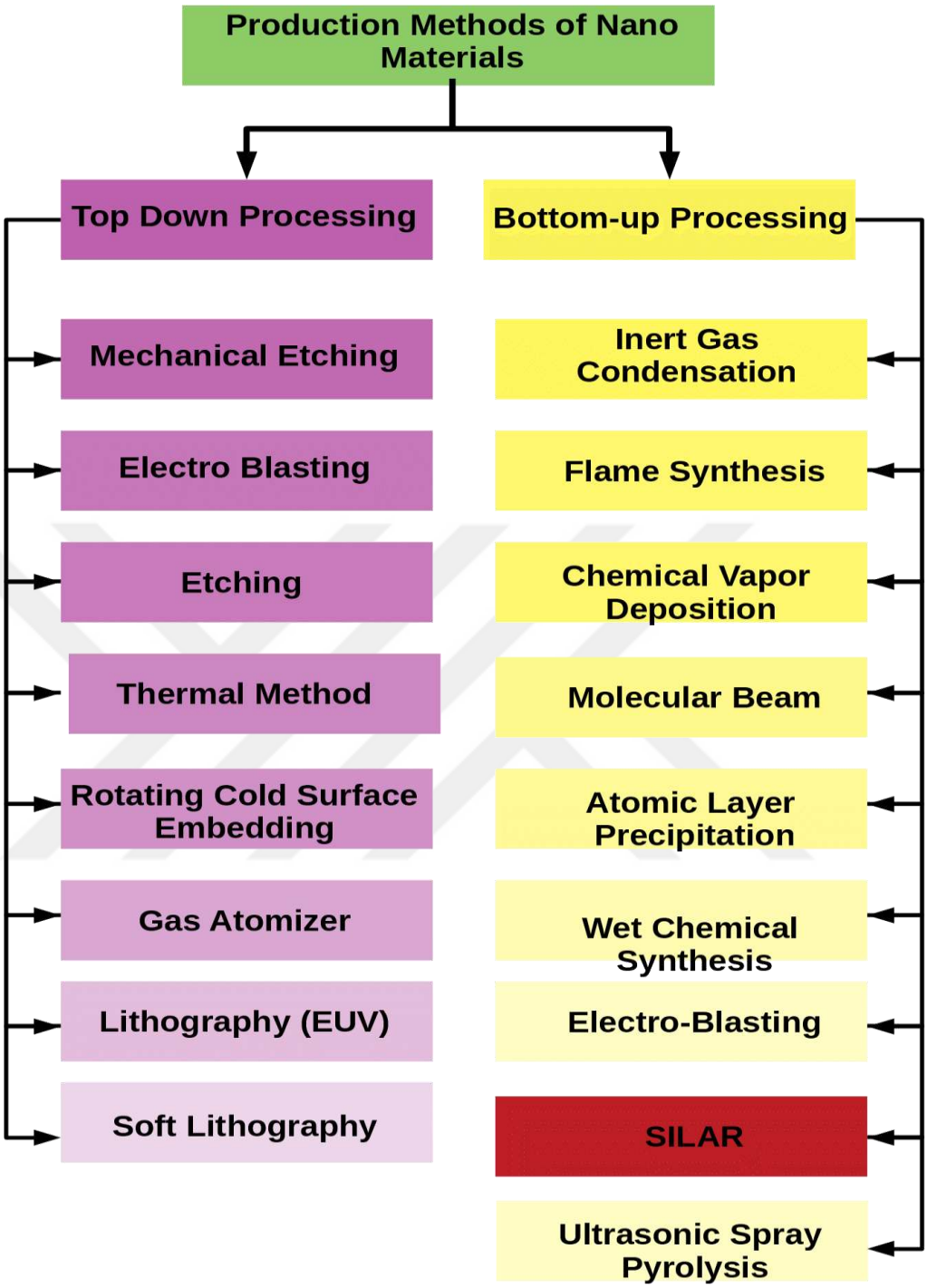

Figure 2.10 Main methods used in nano-size particle production (Hernandez *et al.* 2008)

Nanomaterial growth techniques are widely used in optics, micro-electronics, biomedical applications, packaging applications. With the development of optical, magnetic, electrical, mechanical and chemical fields, which are the fields of use of these produced

nanomaterials, the thin film coating technique has also found application. Thin films are selected according to how they are coated and how they are developed according to the desired properties of the surface to be coated.

In this thesis, the SILAR method is used because of its advantages such as creating a homogeneous structure, not causing air pollution, not requiring high temperature and vacuum, a simple method, being applied to large surfaces, not complicated tools and machines in the process, same coating thickness in all parts of the coated material (Figure 2.11).

2.5 SILAR Method

Successive Ionic Layer Adsorption and Reaction (SILAR) technique is preferred to other compared semiconductor film growth methods, because it does not require a vacuum environment, it is easier, cheaper and less time is spent in the growth phase. Besides, the SILAR method is an ideal method to obtain high quality doped and undoped ZnO thin films. This method involves a four-step process involving cleanroom-substrate immersion in alternating cationic solution, water, anionic solution, and again into room temperature water. In recent years, many scientific studies have been carried out on the preparation of doped and undoped ZnO thin films with the SILAR technique.

The most important advantages of the SILAR method are that the thickness of the target material to be grown on the substrate can be controlled, the number of cycles can be determined, and the thickness of the grown sample can be controlled. The thickness of the grown films increases in proportion to the number of cycles. The film thickness, which is grown up to a certain cycle, becomes stable, but it is known that the quality of the produced sample deteriorates if too many cycles are made. This is due to the fact that when the thickness of the sample reaches a certain value, the ions begin to accumulate on the surface in the form of sediment and it becomes easier to break off from the surface.

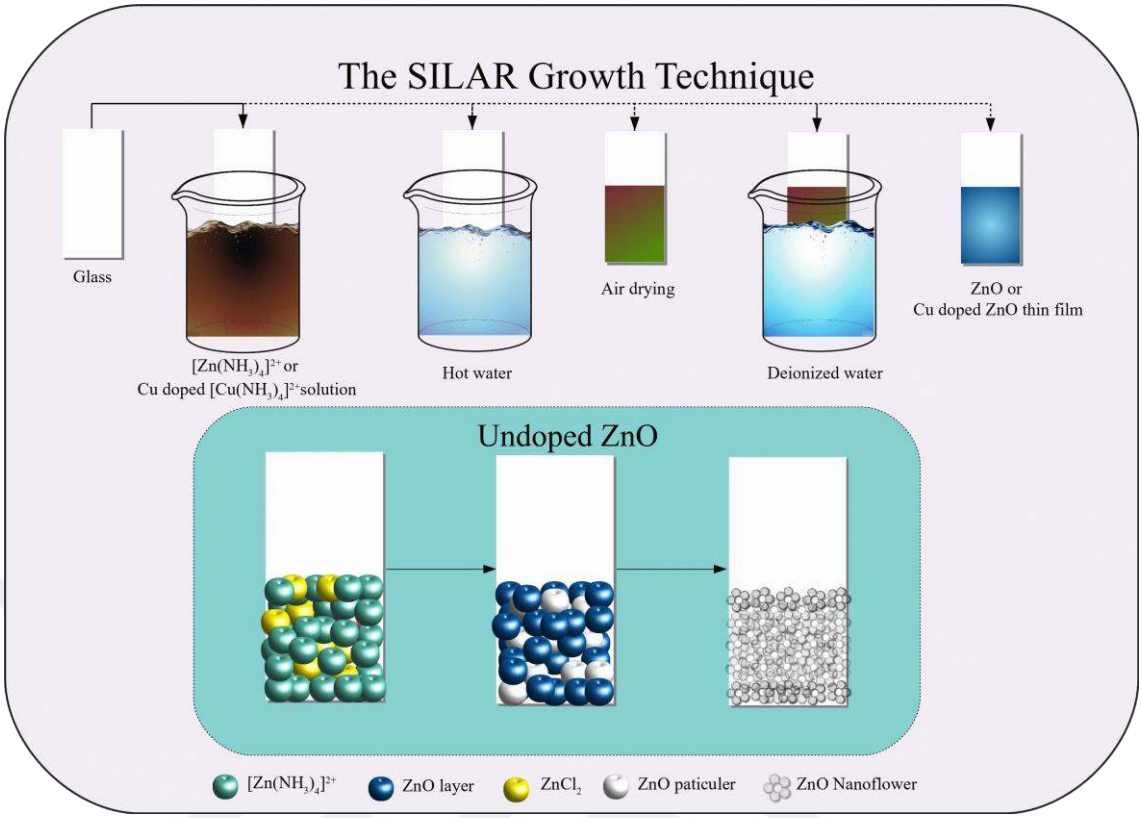

Figure 2.11 Schematic of the SILAR thin film growth method (Kanniainen *et al.* 1996)

These:

- ❖ The growth of thin films does not require a vacuum. This result significantly reduces the cost of thin film growth and provides convenience in terms of growth.
- ❖ To dope with different elements, it is sufficient to add thin films to some forms of cationic and anionic solutions.
- ❖ The thickness of the thin film produced can be easily controlled by changing the number of cycles.
- ❖ There are no restrictions on substrate, dimensions and surface morphology.

2.6 Scanning Electron Microscope (SEM)

A Scanning Electron Microscope (SEM) is an electron microscope that produces images of the sample by scanning the surface with a focused beam of electrons. Electrons interact

with atoms in the sample to produce various signals that contain information about the surface topography of the target sample and the composition of the sample. These captured signals are processed and made meaningful. The commonly used SEM microscope can provide resolution better than 1 nanometer. The structure of the SEM device is given in Figure 2.12 schematically.

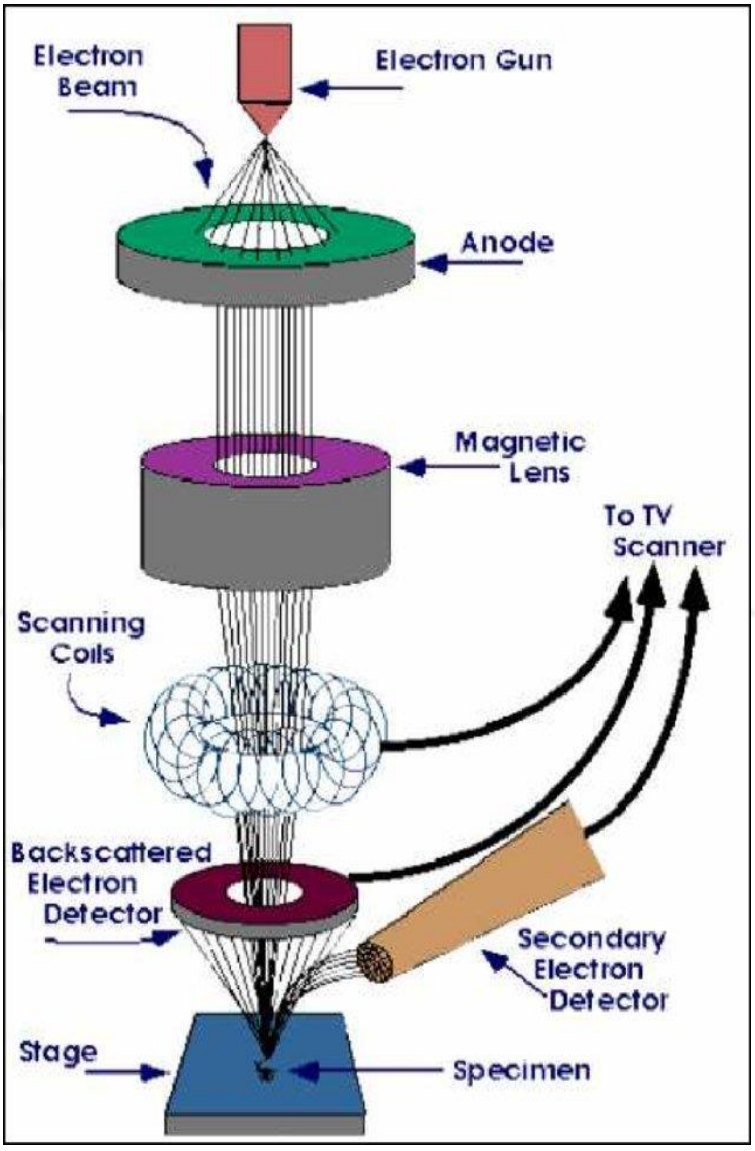

Figure 2.12 Schematic view of the scanning electron microscope (Crewe *et al.* 1969)

As seen in Figure 2.12, the electron gun first sends electrons to the anode plate to accelerate it. Accelerated electrons are transmitted to magnetic lenses to form thin bundles. Scan coils are used to focus these beams. The scattered electron detector is used

to collect the scattered electrons and they are sent onto the sample. Due to the lens systems, the electromagnetic field and the electron beam focus on the sample.

In addition, Energy Dispersive Spectroscopy Analysis (EDS) is used to identify elemental composition on the sample. EDS is a technique generally used in SEM devices. Elemental composition analysis is performed by sending a scanning electron beam on the sample (Figure 2.13).

Figure 2.13 Scanning electron microscope

In this thesis study, SEM and EDS measurements of thin films produced at room temperature were made at Ankara Yıldırım Beyazıt University Central Application and Research Laboratory by using the HITACHI SU5000 field emission scanning electron microscope (FE-SEM) device, whose photo is given in Figure 2.13.

2.7 X-Ray Diffraction Technique (XRD)

X-Ray Diffraction technique (XRD) works on the principle that a crystal phase refracts X-Rays in a characteristic pattern that depends on its unique atomic arrangement. The material used during the XRD analysis does not deteriorate and also a small amount of the material is enough for analysis. Analysis can be done in the form of crystals, powders and polymers of the material. The characteristic patterns of the grown thin films are obtained by XRD device. Based on the peak widths (FWHM) and the intensity of the peaks in XRD patterns, a lot of information can be obtained about the crystallization quality and grain sizes of thin films. X-Ray diffraction can be explained by Bragg's law. The simplest form of Bragg's law is given in Equation (2.4) below.

$$n\lambda = 2d\sin\theta \tag{2.4}$$

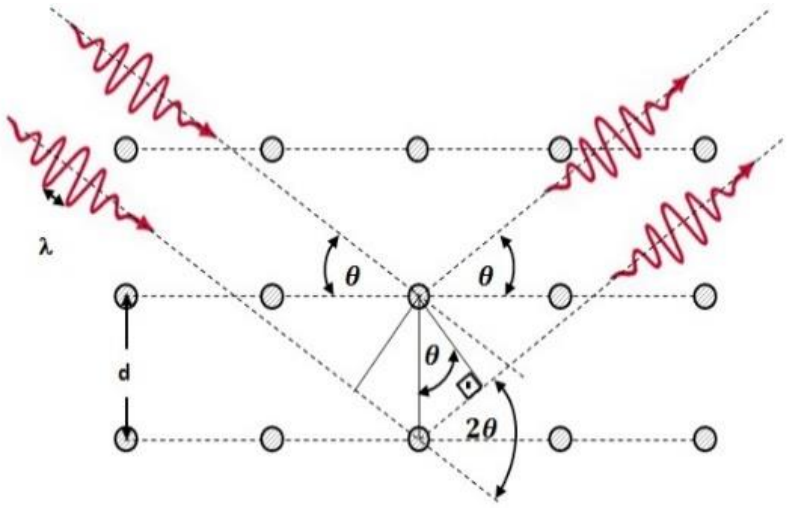

Figure 2.14 Schematic representation of Bragg's law

As can be seen from Figure 2.14, the distance between the lattice planes is d, the θ-bragg angle, n is the scattering order, and λ is the wavelength. It gives information about its atomic structure with XRD technique. The biggest advantages of the XRD technique are that it does not require an elaborate thin film preparation and structure of the material is not broken down by XRD method. It is also an effective method in determining the crystallographic structure of the material. XRD experiment set generally consists of goniometer, tube, tube position, slit system required for measurements, sample carrier and detector. In this thesis study, APD 2000 PRO XRD device in Gazi University Photonics application and research laboratory was used for XRD analysis of the samples produced in the study (Figure 2.15).

Figure 2.15 X-Ray diffraction device

2.8 Optical Absorption Measurement

If the forbidden energy range of the semiconductor is a material suitable for transmitting a beam over the sample to be determined, one of the most used methods is optical absorption measurements. One of the biggest advantages of this method is that it does not cause any damage to the samples during and before measurement. Optical absorption measurements are the spectroscopic technique that measures the absorption of light as a function of frequency or wavelength.

The sample absorbs photons from the transmitted radiation field and changes as a function of frequency, and this variation creates the absorption spectrum. Optical absorption is commonly used to detect the presence and amount of a particular substance in a sample. Perkin Elmer Lambda 2S UV-VIS spectrometer in Gazi University Photonics application and research laboratory was used for optical absorption measurements of the samples produced in this thesis study (Figure 2.16).

Figure 2.16 UV-VIS spectrometer

2.9 Performing the Annealing Process on the Thin Films Produced

The thin films grown by the SILAR method were annealed in the annealing furnace at a temperature of 300 °C for 15 minutes. The samples were placed in the oven at 300 °C for the annealing process. The annealing furnace is shown in Figure 2.17.

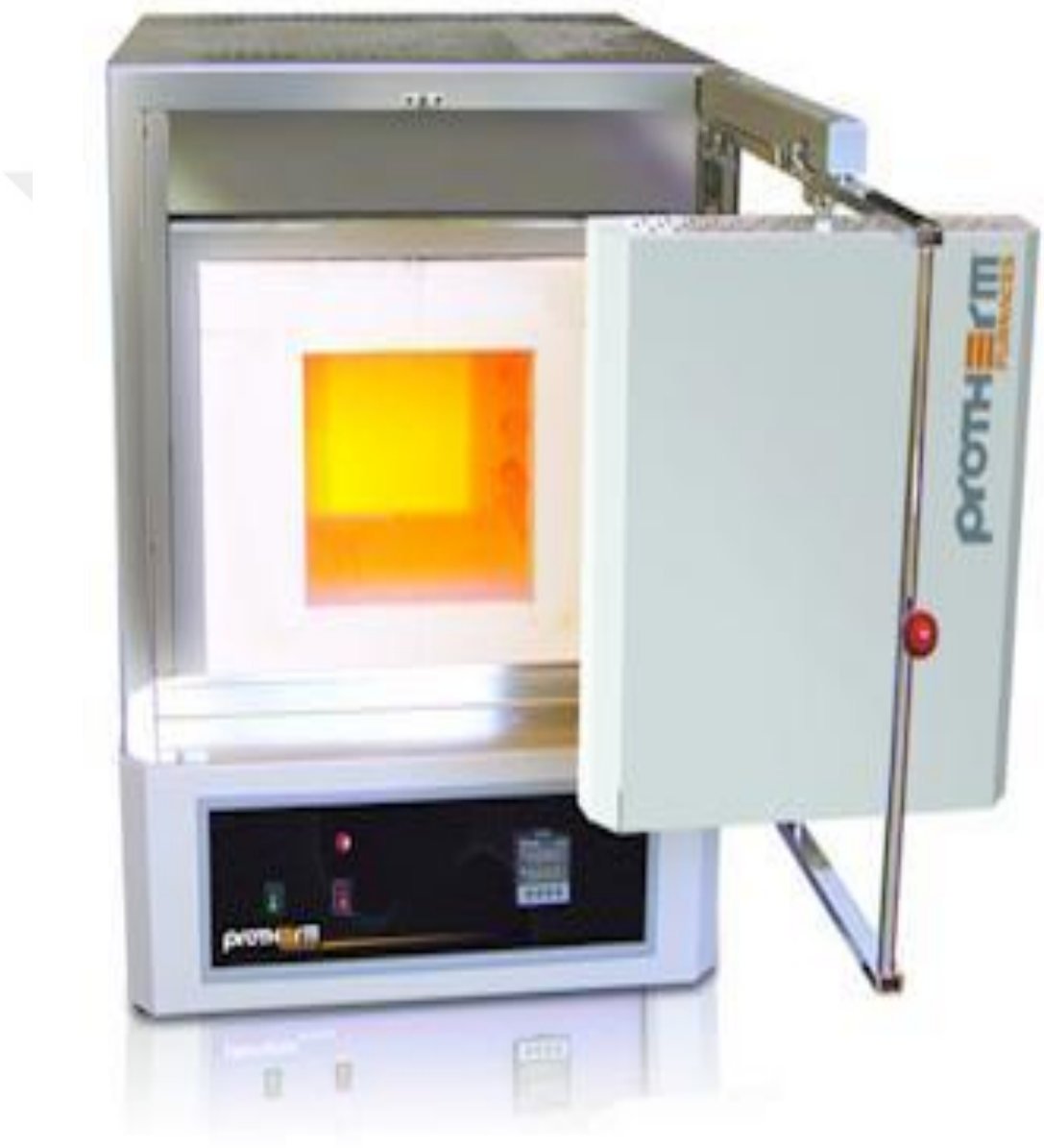

Figure 2.17 Annealing furnace

3. MATERIAL AND METHOD

3.1 Growth of Doped and Undoped Thin Films by SILAR Method

The SILAR thin-film method, which was explored by Nicolau in 1985, is a relatively new method that does not require a vacuum and remains popular today. The SILAR method, which is an ideal growth technique for various substrates such as semiconductors, metals and insulators, is suitable for use at room temperature. The thickness of the produced thin films can be regulated depending on the preparation conditions such as the number of cycles, rinsing time, concentration and adsorption of the solutions.

In this thesis study, SILAR method was preferred in the production of thin film samples. The magnification process is explained in detail in the relevant sections.

3.2 Preparation of Substrate Materials

Thin film growth processes used in the thesis study were performed in Gazi University Chemistry Laboratory. SnO_2:F coated glass was used as the substrate for the samples to be grown. SnO_2:F coated glass materials, TEC8 model, 25 mm x 25 mm, 2 mm has the thickness. Cleaning process was applied to SnO_2:F coated glasses before magnification. In the cleaning process, first of all, SnO_2:F coated glasses were washed in soapy water to remove dirt. After washing, SnO_2:F coated glass substrates were ultrasonically cleaned in acetone for 10 minutes. Then, it was ultrasonically cleaned in a one-to-one (1:1) ethanol-water mixture for 10 minutes.

3.3 Growth of ZnO thin films on SnO_2:F/Glass substrate

($[Zn(NH_3)^4]^{2+}$) zinc-ammonia complex was used to grow ZnO thin films on SnO_2:F/Glass substrate. To prepare the zinc-ammonia solution complex, 0.1M $ZnCl_2$ (pH≈5.5) and 25 - 28 % NH_3 solutions were mixed in 1 to 10 molar ratio [Zn:NH_3=1:10] (Figure 3.1).

The chemical reactions taking place during the growth phase of thin films are given below: Equation (3.1), Equation (3.2), Equation (3.3), and Equation (3.4).

$$ZnCl_2 + 2NH_4OH \leftrightarrow Zn(OH)_2 + 2NH_4^+ + 2Cl^- \quad (3.1)$$

$$Zn(OH)_2 + 4NH_4^+ \leftrightarrow [Zn(NH_3)_4]^{2+} + 2H_2O + 2H^+ \quad (3.2)$$

$$[Zn(NH_3)_4]^{2+} + 4H_2O \rightarrow Zn(OH)_2\,(s) + 4NH_4^+ + 2OH^- \quad (3.3)$$

$$Zn(OH)_2\,(s) \rightarrow ZnO(s) + H_2O \quad (3.4)$$

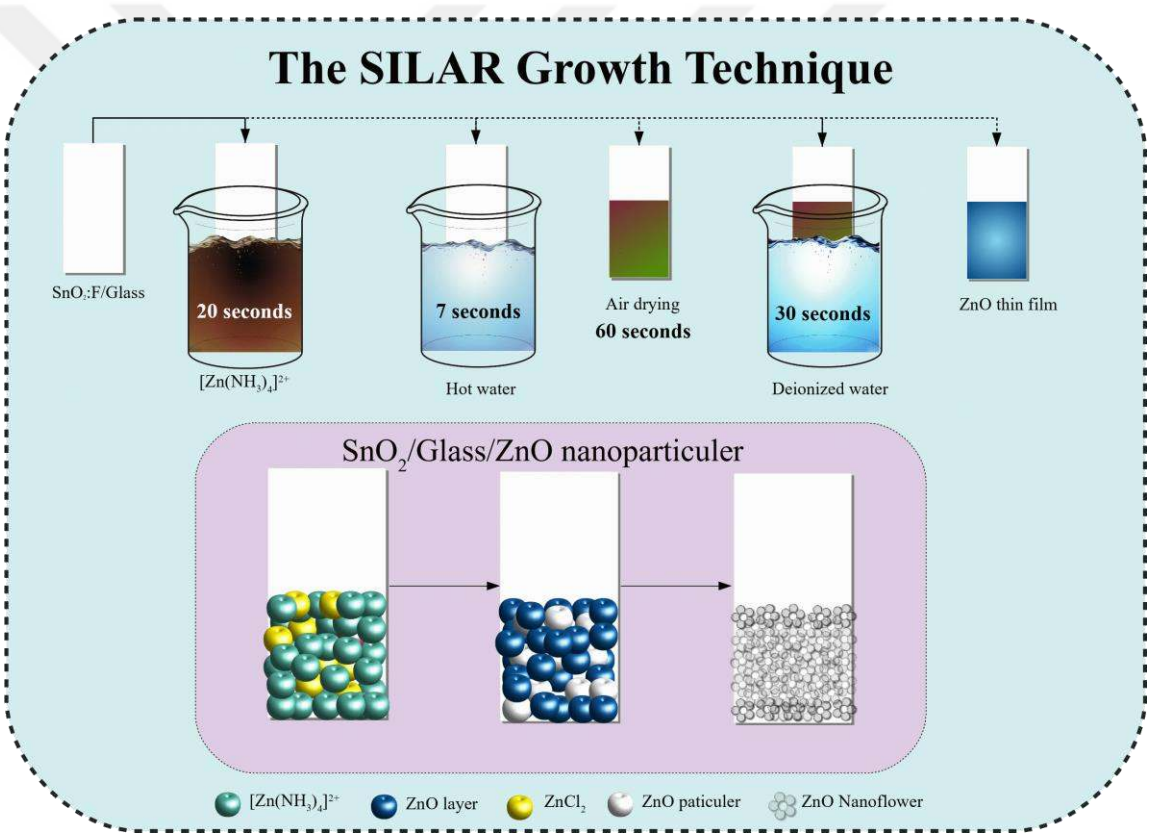

Figure 3.1 Growth mechanism of ZnO thin film on SnO_2:F/Glass substrate by SILAR technique (Kanniainen *et al.* 1996)

SnO_2:F/Glass substrate material is taken out from 90 °C distilled water and then dried in air for 60 seconds. Finally, the SnO_2:F/Glass substrate material is rinsed in distilled water

at room temperature for 30 seconds. Thus, one SILAR round is completed, resulting in a ZnO layer on a solid SnO_2:F/Glass substrate.

3.4 Growth of Sn-Cu Doped ZnO Thin Films on SnO_2:F/Glass Substrate

SnO_2:F/Glass substrate was prepared for the growth of Sn-Cu doped ZnO films, then SnO_2:F/Glass substrate cleaning process was applied. After the cleaning process, solutions were prepared at the desired additive ratio and Sn-Cu doped ZnO thin films were grown on the SnO_2:F/Glass substrate by SILAR method. The chemical reactions that take place during the growth phase are given below: Equation (3.5), Equation (3.6), Equation (3.7), and Equation (3.8).

$$ZnCl_2 + 2NH_4OH \leftrightarrow Zn(OH)_2 + 2NH_4^+ + 2Cl^- \quad (3.5)$$

$$Zn(OH)_2 + 4NH_4^+ \leftrightarrow [Zn(NH_3)_4]^{2+} + 2H_2O + 2H^+ \quad (3.6)$$

$$SnCl_2 + 2NH_4OH \leftrightarrow Sn(OH)_2 + 2NH_4^+ + 2Cl^- \quad (3.7)$$

$$Sn(OH)_2 + 4NH_4^+ \leftrightarrow [Sn(NH_3)_4]^{2+} + 2H_2O + 2H^+ \quad (3.8)$$

The above reactions occur when solutions $ZnCl_2$, $SnCl_2$ and NH_3 are mixed, then $[Zn(NH_3)_4]^{2+}$ and ($[Sn(NH_3)^4]^{2+}$) (pH≈10) complex is formed. $[Zn(NH_3)^4]^{2+}$ zinc-ammonia complex and $[Cu(NH_3)^4]^{2+}$ indium-ammonia complex are used for the growth of Cu doped ZnO thin films. 0.1M ZnCl2 (pH≈5.5), 0.1M CuCl2 (pH≈5.5) and 25 - 28 % NH_3 solutions are used to prepare $[Zn(NH_3)^4]^{2+}$ and $[Cn(NH_3)^4]^{2+}$ complexes.

$[Zn(NH_3)^4]^{2+}$ and $[Cu(NH_3)^4]^{3+}$ complexes were mixed in appropriate proportions according to 1 %, 2 %, and 3 % Cu additive ratios, keeping the 1 % Sn ratio constant. Sn-Cu doped ZnO thin films were grown on SnO_2:F/Glass(FTO) substrate by performing the above growth steps. In this way, Sn-Cu doped ZnO thin films on SnO_2:F/Glass substrate were obtained by SILAR method, according to 1 %, 2 %, and 3 % Cu additive ratios, FTO/Sn-Cu doped ZnO thin films.

4. RESEARCH FINDINGS

ZnO is preferred in many technological applications due to its direct and wide band gap (about 3.4 eV at room temperature), wide exciton binding energy, piezoelectric properties, high transmittance and high electro-optic coefficients. Doped or undoped ZnO is widely used in many industrial applications, such as gas sensors, biosensors, piezoelectric devices, and solar cell applications.

Electro-optical properties of ZnO films can be improved by doping with III-V group elements such as Sn, Cu, Al, Ni, Ga and In. In this study, structural, morphological and optical properties of Sn-Cu doped ZnO films, which were grown by the SILAR method were investigated.

In this section, analysis methods and results of Sn-Cu doped ZnO samples are evaluated. XRD, SEM, EDS and optical absorption analysis of Sn-Cu doped ZnO thin films produced by SILAR method were performed and the results were interpreted.

4.1 Morphological and Optical Properties of Sn-Cu Doped ZnO Thin Films

As a result of the measurements made on the Sn-Cu doped ZnO samples, the samples produced in 40 cycles were annealed at 300 °C temperature. By keeping the 1% Sn ratio constant, Cu doped thin films at 1 %, 3 % and 5 % mass ratios, respectively, were produced by the SILAR method. Structural, morphological and optical analysis of the produced In-doped ZnO thin films were made.

4.1.1 XRD analysis of Sn-Cu doped ZnO thin films

In Figure 4.1, XRD analysis of ZnO thin films produced by 40 SILAR cycles with 1 %, 2 % and 3 % Cu ratio by mass, keeping the 1 % Sn ratio constant, are given.

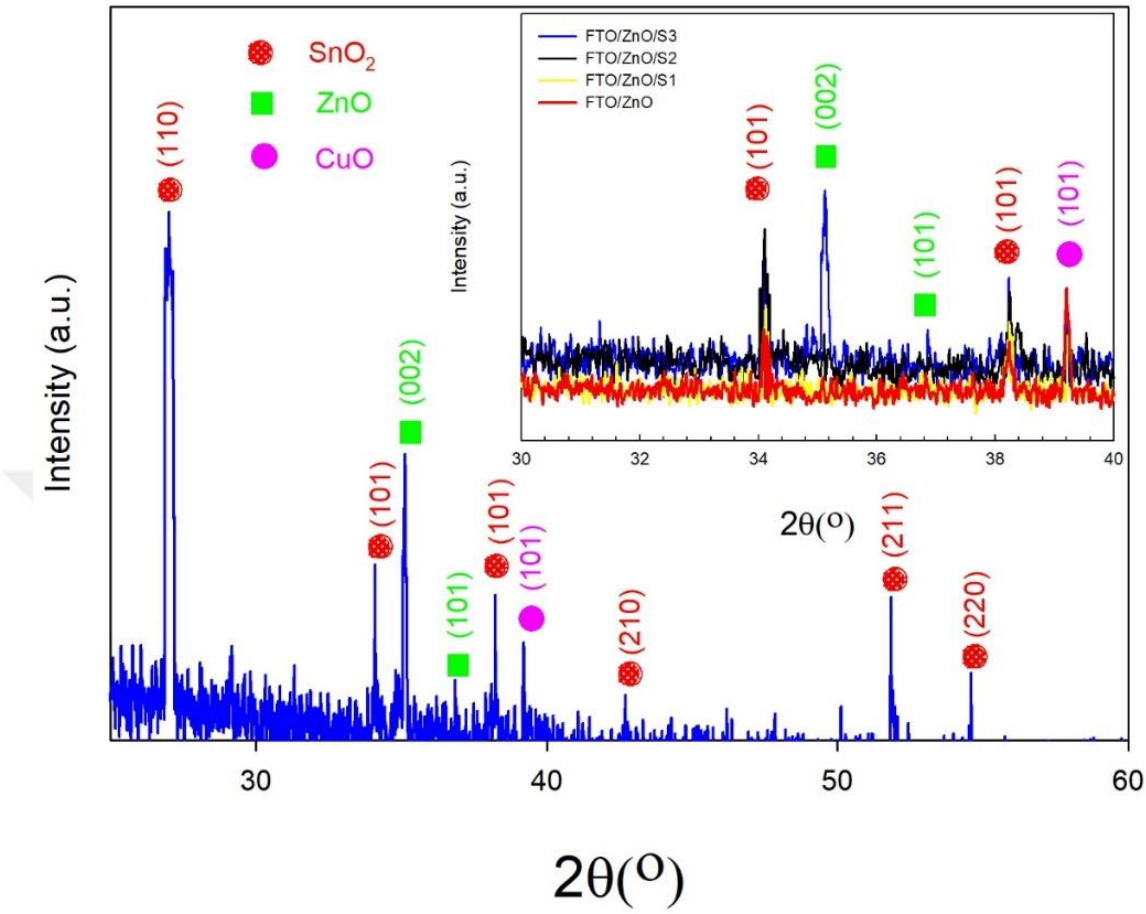

Figure 4.1 XRD analysis of FTO/ZnO, FTO/ZnO/C1, FTO/ZnO/C2, FTO/ZnO/C3 thin films

The dominant diffraction peaks are in the (101), (002) and (211) orientations, indicating the tetragonal crystal structure of SnO_2: F according to the following. It was observed that the peak intensities of the films increased and the half peak widths decreased as the amount of Cu addition increased. In addition, as the doping ratio (x) in the films increased, a decrease in peak intensities and an increase in half peak widths were observed compared to the undoped films (ZnO). Therefore, the crystallization levels of the films vary depending on the Cu doping ratio. When the crystallization levels of the films were examined, the ZnO/Sn-Cu film provided the best compatibility with the SnO_2:F layer.

4.1.2 SEM Analysis of Sn-Cu-doped ZnO thin films

The analysis of the thin films produced depending on each doping ratio were performed sequentially. SEM images of the produced Sn-Cu doped ZnO thin films are given in Figure 4.2.

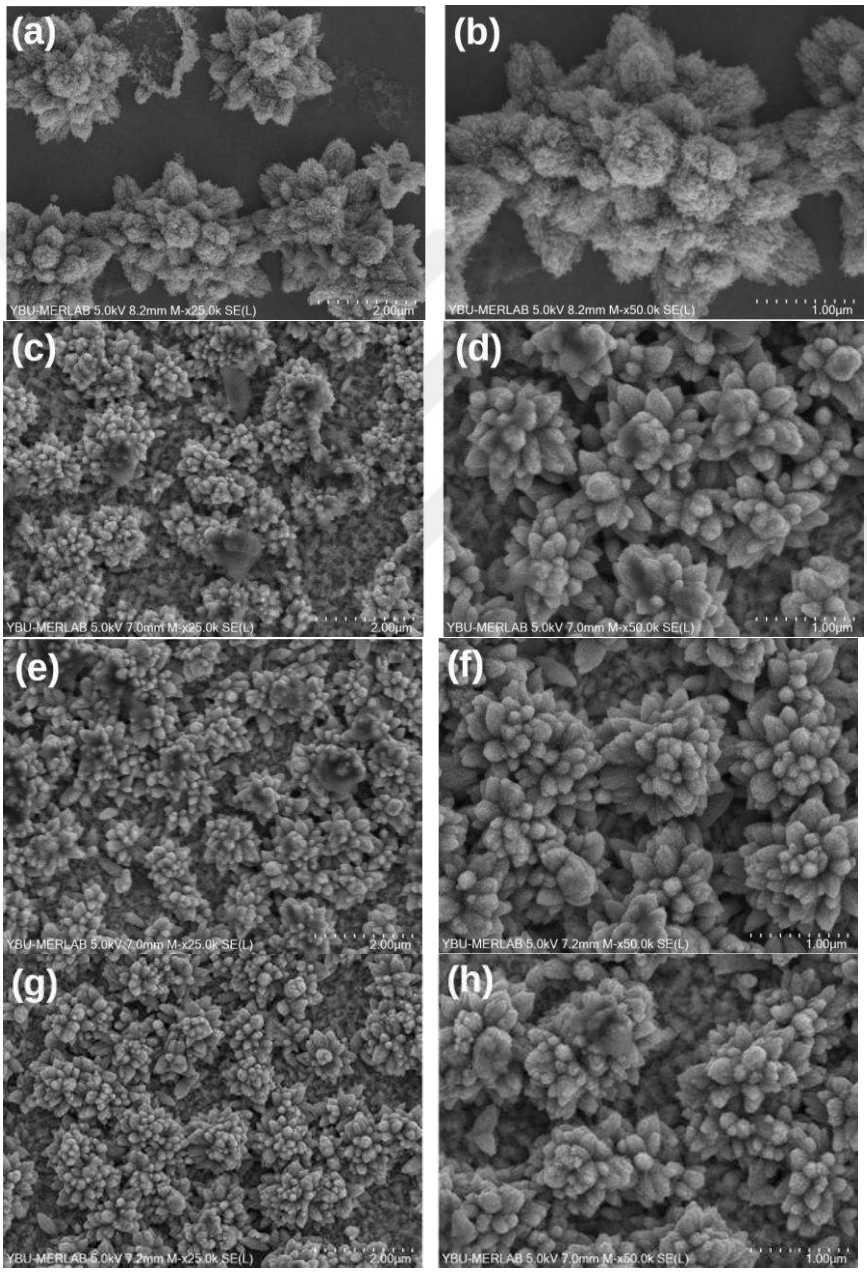

Figure 4.2 SEM analyzes of (a-b) FTO/ZnO, (c-d) FTO/ZnO/C1, (e-f) FTO/ZnO/C2, (g-h) FTO/ZnO/C3 thin films

SEM morphology analysis was performed to better understand the morphology of the produced semiconductor thin film samples. The surface morphologies of undoped and Sn-Cu doped ZnO films are given in Figure 4.2. It was observed that the ZnO thin film structure had a nanoflower structure in the thin film samples produced according to 1 %, 2 % and 3 % Cu additive ratios by keeping the 1 % Sn ratio constant, and the nanoflower structure increased as the Cu addition ratio increased.

Also, it was observed that the average grain size became larger as the Cu content decreased. When the SEM images of all Sn-Cu doped samples were compared, it was observed that the nanoflower structure of the 3 % Cu doped sample was more apparent and some gaps in the structure were reduced. Increasing surface roughness is a desirable feature in some sensor applications. It is known that especially in gas sensor applications, the nanoflower structure increases the sensitivity in gas detection measurements due to the high surface-volume ratio.

4.1.3 EDS analysis of Sn-Cu-doped ZnO thin films

EDS measurements were made to understand the elemental contribution and composition ratios of the grown Sn-Cu doped ZnO samples and their images are given in Figure 4.3. The presence of Si, O, C and Na elements can be seen from the EDS spectrum of the samples. The presence of Si element in the spectrum is due to the precursor materials and glass substrate in the synthesis process. The Na element is due to undesirable impurities during the synthesis of thin films (Figure 4.3).

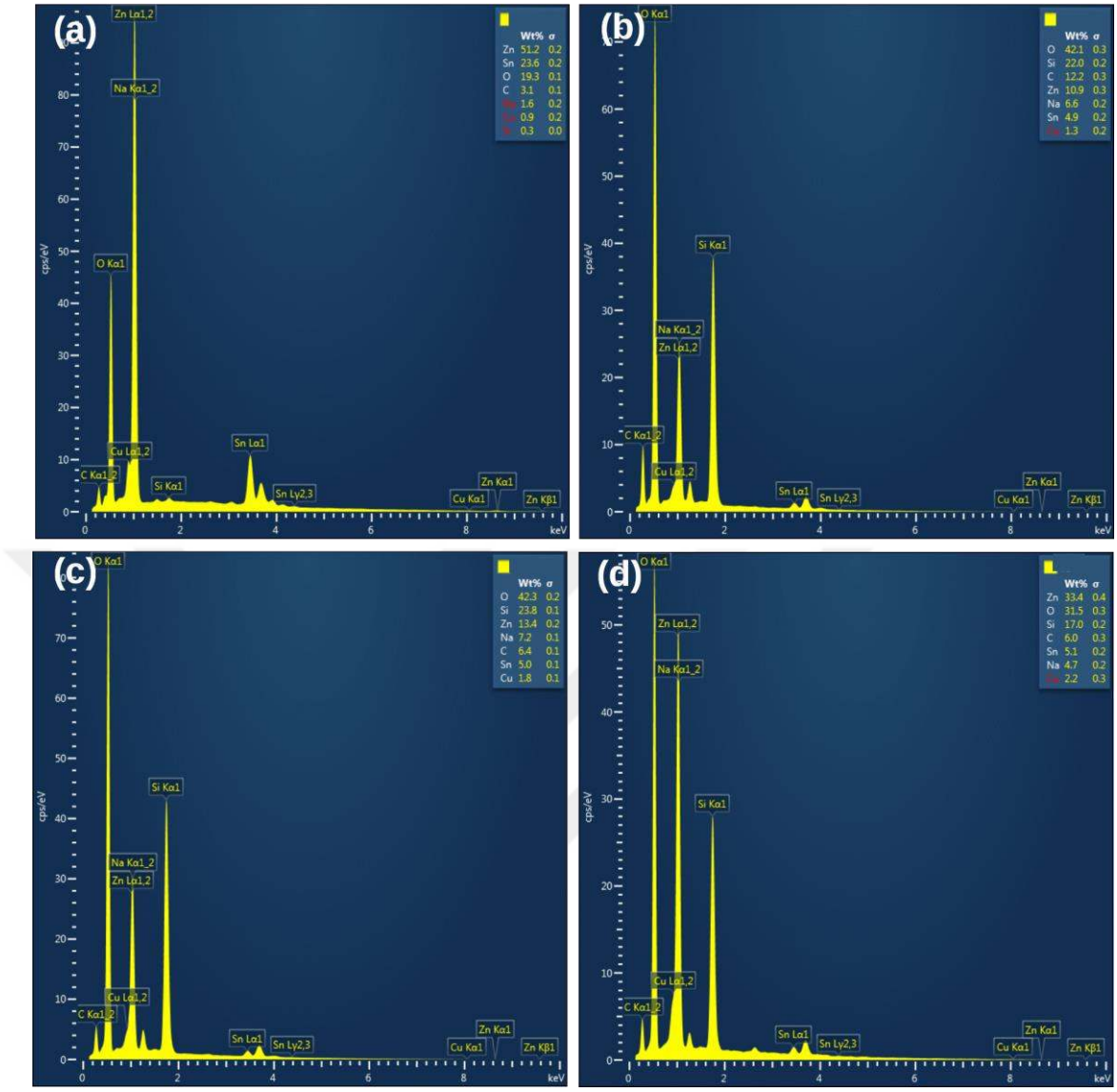

Figure 4.3 EDS analyzes of (a) FTO/ZnO, (b) FTO/ZnO/C1, (c) FTO/ZnO/C2, (d) FTO/ZnO/C3 thin films

EDS analysis of undoped and Sn-Cu doped ZnO samples are given in Figure 4.3. It was observed that there was an increase in Cu element according to the additive ratio of the thin film samples produced according to 1 %, 2 % and 3 % Cu additive ratios by keeping the 1 % Sn ratio constant (As seen in Table 4.1).

Table 4.1 EDS analysis elemental parameters of fructified and Sn-Cu doped ZnO thin films.

Sample Name	Zn Wt%	Si Wt%	O Wt%	C Wt%	Na Wt%	Cu Wt%	Sn Wt%
FTO/ZnO	51.2	0.3	19.3	3.1	1.6	0.9	23.6
FTO/ZnO/C1	10.9	22.0	41.1	12.2	6.6	1.3	4.9
FTO/ZnO/C2	13.4	23.8	42.3	6.4	7.2	1.8	5.0
FTO/ZnO/C3	33.4	17.0	31.5	6.0	4.7	2.2	5.1

4.1.4 Optical analysis of Sn-Cu-doped ZnO thin films

The absorption spectrum for the thin film of undoped and Sn-Cu doped ZnO films grown by SILAR technique, drawn using the absorption measurements taken at room temperature, is given in Figure 4.3. In addition, using the absorption measurements, the energy dependent graph of $(\alpha hv)^2$ $(eVcm^{-1})^2$ is given in Figure 4.3, and the forbidden energy gaps (E_g) of the films are calculated.

In Figure 4.4, the Urbach energy (E_u) versus $ln\alpha$ (hv) was calculated from the slopes of the linear regions. Obtained values and *Eg*, *Eu* energies of the produced films according to the indium additive ratio are given in Table 4.2 below.

Figure 4.5 shows the energy dependent graphs of $(\alpha hv)^2$ $(eVcm^{-1})^2$ drawn using optical absorption measurements of annealed thin films produced according to 1 %, 2 % and 3 % Cu doping ratios, keeping the 1 % Sn ratio constant.

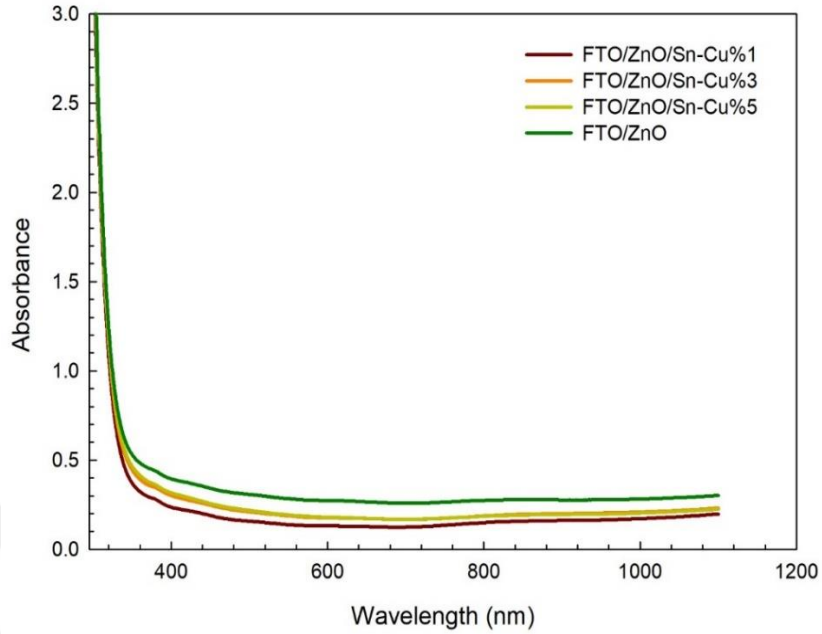

Figure 4.4 Energy dependent plots of $(\alpha hv)^2$ $(eVcm^{-1})^2$ plotted using optical absorption measurements of FTO/ZnO, FTO/ZnO/Sn-Cu 1%, FTO/ZnO/Sn-Cu 2%, FTO/ZnO/Sn-Cu 3% thinfilms

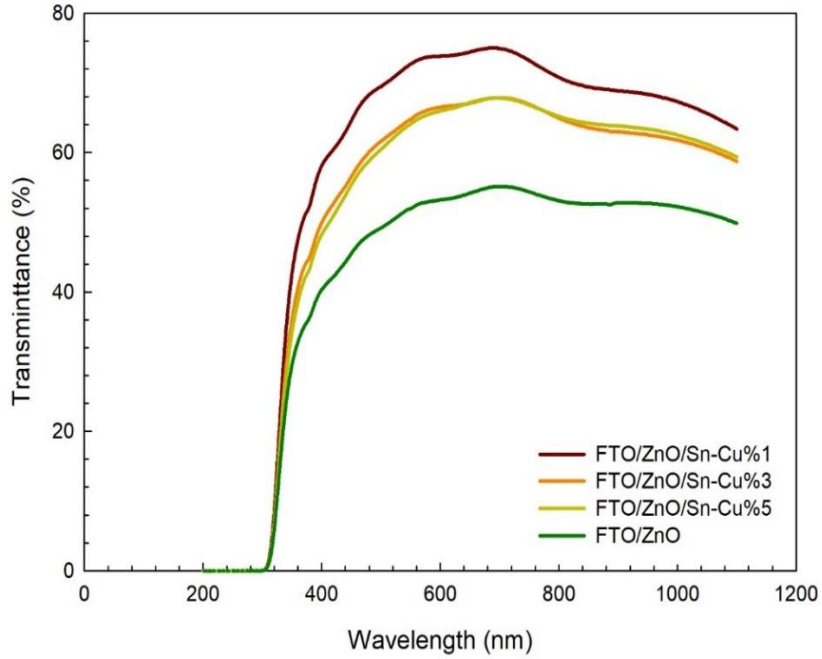

Figure 4.5 Energy dependent graphs of $(\alpha hv)^2$ $(eVcm^{-1})^2$ plotted using optical transmittance measurements of FTO/ZnO, FTO/ZnO/Sn-Cu 1%, FTO/ZnO/Sn-Cu 2%, FTO/ZnO/Sn-Cu 3% thin films.

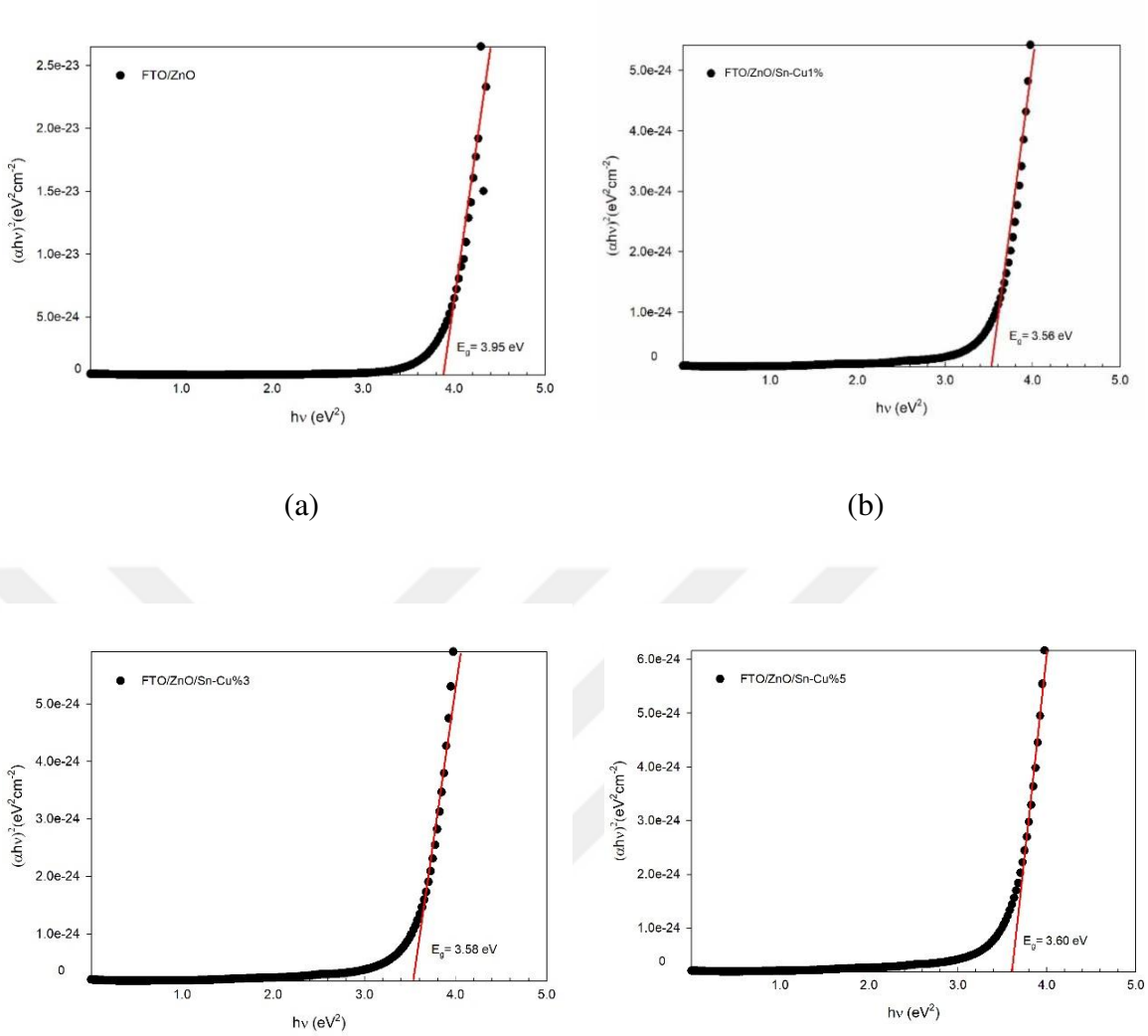

Figure 4.6 Energy-dependent band gap of $(\alpha hv)^2$ $(eVcm^{-1})^2$ plotted using optical absorption measurements of (a) FTO/ZnO, (b) FTO/ZnO/Sn-Cu 1%, (c) FTO/ZnO/Sn-Cu 2%, (d) FTO/ZnO/Sn-Cu 3%thin films

Forbidden energy values which are calculated from the hυ (energy) dependent graphs of $(\alpha hv)^2$ $(eVcm^{-1})^2$ drawn using optical absorption measurements of FTO/ZnO, FTO/ZnO/C1, FTO/ZnO/C2, FTO/ZnO/C3 thin films are given in Table 4.2. It was determined that the forbidden energy gap values of the films changed with doping. The forbidden energy gap values of the thin films which are produced by doping decrease, and it has been observed that the absorption edge becomes sharper and the absorption

intensity increases (Figure 4.6). The reduction of the forbidden energy gap by doping can be attributed to the improvement of the film crystallinity and surface properties and the increase in grain size (Figure 4.7).

Table 4.2 The forbidden energy (E_g) and Urbach (E_u) values calculated from the energy dependent graphs of $(\alpha hv)^2$ $(eVcm^{-1})^2$ drawn using optical absorption measurements of FTO/ZnO, FTO/ZnO/Sn-Cu 1%, FTO/ZnO/Sn-Cu 2%, FTO/ZnO/Sn-Cu 3%thin films

Sample	**E_g (eV)**	**E_u (meV)**
FTO/ZnO	3,95	360.22
FTO/ZnO/Sn-Cu 1%	3,56	371.25
FTO/ZnO/Sn-Cu 2%	3,58	375.57
FTO/ZnO/Sn-Cu 3%	3,60	393.61

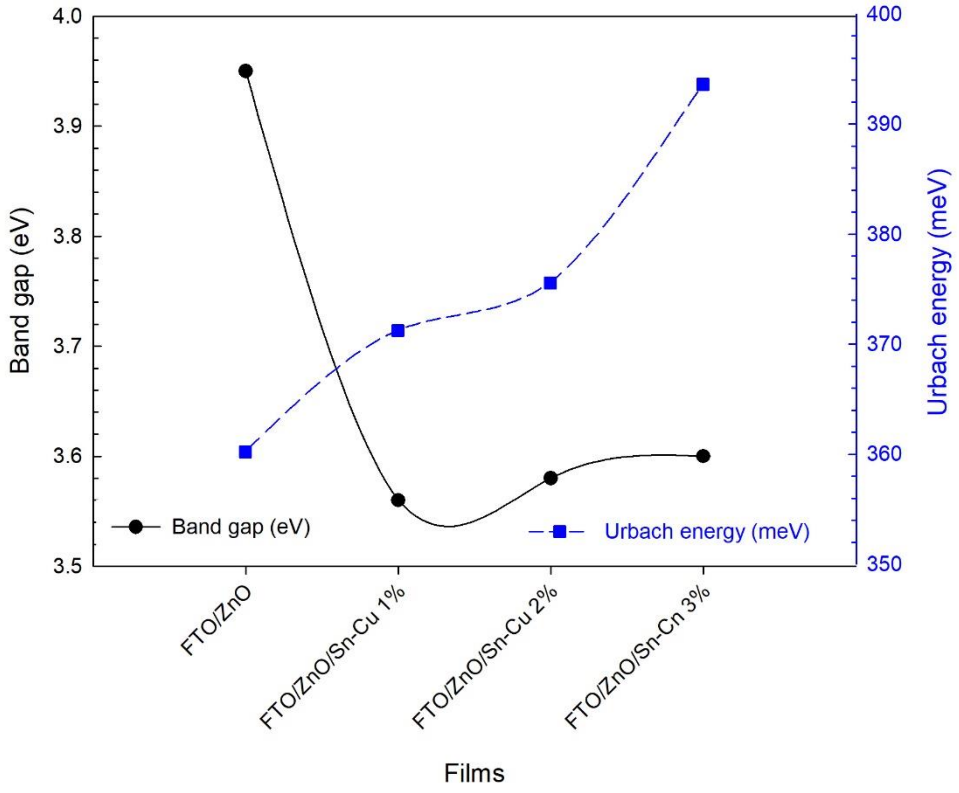

Figure 4.7 Band gap and Urbach energy versus of FTO/ZnO, FTO/ZnO/Sn-Cu 1%, FTO/ZnO/Sn-Cu 2%, FTO/ZnO/Sn-Cu 3% films

As seen in Table 4.2, it was observed that the forbidden energy gaps of the thin films decreased with an increase in the 1 %, 3 % and 5 % Cu additive ratio, keeping the 1 % Sn ratio constant. At the same time, an increase in E_u values was observed according to the Cu doping ratio of the produced thin films.

As shown in Figure 4.8, a decrease in E_g values depends on the Cu additive rate, but an increase in E_u values occurs. It is expected that E_g decreases and E_u increases with Cu doping (Sharma *et al.* 2017). The forbidden band energy of Cu-doped ZnO thin films is smaller than non Cu doped ZnO thin films, which can be explained by the Bursteine-Moss shift. Moreover, with increasing Cu contribution, the Fermi energy level of ZnO/Sn-Cu shifts towards the conduction band, and therefore an increase in the forbidden energy gap is observed in Figure 4.8.

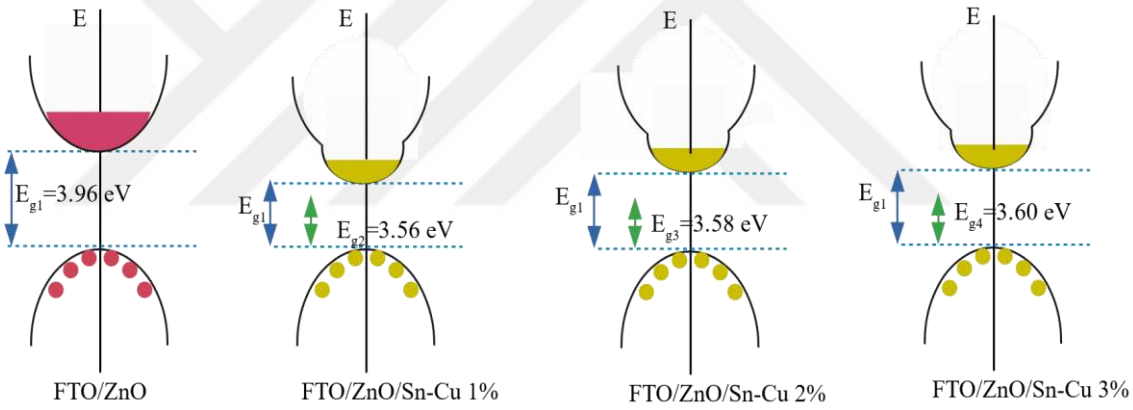

Figure 4.8 The schematic representation of the band diagram of FTO/ZnO, FTO/ZnO/Sn-Cu 1%, FTO/ZnO/Sn-Cu 2%, FTO/ZnO/Sn-Cu 3% films

5. DISCUSSION AND CONCLUSIONS

In this thesis, SILAR method was used in the production of ZnO films produced according to 1 %, 2 % and 3 % Cu doping ratios, keeping the undoped ZnO and 1 % Sn ratio constant on FTO substrate. The thin films produced were annealed at 300 °C and in a nitrogen gas environment for 13 minutes after 40 cycles. Considering the XRD, SEM and EDS analysis of the produced thin films, it was seen that the growth occurred on the FTO substrate. In this study, it was aimed to examine the structural, morphological and optical properties of ZnO films produced according to 1 %, 2 % and 3 % Cu doping ratios by keeping the undoped ZnO and 1% Sn ratio constant.

XRD analysis;

In XRD analyzes of ZnO films produced according to 1 %, 2 % and 3 % Cu doping ratios by keeping the undoped ZnO and 1% Sn ratio constant, it was observed that the peak intensities of the films increased and the half peak widths of the films decreased as the Cu doping ratio increased. In addition, as the doping ratio (x) in the films increased, a decrease in peak intensities and an increase in half-peak widths were observed compared to the undoped films (ZnO). It was observed that there was a transition towards tetragonal ZnO phase in Cu doped thin films. The dominant diffraction peaks were observed to be in the (101), (002) and (211) orientation, indicating the tetragonal crystal structure of SnO_2:F.

When the crystallization levels of the films were examined, it was observed that the crystal structures improved and the samples became more stable depending on the Cu contribution ratio. According to the results, it was seen that the ZnO/Sn/C3 film provided the best compatibility with the SnO_2:F layer.

SEM analysis;

From the SEM image of the unadulterated ZnO thin films, it is seen that there is a less dense layering and growth disrupting the homogeneity on the substrate surface. It was observed that as the additive ratios increased, the voids and surface roughness on the substrate surface decreased, and a more homogeneous and uniform stratification was formed by merging the regional agglomerations with each other. It is observed that the morphological properties of thin films produced by doping have changed significantly. While the surface roughness of the produced samples decreases, there are partial agglomerations in some regions.

When the SEM images of the 1 %, 2 % and 3 % Cu doped ZnO samples which have constant 1% Sn ratio were examined, it was seen that the ZnO thin film structure had a nanoflower structure and the nanoflower structure of the 3 % Cu doped sample was dominant on the substrate surface. However, it was observed that the average grain size became smaller as the Cu addition ratio increased. When the SEM images of the 1 %, 3 % and 5 % Cu doped ZnO samples which have constant 1 % Sn ratio were compared, it was seen that the nanoflower structure of the sample with 3 % Cu doped was more prominent and the voids were reduced at low doped ratios in the structure.

EDS analysis;

When the EDS analyzes are examined, changes are observed in the ratios of Zn, O, C, Sn and Cu elements in the samples depending on the additive ratio. The presence of Si and C elements in EDS analyzes is due to the substrate material. The presence of the element Na is due to undesirable impurity.

In addition, EDS analyzes show that ZnO/Sn/Cu samples were produced with the SILAR method at stoichiometrically appropriate doping ratios.

Optical analysis;

As a result of the optical absorption measurements of the ZnO films produced according to the 1 %, 2 % and 3 % Cu doping ratios by keeping the 1% Sn ratio constant on the undoped ZnO, a decrease in the forbidden energy gap of the films is observed with the increase in the doping ratio. With the increase of doping ratio, a decrease in the forbidden energy range of ZnO (E_g = 3.95 eV for undoped ZnO at room temperature) (E_g = 3.58 eV - 3.60 eV for doped ZnO at room temperature) was observed. The band gap values of the 1 %, 2 % and 3 % Cu doped ZnO samples which kept the constant 1 % Sn ratio decreased, and it was observed that the absorption edge became sharper and the absorption intensity increased. The decrease in the forbidden energy gap can be attributed to the improvement of the produced film crystallinity and surface properties, to the increase in particle size. It is expected that the forbidden energy gaps will decrease with Cu doping. The forbidden band energy of Cu doped ZnO thin films is smaller than the band energy of undoped ZnO thin films, which can be explained by the Bursteine-Moss shift.

When all the obtained results are evaluated, it has been observed that the characteristic properties of the films produced according to the 1 %, 2 % and 3 % Cu doping ratios by keeping the 1 % Sn ratio constant, change depending on the doping ratios. It is clearly seen that the Sn and Cu doped ZnO material has a more regular and stable structure than the undoped ZnO material. It was observed that there was a structural improvement with the effect of Cu doping. It has been determined that there are significant changes in the morphological properties of thin films with the effect of Cu doping.

Structural, morphological and optical properties of Undoped ZnO and also ZnO film samples produced according to 1 %, 2 % and 3 % Cu doping ratios, keeping the 1 % Sn ratio constant were investigated in this master thesis. In this way, it is clearly seen that this thesis will be useful for many applications in this field.

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