

**T.R.
SAKARYA UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**SYNTHESIS AND CHARACTERIZATION OF CZTS THIN-FILM
AS ABSORBER LAYER FOR SOLAR CELLS**



MSc THESIS

SAAD RAQEEB MOHAMMED

Fizik Department

MARCH 2023

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Thesis Advisor: Dr. Öğr.Üyesi YUSUF KARAKUŞ

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The thesis work titled “SYNTHESIS AND CHARACTERIZATION OF CZTS THIN-FILM AS ABSORBER LAYER FOR SOLAR CELLS” prepared by SAAD RAQEEB MOHAMMED was accepted by the following jury on 7/3/2023 by unanimously/majority of votes as a MSc THESIS in Sakarya University Graduate School of Natural and Applied Sciences, Fizik department.

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(...../...../2023)

Saad Raqeeb Mohammed MOHAMMED



ACKNOWLEDGMENTS

Praise be to God, lord of the worlds, prayers and peace be upon our master Muhammad, the seal of the prophets and messengers.

A big thanks to the inspirer teacher and supervisor Dr. Öğr.Üyesi Yusuf Karakuş, the scientific supporter who was with me every step of my project and research, the owner of the genius thought.

Special thanks to Sakarya University, specifically the institute of science and technology, this great scientific edifice. And the head of the department of physics and all the professors of the department.

I thank my father and mother for their support throughout my studies.

I thank my wife and children for their moral support and standing by my side until I reached this stage.

Thanks to my brothers and sisters.

Special thanks to everyone who helped me, students and friends.

Saad Raqeeb Mohammed MOHAMMED
SAKARYA, 2023



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SYMBOLS

n	: An integer representing the diffraction order
d_{hkl}	: The distance between the planes
θ	: Bragg's diffraction angle
λ	: The wavelength [nm] of the incident ray
a_o, c_o	: Lattice constants
hkl	: Miller's coefficients
D	: Crystallite size [nm]
k	: Shape factor
β	: Full width at half maximum (FWHM) in radial units.
T_c	: Texture coefficient
N	: Peaks count visible in X-ray diffraction
$I_{(hkl)}$	: Measured relative intensity of the plane (hkl)
$I_o(hkl)$	: Intensity standard of the plane (hkl) taken from the card (ICDD)
δ	: Dislocation density
N_0	: Number of crystallites per unite area
t	: Thickness of film
I_A	: Absorbed intensity
I_R	: Reflected intensity
I_T	: Transmitted intensity
P	: Constant that is determined by the substance's nature
$h\nu$	: Photon energy [eV]
E_g	: Optical energy gap
r	: An exponential factor that determines the nature of transition
α_o	: Proportionality constant
E_u	: Urbach energy
n_o	: Refractive index
K_o	: Extinction coefficient
B_o	: A constant that is determined by the substance's nature.

B_1	: Constant depends on the type of material
E_{ph}	: Phonon energy
ϵ	: Complex dielectric constant
ϵ_1	: Real part of dielectric constant
ϵ_2	: Imaginary part of dielectric constant
R_H	: Hall coefficient
V_H	: Hall voltage
B_z	: The intensity of the applied magnetic field
ϕ	: Scattering factor
n_H	: Concentration of charge carriers
μ_H	: Hall mobility
σ	: The conductivity
W_t	: Solute weight [g]
M	: Molar concentration [mol/L]
V	: Solvent volume [ml]
M_{wt}	: Molecular weight of material [g/mol]

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SYNTHESIS AND CHARACTERIZATION OF CZTS THIN-FILM AS ABSORBER LAYER FOR SOLAR CELLS

SUMMARY

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were deposited on glass substrates at temperature 350°C using chemical spray pyrolysis technique. The structural, optical and electrical properties of the CZTS films were studied using X-ray diffraction (XRD), Raman spectroscopy, Field emission scanning electron microscopy (FESEM), UV-visible spectrophotometry and Hall Effect measurements.

The X-ray diffraction results showed that the prepared films have a polycrystalline structure of the tetragonal type, kesterite phase. The size of the crystals was calculated using Scherer's method and it was found that the crystal size increased with the increase of the thickness. Raman spectroscopy showed the main peak around ($324, 338, 330, 325, 334\text{ cm}^{-1}$) for all samples, which confirms the formation of tetragonal (CZTS) compound.

The results of the field emission scanning electron microscope (FESEM) showed that the prepared films were formed as beautifully and homogeneously intertwined twigs.

The optical properties were studied using UV-visible spectrophotometry, and the optical energy gap values were calculated using the (Tauc plot) and it was found that it decreases from (1.72 to 1.56 eV) with the increase in thickness. High values of the absorption coefficient ($\alpha > 10^4\text{ cm}^{-1}$) are obtained which is suitable for the solar cell applications.

The measurements of Hall coefficients showed that the prepared films are p-type. As the thickness increased from 0.59 to $3.3\text{ }\mu\text{m}$, the mobility of charged particles increased from 1.33 to $30.5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and the conductivity of CZTS samples increased from 0.015 to $0.069\text{ (}\Omega\cdot\text{cm)}^{-1}$.



GÜNEŞ HÜCRELERİ İÇİN EMİCİ TABAKA OLARAK CZTS İNCE FİLMİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Farklı kalınlıktaki $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) ince filmler, kimyasal spreylendirme yöntemi kullanılarak 350°C sıcaklıkta tutulan cam altlıklar üzerine hazırlanmıştır. CZTS ile hazırlanan filmlerin yapısal, optik ve elektriksel özellikleri, X-ışını kırınımı (XRD), Raman spektroskopisi, Alan emisyon taramalı elektron mikroskobu (FESEM) ve UV-görünür spektrofotometri kullanılarak incelenmiştir.

X-ışını kırınım sonuçları, hazırlanan filmlerin tetragonal tipte, kesterit fazında polikristal bir yapıya sahip olduğunu gösterdi. Kristallerin boyutu Scherrer yöntemi kullanılarak hesaplandı ve kalınlıktaki artışla kristal boyutunun arttığı tespit edildi. Raman spektroskopisi, tüm numunelerde CZTS bileşiğinin ana pikleri olan 324, 338, 330, 325, 334 cm^{-1} değerlerini gösterdi ve tetragonal oluşumu doğruladı.

Alan emisyon taramalı elektron mikroskobu (FESEM) sonuçları, hazırlanan filmlerin güzel ve homojen bir şekilde birbirine dolanmış ince dallar halinde oluştuğunu gösterdi.

Optik özellikler UV-görünür spektrofotometri kullanılarak incelendi ve yasak enerji aralığı (E_g) değerleri, Tauc grafiği kullanılarak hesaplandı ve kalınlık artışıyla (1.72'den 1.56 eV'ye) düştüğü tespit edildi. Hazırlanan numunelerin yüksek soğurma katsayısına $\alpha > 10^4 \text{ cm}^{-1}$ sahip olduğu görüldü. Bu yüksek soğurma katsayısı güneş pili uygulamaları için gereklidir.

Hall etkisi ölçümleri, hazırlanan filmlerin (p-tipi) olduğunu ve film kalınlığındaki artışla (0.59 μm - 3.3 μm) yüklü parçacıkların mobilitesinin 1.33 ten 30.5 $\text{cm}^2/\text{V.s}$ ve iletkenliğinde 0.015 den 0.069 ($\Omega.\text{cm}$) $^{-1}$ arttığı gözlemlendi.

(CZTS) film hazırlamak için, molar kütleli Bakır klorür (CuCl_2) (134,45 g/mol), Çinko asetat dihidrat ($\text{C}_4\text{H}_{10}\text{O}_6\text{Zn}$) (219,5 g/mol), Kalay (II) klorür (SnCl_2) (189,6 g/mol) ve Kükürt kaynağı olarak tiyoüre ($\text{CH}_4\text{N}_2\text{S}$) (76.12g/mol), oda sıcaklığında saf su (H_2O) ile Etanol ($\text{C}_2\text{H}_6\text{O}$) ile çözülüp.

Molar konsantrasyonlar şu şekilde kullanıldı, 0.2 molar bakır klorür, 0.1 molar çinko asetat dihidrat, 0.1 molar kalay (II) klorür ve 1 molar tiyoüre. Sülfür iyonlarının (tiyoüre) konsantrasyonu, filmin büyümesinin son reaksiyonu sırasında cam alt tabakaların ısınması nedeniyle büyük bir miktarı buharlaşacağından, birden çok kez iki katına çıkar, formül $[\text{Cu}/(\text{Zn}+\text{Sn})]=1$ karşılar bileşik (CZTS) için denklik formülü. Nihai çözeltinin hacmi (50 ml) idi.

Kimyasal spreylendirme yöntemi kullanılarak çözelti 350°C 'de 10 saniye ısıtılan cam yüzeyler üzerine püskürtüldü ve daha sonra numuneler orijinal sıcaklığına dönene kadar 1 dakika bırakıldı, ardından filmin kalınlığına bağlı olarak birkaç kez püskürtmeye devam edildi hazırlıklı olmak Püskürtme işlemi sırasında numuneler hareket eder (döner) ve en iyi film homojenliğini elde etmek için püskürtme miktarını düzenler. Püskürtme işleminden sonra hazırlanan filmlerin kristal büyütme sürecini tamamlaması için numuneler elektrikli ısıtıcı üzerinde bırakılır. Daha sonra ani

soğumanın hem filmlere hem de yüzeylere olumsuz etkisi olmasın diye kademeli olarak soğumaya bırakılır.

Kimyasal spreylere piroliz tekniği kullanılarak cam altlıklar üzerine farklı kalınlıklarda biriktirilen (CZTS) filmlerin yapısal, optik ve elektriksel ölçümlerinin sonuçları, bu tür malzemelerin davranışını açıklayan teorik ilkelere göre sunulacak ve analiz edilecektir. değişen kalınlığın şekillendirilmiş (CZTS) filmlerin fiziksel özellikleri üzerindeki etkisini bilmek için.



1. INTRODUCTION

Modern electronic devices depend in their work on materials with special physical and chemical properties with semiconducting materials that have the properties of insulators at low temperatures (zero absolute) and has the ability to conduct electricity when its temperature rises to a certain extent, as well one of the important topics is the study of the properties of materials in the form of thin films.

thin films are a phrase used to indicate one or more layers of atoms in a substance. They must be deposited on a solid substance such as glass, Silicon, salts, or polymers since they are thin and brittle (easy to break). Thin films have traits and features that aren't found in other material's structures. The fact of their very thin thickness and a distinctive physical structure that sometimes resembles that of a single crystal because of their enormous "surface to volume" ratio [1].

1.1. Historical Background of Solar Cell

Solar cells or photo-voltaic devices converts the sun light (photon energy) into electrical or heat energy. Figure 1.1. is showing schematic representation of a solar cell device [2].

The work of solar cells depends on the photovoltaic phenomenon that converting sunlight into electrical energy. Solar cells, that it is characterized by not having moving parts, so it is not prone to failure and works efficiently when used in the satellites also operate silently and do not need maintenance, repairs or fuel, but they are requires cleaning them from dust, which reduces the efficiency of solar cell.

This phenomenon was first published in 1896 by the scientist Becquerel, who noticed that the electric potential difference between the electrodes immersed in an electrolytic solution depends on the incident light [3]. In 1876, this phenomenon was observed in all devices containing selenium (Se). This was followed by the invention of photovoltaic cells made of this material and copper oxide, and although the first thing that was published about the silicon cell was in 1941, the silicon cell was not known in its current form until 1954, and this device was considered one of the

greatest innovations during that period because it was the first a photovoltaic installation that converts incident light into electrical energy with an acceptable efficiency, these cells were also used in 1958 for space purposes and at the beginning of the sixties of the last century, the use of silicon cells for space purposes is becoming commonplace and this remained one of its most important uses for a decade.

The beginning of the seventies of the last century witnessed a period of development of silicon cells, with a clear increase in the efficiency of energy conversion. At about the same time there was an increase in interest in the use of these devices in terrestrial applications. At the end of the seventies, the volume of cells produced for land uses exceeded those this increase in production is accompanied by a significant decrease in the prices of cells solar. The beginning of the eighties of the last century witnessed the experimental production of modern technologies at that time aimed at reducing Solar cell costs for the coming decades. This drop in prices encourages the continued expansion of commercial applications to exploit solar energy [4].

The technology of using thin films to produce solar cells has also emerged recently, while raising the external capacity per unit area for these cells. Amorphous silicon solar cells have been commercially available since 1980, whose performance in the laboratory is almost as good as that of cells made of good quality crystalline silicon, and studies are now continuing with the aim of obtaining this performance outside the laboratory on space stations [5]. It is commonly used to improve the surface properties of solid materials [6].

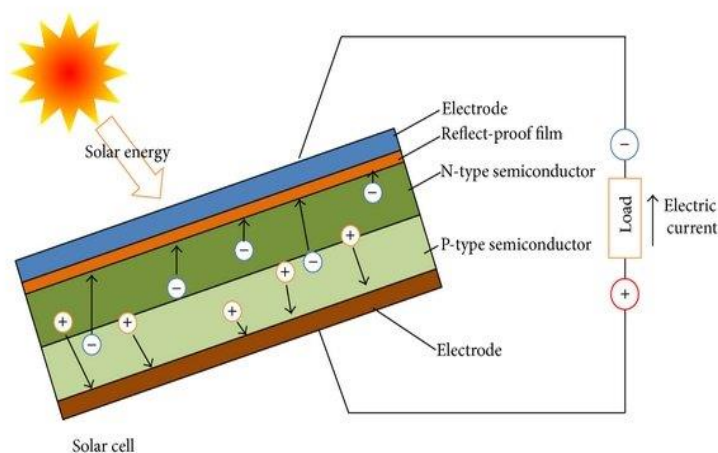


Figure 1.1. Schematic representation of a solar cell device [2].

1.2. Solar Cells as A Renewable Energy Source

Research into thin-film materials is carried out by various research groups and categories. The goal of this project is to investigate the characteristics of CZTS films, for use as an absorption layer in solar cells that convert solar energy into electrical energy directly.

Photovoltaic technology with direct conversion of sunlight into electricity has very high possibilities to cover the global demand for electricity, as (90) minutes of sunlight that it reaches the earth enough to generate the energy needed for the need of the whole world for one year. The electrical energy generated by photovoltaic cells contributed only 0.5% of the consumption electricity in the world. The obstacle to further expanding the share of photovoltaic energy is due to the cost compared to traditional carbon-based technology. More than 80% of photovoltaic cells rely on silicon technology. Devices appear the silicon-based performance is very stable, as it recorded a record efficiency of 20 and 25% for laboratory cells polycrystalline and bulky respectively [7].

1.3. Literatures Review of CZTS Thin Films

- In 2011, the researcher (Yoo) and others prepared CZTS films by using the (Rf sputtering deposition) technique, and then plasticized at a temperature of (570 °C) by passing sulfur vapor. The researchers examined the impact of the different deposition sequences on the properties of the prepared films. They discovered that all the films have good growth and high crystallization, and this may refer to high temperature treatment. They also found that the difference in the sedimentation sequence of the elements affects the nature of the films, and Raman spectroscopy revealed the presence of Cu_{2-x}S compounds as phases. Secondary with the base compound and that the deposition of copper as a first layer over the glass bases led to the formation of films with a porous structure because of the migration of copper atoms towards the surface of the film during the sulfur treatment process. In terms of the "Chemical Spray Pyrolysis" films, the technique of X-ray diffraction during the analysis of the samples showed the disappearance of certain peaks at one of the concentrations after treating the films with sulfur, this is

followed by the emergence of further peaks at different concentrations, which indicates the effect of the sulfur element in the composition of the films. The researchers also noticed a creep in the locations of the diffraction angles and Raman peaks during the change in the concentration of copper, due to the surface clearance or the pressure stresses generated when the concentration changed, and that the treatment of the films with sulfur led to an increase in crystallization without a change in the locations of those angles [8].

- In 2011, researcher (Shin) et al. prepared $\text{Cu}_2\text{ZnSnS}_4$ films of thickness (1.5 μm) and then annealed at (550 $^\circ\text{C}$) for 15 minutes. All the peaks shown by the X-ray diffraction technique belong to CZTS and are polycrystalline in nature. Raman spectroscopy showed a clear peak belonging to the same compound, while one of the samples showed a peak belonging to SnS_2 compound, which agreed with the X-ray diffraction results. The FE-SEM measurements of one of the samples showed a regular surface free of voids, a large particle size and a high efficiency due to the large particle size, while the other samples showed several voids and secondary phases. The researchers also found that the voids in the absorbent layer generate a decrease in the conversion efficiency, as all conductive films showed of the positive type and high mobility depending on the structure and secondary phases, the prepared films have a high coefficient of absorption greater than (10^4 cm^{-1}) in the visible light range and a direct energy gap located in the range (1.1 - 1.5 eV) [9].
- In 2013, the researcher Chung et al. was able to study the properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films prepared by Sol-Gel method and using two types of solvents 2-Methoxyethanol (metho-2) and methanol, the produced films have a kesterite composition, according to X-ray diffraction data., and with the prevailing trend (112) for the two solvents, and from the results of Raman spectroscopy, the appearance of secondary phases of them ($\text{Cu}_2\text{ZnSnS}_3$ and SnS_2) was observed when using methanol because they contain a synthetic ratio closer to the ideal value, as for the optical and electrical tests for the films prepared with 2-Methoxyethanol and methanol, it was found that the permissible energy gap is 1.27 – 1.36 eV and the specific resistance is ($2.7 \times 10^{-1} - 12.2 \times 10^{-1} \Omega.\text{cm}$) respectively [10].

- Malerba et al. deposited layers of Cu, Sn, and ZnS in 2014 using (e-beam evaporation) technology on glass bases at 150°C and then treated with sulfur at 550°C. The researchers studied the effect of changing the concentrations of the elements on the value of the energy gap, as they found an increase in the presence of Sn_xS_y as a secondary phase with an increase in the film content of the element tin when the concentrations of copper and zinc were fixed. It was also found that the permeability was not affected by the change in the concentration of zinc, while the value of the permeability was shifted towards the shorter wavelengths when the content of tin was increased in therefore, the value of the energy gap was not affected by the change in the content of the films from zinc, while its value increased with an increase in Sn/Cu [11].
- In 2014, Farinella et al. prepared CZTS films using electrodeposition at room temperature. The researchers found that CZTS layer uniformly covers all the base area exposed to the solution, the deposited films are random in structure, according to the X-ray diffraction data. And their composition changes to polycrystalline after heat treatment, the composition of the deposited films was calculated by EDX analysis, which showed a spectrum of peaks of Zn, Sn, Cu and S, belonging to the $\text{Cu}_2\text{ZnSnS}_4$ complex, and a peak belonging to the glass. The measured energy gap value is higher than that of crystalline CZTS it is 2eV due to the stochastic nature of the film [12].
- In 2015, researcher Kermadi and others, examined the impact of copper content and sulfur treatment on the growth and composition of optical properties of CZTS films deposited on glass bases using Chemical Ultrasonic Spray Pyrolysis technology with several concentrations of copper at 310°C. The samples showed better homogeneity after annealing, as the grains appeared to be fused, and it was noted that aggregates consisting mainly of copper compounds with little to CZTS compound appeared. The atomic force microscopy (AFM) tests also showed an increase in the grain size rate from (100 to 300 nm) when the copper content was increased. XRD patterns showed that all diffraction angles belong to the kesterite phase of the CZTS complex. Raman spectroscopy measurements also showed a common peak for all concentrations before and after the heat treatment, which lies in the range of $333\text{-}339\text{ cm}^{-1}$ and it represents the main peak that describes the CZTS compound. The study showed that there is no clear relation between

the energy gap and the film content of copper, and this is due to the factors that automatically affect the energy gap value of CZTS, including: unevenness in the composition of materials, the number of secondary phases, and the change in shape and composition. All compositions showed a decrease in the energy gap value after annealing, and the decrease in its value increased after sulfur treatment, which confirms the occurrence of a chemical change in the films. The electrical measurements showed that all the films have positive conductivity and suffer from a decrease in the resistance value after the annealing process [13].

- In 2016, Yeh et al. researchers prepared $\text{Cu}_2\text{ZnSnS}_4$ films by depositing them on glass bases with Spin Coating technique to studying the effect of annealing for optical, structural, topographical and electrical properties. The results showed that the prepared films are polycrystalline with an energy gap of (1.7 - 1.35 eV) and were used as a solar cell by depositing it on (n-Si) with a conversion efficiency (1.13 %), with ($V_{oc} = 520$ mV), ($J_{sc} = 3.28$ mA/cm²) and (Fill-Factor (FF) = 66 %) [14].
- In 2016, the researcher Moreno et al. prepared $\text{Cu}_2\text{ZnSnS}_4$ films using the Spray Pyrolysis and Co-evaporation methods using a solution consisting of (0.01 Molar) copper chloride, (0.005 Molar) Zn chloride, (0.005 Molar) tin chloride and (0.04 Molar) thiourea as a source of sulfur and disulfide. DMSO methyl sulfoxide as a solvent. The solution was deposited on Soda-lime glass at 350 °C and the prepared films were plasticized at 500 °C for 30 minutes. The researchers studied the effect of different preparation method for the structural and the optical properties of prepared films, The outcomes revealed that the value of the full width half maximum was affected by the preparation method, which caused the change in the values of crystal size and consequently the change in the values of the energy gap. The researchers also found that the values of lattice stresses and Urbach energy for films prepared by thermal evaporation method are lower than their counterparts for films prepared by thermal chemical decomposition method. This indicates that the thermal evaporation method is less dense for structural defects than the thermal chemical decomposition method, because Urbach energy is due to the density of local levels induced by structural defects. Raman spectroscopy also revealed peaks of CZTS for both preparations but the peaks resulting from

the thermochemical decomposition process suffer crawling towards the lower wavelengths from their locations for the films prepared by evaporation method [15].

- In 2017, the researcher Zhao and others, examined the impact of increasing the base temperature for the general properties of $\text{Cu}_2\text{ZnSnS}_4$ films prepared by Rf magnetron sputtering technique. The researchers found that with the increase in temperature the X-ray diffraction peaks become stronger and more intense, accompanied by a decrease in the value of the full width half maximum, an increase in grain size leads to a drop in the energy gap's value. This shows that increasing the temperature improves the crystallization process of the films and makes them more dense and more sticky. Raman spectrometry showed that the base CZTS crest becomes more intense and suffers creep towards larger wave numbers, in the range ($332\text{-}336\text{ cm}^{-1}$) when the temperature rises [16].
- In 2018, researcher Jahan et al. prepared thin films of CZTS of different thicknesses on glass bases by utilizing the spin coating method. The optical measurement results of the prepared films showed that the energy gap is about (1.7 eV). The results of the (SEM) showed that the prepared films possess is good homogeneity through the uniform distribution of granular agglomerates [17].
- In 2019, the researcher Khodair and others, examined the impact of temperature and thickness on the optical and structural properties of (CZTS) film prepared on glass substrates by (chemical pyrolysis) method at different temperatures (300, 350 and 400 °C) and thickness (140, 425 and 530 nm). The X-ray diffraction results show that the produced films were discovered to have a tetragonal polycrystalline structure, with a dominant orientation 112. The maximum crystal size ranges from (11.71 to 15.47 nm) at a temperature of 350 °C and a thickness of 530 nm. The results of the optical measurements showed that the transmittance increases with increasing substrate temperature and decreases with increasing thickness. And the energy gap's value decreases with increase the temperature of the substrate and increases with the increase the thickness [18].

- In 2020, Balaji and others were able to prepare a thin film of CZTS compound by Radio Frequency Magnetron Sputtering method at a temperature of 300°C on glass substrates, and then annealed at 350°C in a hydrogen sulfide oven for 60 minutes. The CZTS films were found to be in the kesterite phase, according to the findings, and the preferred direction of growth is 112 and 220. Optical measurements showed that the energy gap is 1.477 eV. The electrical Hall Effect measurements showed that the P-type conductivity of the prepared films can be used as absorption layers in the solar cell applications [19].



2. THIN FILMS

One of the most significant disciplines of solid-state physics is thin film, that led to the advancement of semiconductor research and provided a thorough understanding of several physical features of materials. As the solid material is formed as though it were a thin film when prepared in the form of layers deposited on a solid basis by one of the physical methods or chemical or electrochemical reactions, as thin films describe a layer or several layers of atoms whose thickness does not exceed one micron [20].

Thin films are given great care for their use in several fields, as they are used in the manufacture of many components of thin electronic devices, interference filters and detectors, and are used in many optical fields, such as the manufacture of mirrors and glass panels sensitive to electromagnetic waves and are used in the manufacture of integrated electrical circuits. It is not present in other types of materials, as its infinitesimal thickness gives it a rare crystalline structure that approaches the characteristics of monocrystalline structures and may sometimes surpass it, as the composition of the material in the shape of a thin film differs from its regular structure in that the size of crystals in thin films is smaller of its normal size in the material. Thin films may also contain a much higher percentage of impurities than in the material in its natural form resulting from the preparation method. Thin films have more point defects than crystals of the natural material, especially at degrees higher than $T = 0\text{ K}$ due to the vibrational movement of the material atoms in their positions, thus causing point defects [21].

2.1. Thin Films Preparation Methods

The wide applications of thin films prompted researchers to find new preparation methods, as they witnessed great developments as a result of scientific and technological development, and they became very accurate to determine the thickness and homogeneity of the film, and that each method has its advantages and specificity to serve the purpose for which it was used. The choice of the method in which the thin film is prepared relies on a number of elements, the most significant

of which are the application's nature and kind, the cost of preparation and the type of materials used in the preparation [22]. Figure 2.1. shows the common thin film deposition methods [23]. These methods can be divided into two general class types:

- Chemical Methods
- Physical Methods

2.1.1. The commonly used techniques:

- Chemical spray pyrolysis.
- Sol gel.
- Chemical vapour deposition (CVD).
- Pulsed laser deposition (PLD).

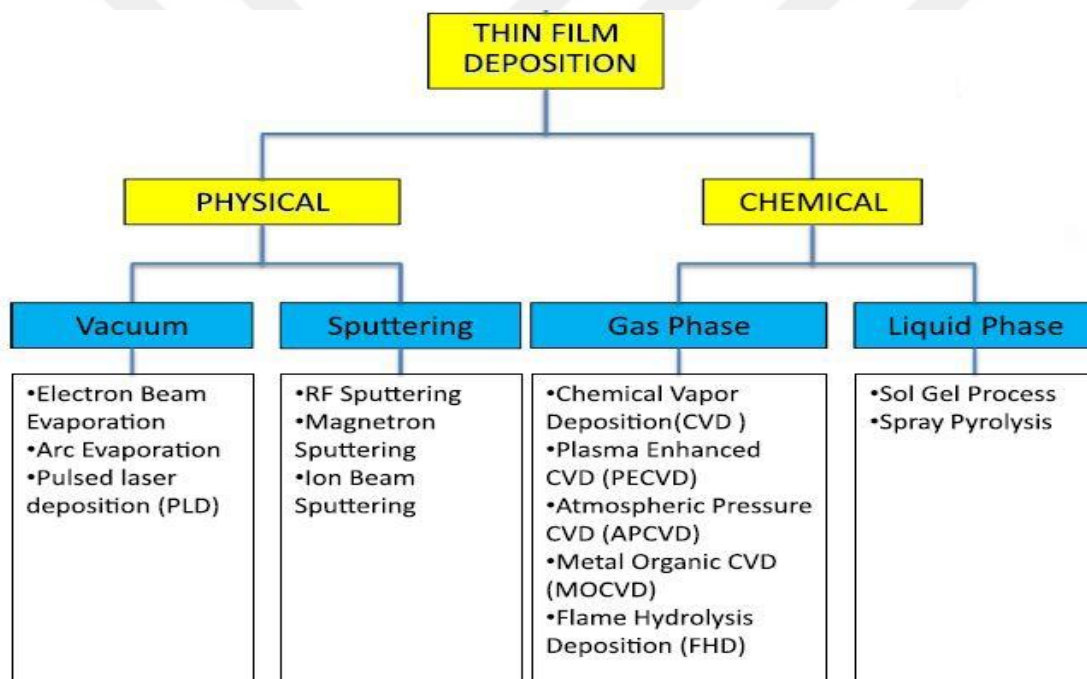


Figure 2.1. Thin films deposition methods [23].

2.2. Spray Pyrolysis Method

Spray pyrolysis is one of the most common methods among many chemical techniques, it is like vapor deposition, isn't necessary vacuum or excellent targets at any step, which is the technique's major benefit in workplace [24], [25]. Figure 2.2. show the spray pyrolysis technique [26]. The versatility of this technique lies in its many advantages:

- Controlling the spray settings allows you to simply manage the deposition rate and film thickness.
- Doping is simple since the appropriate amount of dopant may be applied with a single right amount of dopant solution.
- The thin films may be deposited at a modest substrate temperature range.
- The size and form of the substrate are unrestricted.
- Multilayer and multi-compositional thin films are both possible to make.
- The spray pyrolysis technology allows for large-area setup.

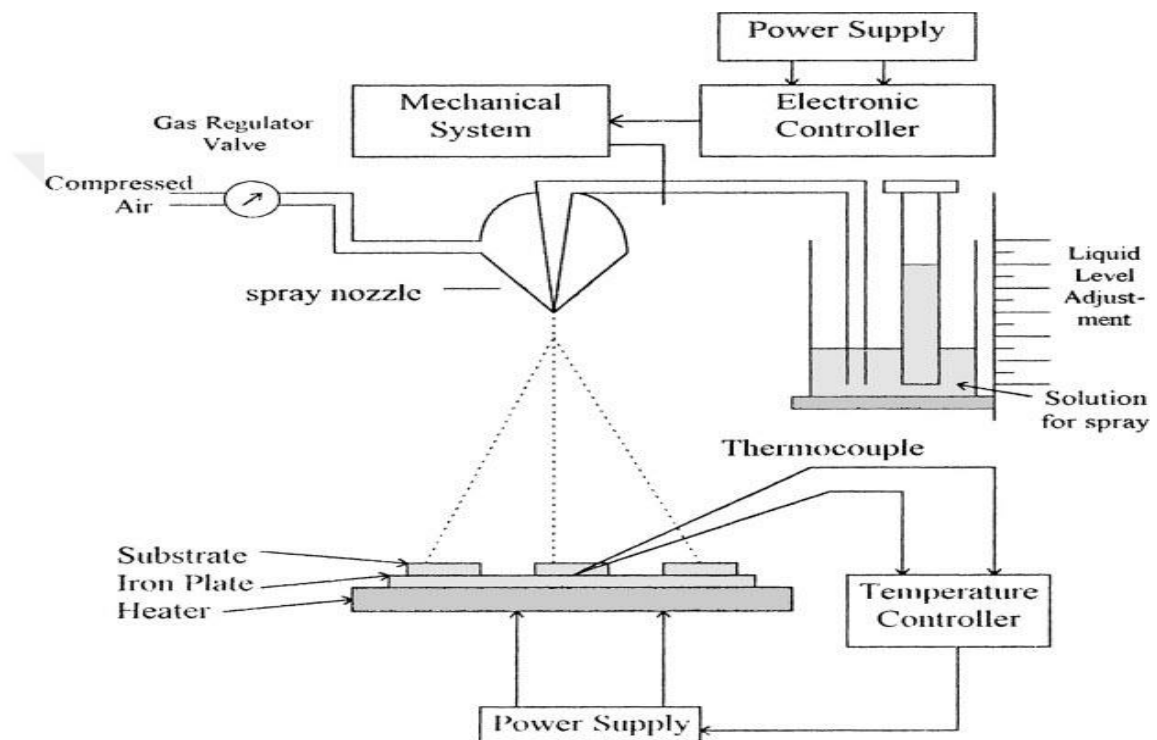


Figure 2.2. Spray pyrolysis technique [26].

The chemical spray pyrolysis method also has disadvantages [27]

- It requires a lot of effort and time to obtain homogeneous films.
- The films do not form easily, it may be deformed, or spots may form on the base.
- Use only with substances soluble in distilled water or solvents.
- Do not use in alloy or powder material directly.
- probability to unformed the substance due to a difference in the chemical reaction.

2.3. Spray Pyrolysis Components

Spray pyrolysis is made up mostly of Spray nozzle, Rotator, Solution pump, Gas flow meter, Heater, Metallic chamber etc. [28]

- Spray nozzle: The shape of the spray nozzle determines the spray pattern, droplet size, and spray rate. It is divided into two sections (Solution tube and Carrier gas tube). In this study N₂ gas is employed as a carrier gas, The system begins by injecting high-pressure N₂ into the carrier gas tube, while simultaneously pushing solution through the solution pump to the nozzle's end.
- Rotator: The nozzle was oscillated horizontally across the substrates using the make control as a rotor, its fluid motion assists in maintaining a steady temperature for uniform film deposition.
- Solution pump: The rate of spraying at a constant N₂ gas pressure is determined by the pressure produced. The spray rate changes as the assembly height changes.
- Gas flow meter: The air pressure is subject to a mechanical valve and the air pressure variance is subject to the flow meter.
- Heater: During the spraying operation, it may adjust the temperature and keep the substrate at the desired temperature.
- Metallic chamber: To prevent being exposed to the harmful fumes that emerge during the thermal degradation of the components, the system is housed in an airtight metallic chamber of 1 m³. To keep the environment safe, the chamber is equipped with an exhaust system.

2.4. Thin Film Formation Mechanism

The structure of thin films is characterized by a high degree of complexity with compare to the bulk materials. Either it was monocrystalline or polycrystalline, because it is very small granular sizes materials, thus it will possess areas of irregularity, density and defects are much larger than in bulk materials. On top of the factors mentioned above there are many other factors that determine the regularity and crystalline structure of the films, such as the size of the drop, the density of distribution (drops per unit area), gas pressure, decomposition device, and nozzle

diameter. In general, all these factors are affecting directly to the homogeneity of the film and its structure, which is reflected on the electrical and optical properties [29].

2.4.1. Main steps of the film's preparation process

The main steps of the film preparation are:

1. Production of atoms, molecules or ions for the decomposition solution of the film material.
2. Its transfer to the prepared substrate through a carrier medium (such as air).
3. Deposition of solutions on the substrate.

The process of film growth begins with the nucleation stage. Nucleation is formed when atoms molecules or ions move to the deposer substrate. The nuclei attached to the substrate are characterized by their small size. And then the nucleus growth phase begins, as it grows in three dimensions, and the growth is parallel to the substrate, i.e., the growth is horizontal rather than vertical due to the superficial spread of atoms [30].

After the growth stage, the nuclei are connected to one another, forming islands. The factors that affect the formation of islands are, the temperature of the substrate and the availability of nucleation sites on the surface.

As the islands continue to coalesce, they begin to change their shape, extend and elongate linked and form narrow areas near the area of attachment to each other, this area is long and irregular, known as ducts. Continuing with the deposition process, nuclei, islands, and ducts are produced, and they rapidly fuse on contact with the walls of the channels, forming bridges, leaving cavities within the film. During the continuation of the formation of secondary islands touching the edges of the vacuoles and merging with the main film, Figure 2.3. shows the thin films formation steps [31].

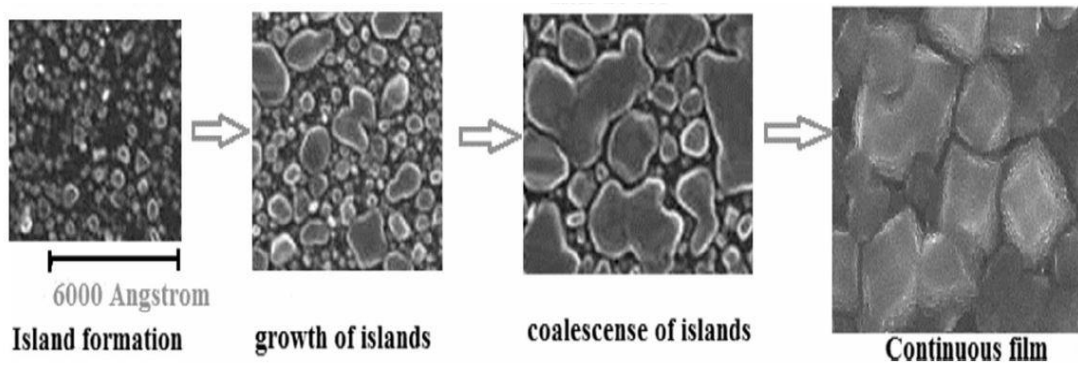


Figure 2.3. Thin films formation steps [31].

Thin-films formation by the method of chemical pyrolysis depends on the collision of droplets with the substrate and the evaporation of the solution. Chemical pyrolysis of the raw materials is happened on the substrate's surface. The chemical pyrolysis of the materials and the atomization of the droplets must be controlled to obtain the required droplet size. It should be noted that the failure to obtain equal sizes of droplets is reflected in the thermal behavior that depends Turn on the droplet block. As it is shown in Figure 2.4. decomposition states can be classified as A, B and C depending on the size of the droplets formed [32].

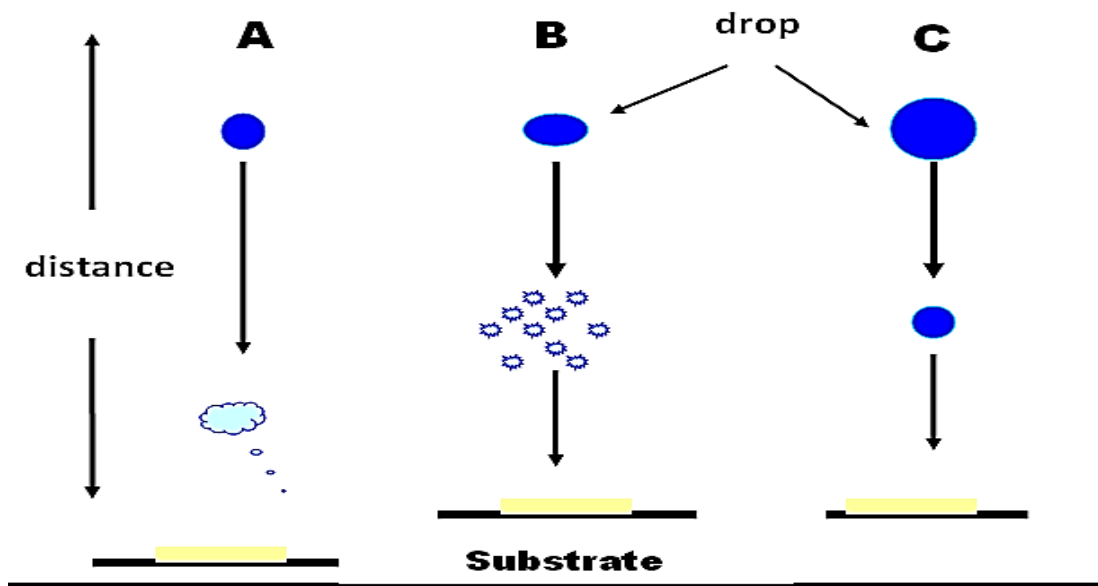


Figure 2.4. Deposition states of A, B, C with respect to droplet [32].

Case A: The drops become dry before they reach the substrate and are in the form of a powder it spread and condense in the form of fine granules on the surface of the substrate that can be removed easily due to their poor adhesion to the substrate, this situation occurs when the deposition distance is large.

Case B: It represents the perfect state of chemical pyrolysis in which the desired properties of the film are obtained. In this case, the solvent evaporates shortly before reaches the substrate and the granules reach the hot substrate in the form of steam. This enables it to gain enough heat to raise its temperature and interaction with the substrate.

Case C: If the size of the droplets is relatively large, so the heat absorbed is not sufficient to evaporate the solvent. When the drop hits the substrate, a solid precipitate is formed after the solvent evaporates. As a result of decreasing the temperature at a large rate, internal stresses occur and a heterogeneous film is formed, and thus this negatively affects the physical properties of the film.

2.5. Grain Growth

Atoms move in both directions across the grain boundary and inside crystals, and the movement of atoms across the grain boundary wall is usually balanced, which means that the number of atoms crossing the wall in one direction is equal to the number of atoms crossing the wall in the opposite direction, and when the wall is curved, there will be two areas around the arc, one concave and the other convex, the concave region is more compact with atoms than the convex region, as shown in Figure 2.5. Atoms across grain boundaries are not equal, as atoms move to concave surfaces that are more stable [33].

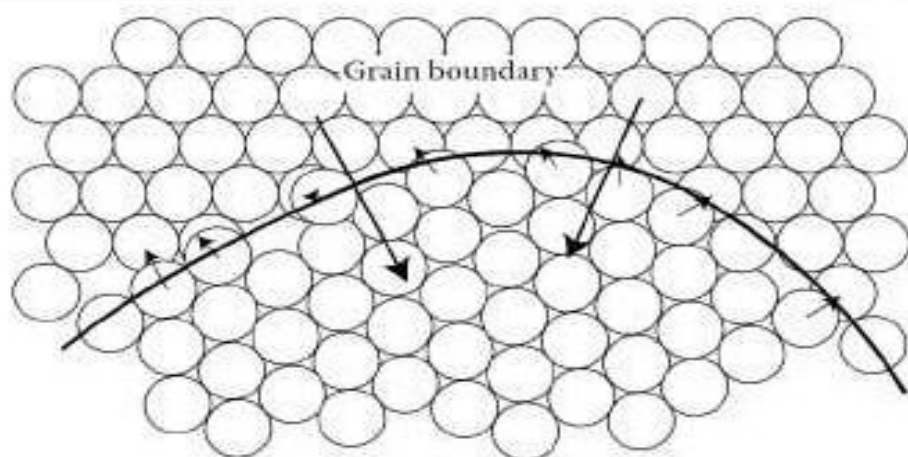


Figure 2.5. Movement of the grain boundary towards the center [33].

The growth of crystals is spontaneous growth and the reason for this is due to the tendency of materials to reduce their free energy to the least possible amount because this leads to an increase in their stability and this growth is at the expense of small crystals as large crystals are more stable from the point of view of thermodynamics [34].

2.6. Copper Zinc Tin Sulphide

The compound ($\text{Cu}_2\text{ZnSnS}_4$) is one of the most important materials because of its less expensive and has outstanding capabilities in optical applications, and it is derived mainly from (CIGS) as it replaces indium (III) with zinc (II), and gallium (III) with tin (IV), and selenium (VI) with sulfur (VI) [35]. Copper, zinc, tin, and sulfur are all present in small amounts in the earth's crust (50 ppm, 75 ppm, 2.2 ppm, and 260 ppm, respectively), and at the same time, indium is found in the earth's crust with a concentration of (0.049 ppm), which is quite low when compared to zinc and tin [36].

2.7. Crystal Structure and General Properties Of (CZTS)

CZTS is P-type semiconductor made of abundant and non-toxic elements compared to indium (In) and cadmium (Cd) [37]. Its absorption coefficient is rather high ($\alpha > 10^4 \text{ cm}^{-1}$), the energy gap between (1.45 to 1.51 eV) which is perfectly suited to the range of the solar spectrum and the applications of photovoltaic cells [38], [39]. It is mainly derived from CuInS_2 by replacing two atoms of indium with one atom of zinc and one atom of tin, this isoelectronic substitution produces a material that shares several properties with the parent material without the need to use rare and expensive elements, Figure 2.6. shows the unit cell of (CIS) [40].

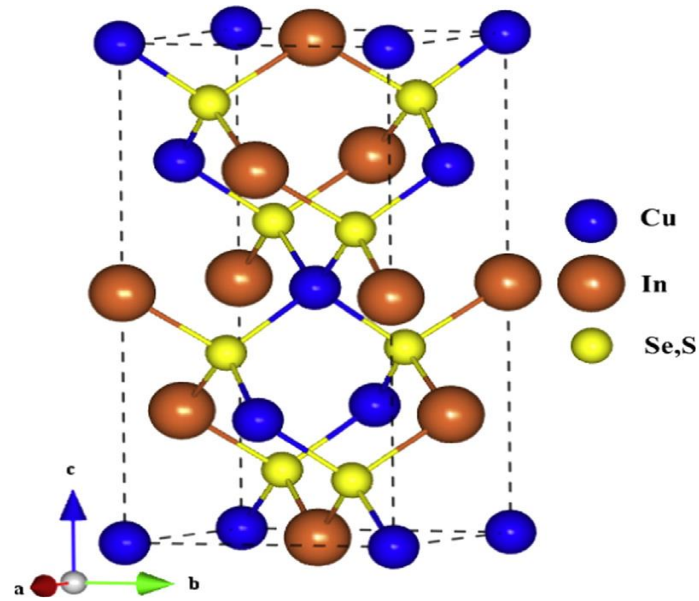


Figure 2.6. The chalcopyrite (CIS) crystal structure [40].

CZTS exists in two main crystalline structures: (Kesterite) and (Stannite) they both have a standing quadrilateral structure (Tetragonal), it consists of a closed cubic set included [41] the negative ion represented by sulfur (S) and positive ions that occupy half of the tetrahedral space, with a similar arrangement of (Zinc Blend) The structural differences are related to the positive ions in the steric layer. In (Kesterite) structure, the positive layers are arranged from CuSn, CuZn, CuSn, CuZn, where $Z = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$, respectively, while in (Stannite) structure ZnSn and Cu₂ layers are arranging respectively, and the sulfur and tin ions occupy fixed positions in the lattice with both structures. See Figure 2.7. [42].

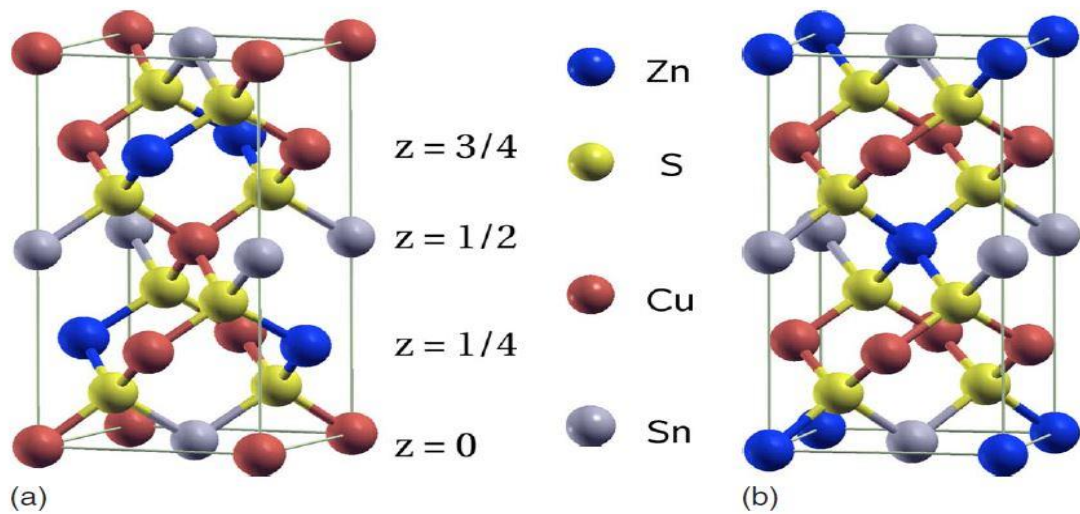


Figure 2.7. Schematic representation of (a) [Kesterite] and (b) [Stannite] structures [42].

The formation of a pure phase of (CZTS) is a challenge because of the secondary phases of the binary and ternary compounds represented by ($\text{Cu}_x\text{S}/\text{Zn}_x\text{S}/\text{Sn}_x\text{S}/\text{Cu}_x\text{SnS}_y$) that are formed during and after the growth of (CZTS) crystals that cause heterogeneity and may also contribute to the decrease in the efficiency of the solar cell. Which is usually done using X-ray diffraction (XRD), also for the (CIGS) compound. There is some of common peaks between CZTS and (Cu_2SnS_3) and (ZnS) as shown in Figure 2.8., as X-ray diffraction is often used to describe the (CZTS) films and other films [43].

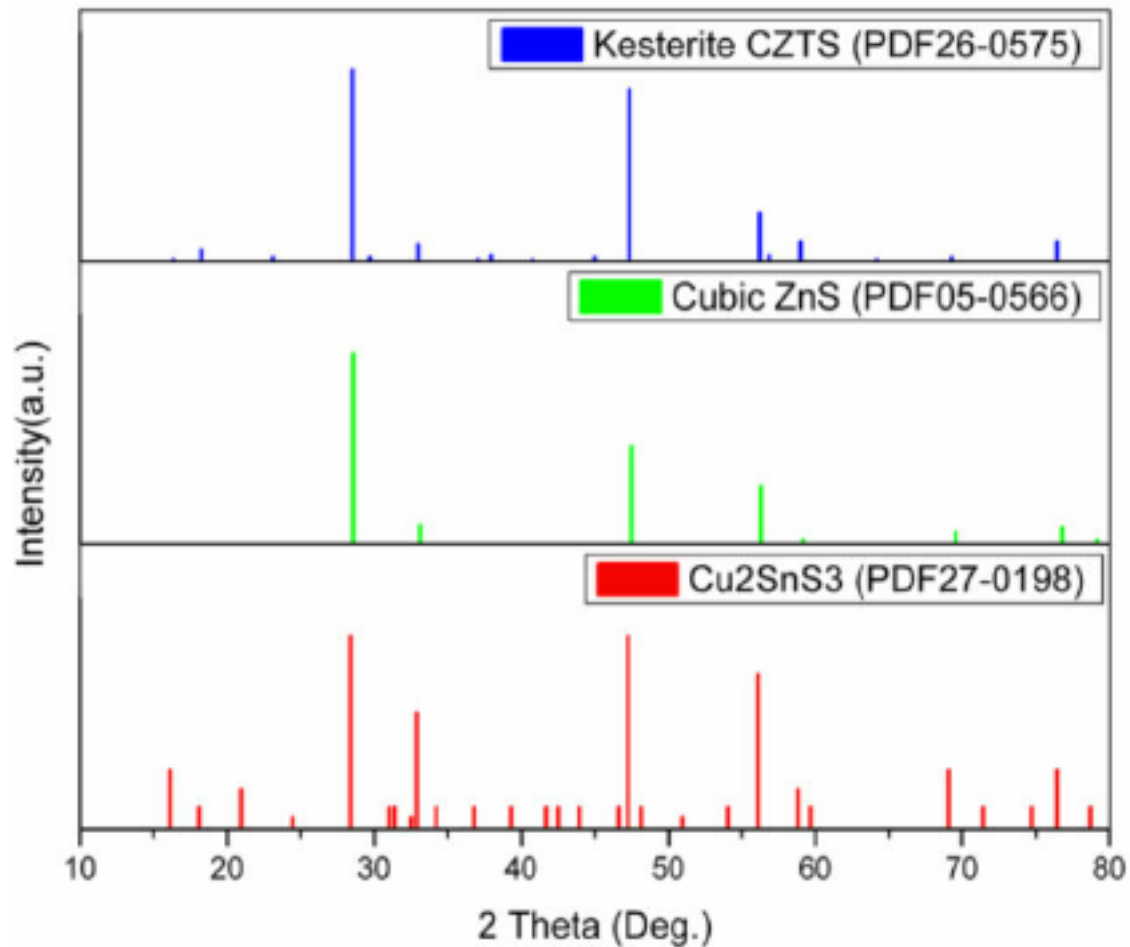


Figure 2.8. Comparison of XRD peaks of CZTS, ZnS, and Cu_2SnS_3 [43].

2.8. Interaction of Light with Semiconductor

When shining the light with its energy ($h\nu_0$) it can irritate electrons and move them to the conduction band (CB) from the valence band (VB), thus causing optical conduction. The incident photons' energy must be larger than or equal to the forbidden energy gap's value (E_g), meaning ($h\nu \geq E_g$) and when (E_g) is equal to ($h\nu_0$),

then ($\nu_0 = E_g/h$) since (ν_0) is known as the threshold frequency. But when the absorbed photon's energy is higher than the energy gap's value, the transition process will take place, and the additional energy ($h\nu - E_g$) is dissipated in the form of heat. However, if the incident photon's energy is less than the energy gap, the photon is not absorbed, but rather penetrates the semiconductor.

The ratio of light absorption inside a semiconductor and intensity of the light are directly proportional at a particular wavelength, as a result, the intensity of monochromatic light decreases exponentially while passing through a crystal, and this is expressed by the Lambertian relation [44].

$$I_t = I_0 e^{-\alpha t} \quad (2.1)$$

α : the wavelength function of the incident radiation and it known as the absorption coefficient.

I_t/I_0 : The ratio of the transmitted light's intensity to the incident light's intensity, as it is proportional to thickness of the material (t).



3. (CZTS) CHARACTERIZATION TECHNIQUES

3.1. Intrinsic Defects and Electronic Properties of (CZTS)

The quaternary compound (CZTS) can contain several types of point defects represented by:

- Interstitial defects “ $\text{Cu}_i/\text{Zn}_i/\text{Sn}_i$ ”.
- vacuums which include “ $\text{V}_{\text{Cu}}/\text{V}_{\text{Zn}}/\text{V}_{\text{Sn}}/\text{V}_s$ ”.
- Substituting atoms “ $\text{Cu}_{\text{Zn}}/\text{Zn}_{\text{Cu}}/\text{Cu}_{\text{Sn}}/\text{Sn}_{\text{Cu}}/\text{Zn}_{\text{Sn}}/\text{Sn}_{\text{Zn}}$ ”.

Within the energy gap, these defects might occupy shallow or deep levels, exhibiting acceptor or donor behavior and thus affecting the optoelectronic properties for the additives. CZTS shows auto-connectivity of positive type, this behavior is due to the appearance of self-sustainable defects with low formation energy as in Figure 3.1. Vacuums of copper (V_{Cu}) are predominant and are generated in acceptor surface planes, located above the valence band, while Cu_{Zn} is produced with a higher energy level of (0.12 eV). As well as Cu_{Zn} , there are other types of defects that require a relatively low forming energy for CZTS with low copper concentration (Cu-Poor) typical for use in solar cell applications. (V_{Cu} , Zn_{Sn} , V_{Zn} , and Cu_{Sn}) are the defects in ascending order of formation energy [45].

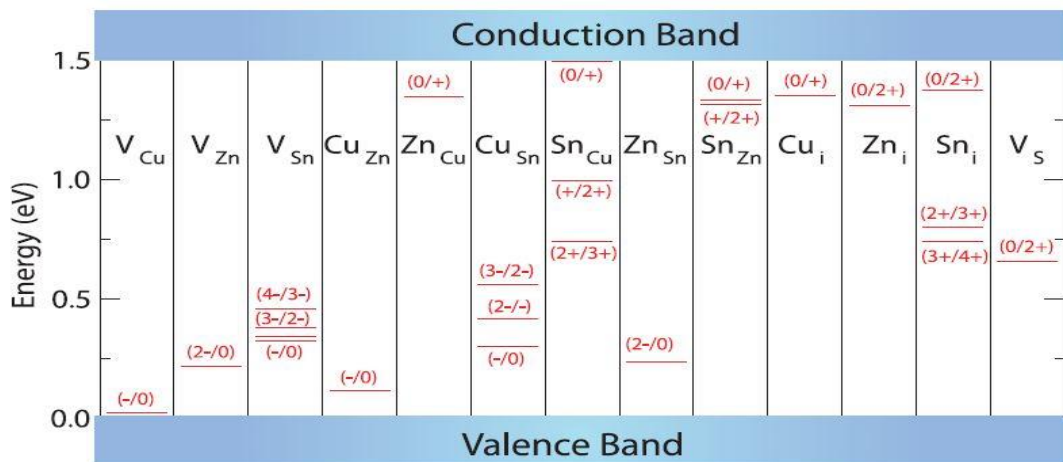


Figure 3.1. Intrinsic defect ionization levels in the bandgap of $\text{Cu}_2\text{ZnSnS}_4$ [46].

The recorded theoretical results contributed to understanding the electronic properties of CZTS compound and its relation to the actual defects of the material. The intrinsic defects contribute significantly to the performance of the semiconductor as an absorption layer, the deep levels are not suitable for photovoltaic cell applications because they generate centers for (electron-hole) pair recombination. The studies have shown that the $\text{Cu}_{\text{Sn}}^{-3}$ defect is capable of being a deep plane having energy near to the (mid-gap) and low formation energy, it is anticipated to be the focal point of the activist (electron-hole) pair reassemble in the CZTS complex.

Recent studies have also shown that $(\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}})$ defect are expected to be detrimental to the performance of photovoltaic cells, which exhibit comparatively low energy of forming and produce deep levels of donor. Accordingly, “Cu-poor” and “Zn-rich” compounds will be desirable to put an end to the appearance of destructive flaws. This might explain why CZTS with this structure has historically generated the finest solar cells [47].

3.2. Properties of Structure

3.2.1. X-ray diffraction (XRD)

It is possible to obtain certain information about the crystal structure of solids through ocular or microscopic observations of the external shape of the crystal. But if we want to obtain accurate information about the crystal structure, we must use techniques that depend on ray diffraction. One of the most popular techniques for examining materials structure and determining their crystallization or randomness is the X-ray diffraction technique. As diffraction is affected by both crystal structure and wavelength of the rays used, and one of the conditions for choosing the rays is that their wavelength be same as or close to the “lattice constant”.

X-rays are electromagnetic waves with a specific wavelength ranging from (0.1-10 Å), the samples of CZTS compound can contain associated secondary phases, and the most common of them are those that result from the exchange of sites between zinc and copper atoms, and this in turn is due to the Isoelectronic of zinc and copper in the CZTS compound [48]. When single-wavelength X-rays are irradiated with a certain range of angles on a specific material, peaks appear due to Bragg’s reflections

from parallel crystal surfaces. Figure 3.2. shows a schematic diagram of X-ray characteristic [49].

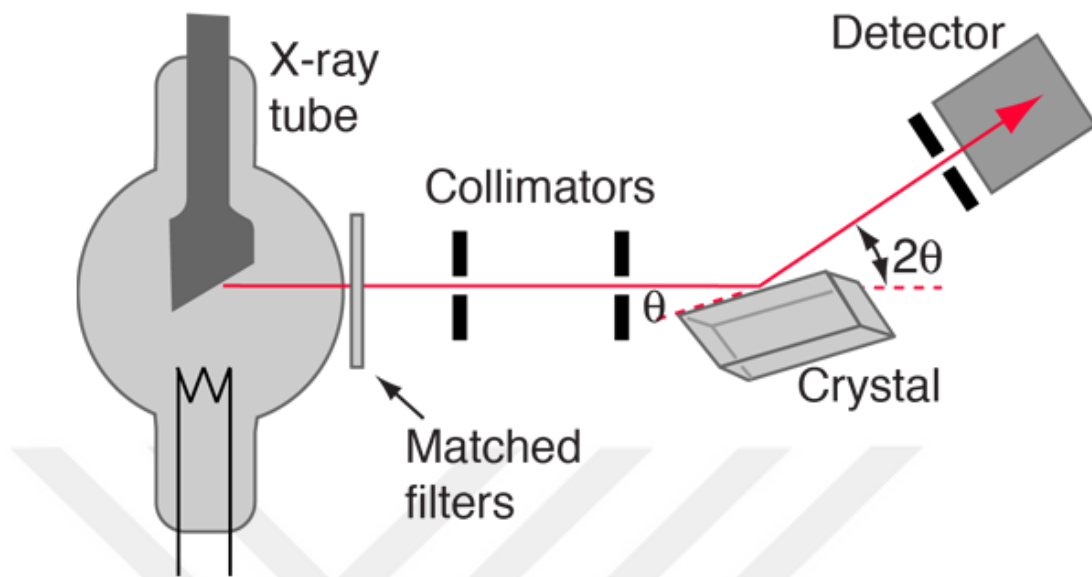


Figure 3.2. Characterization by X-ray [49].

The X-ray diffraction technique describes the crystallization or randomness of materials as follows:

1. X-ray diffraction (XRD) shows various peaks at different angles for polycrystalline materials, as in Figure 3.3a.
2. X-ray diffraction (XRD) shows sharp reflections (single sharp peak) in monocrystalline materials, as in Figure 3.3b.
3. X-ray diffraction (XRD) shows a several broad peaks in amorphous crystallized materials, as the reflection of a single crystal does not appear, Figure 3.3c. shows that.

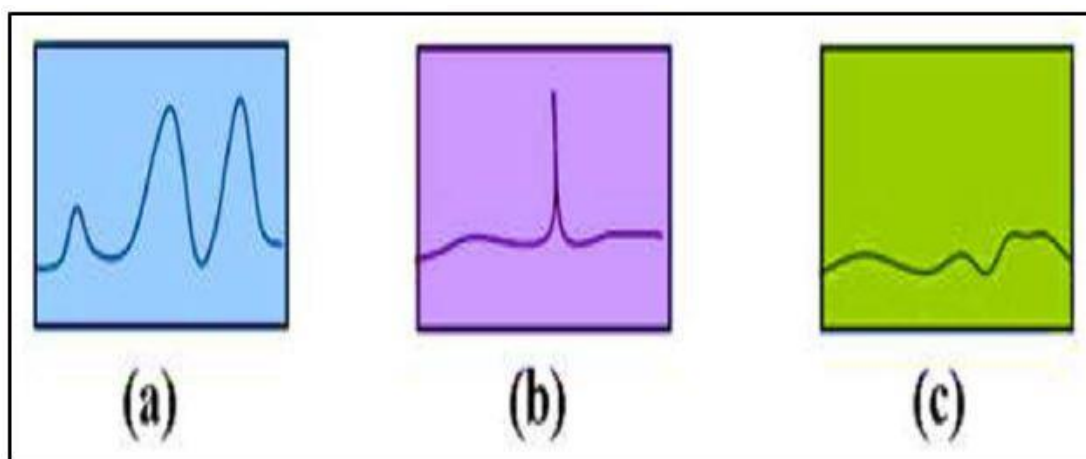


Figure 3.3. X-ray diffraction patterns [50].

3.2.2. Bragg's Law

The molecules are regularly spaced within the crystal lattice and are affected by the fall of the rays on it, as the incident rays suffer deviation from their path due to their interaction with the material, when a scattered photon or particle loses some of its kinetic energy, it is called inelastic scattering, and when there is no change in energy then it is called elastic scattering [51]. Bragg was able to deduce his law based on the fact that the path difference between incident and reflected rays is equal to the length of one wave or an integare number of wavelengths. The condition for the occurrence of the Bragg inversion is the realization of the inequality ($\lambda \leq 2d$), and the Bragg law is represented by the following equation:

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.1)$$

n : An integare representing the diffraction order.

d_{hkl} : The distance between the planes.

θ : Bragg's diffraction angle.

λ : The wavelength (nm) of the incident ray.

Figure 3.4. represents the pattern of X-ray diffraction as they fall on the surface of the crystal.

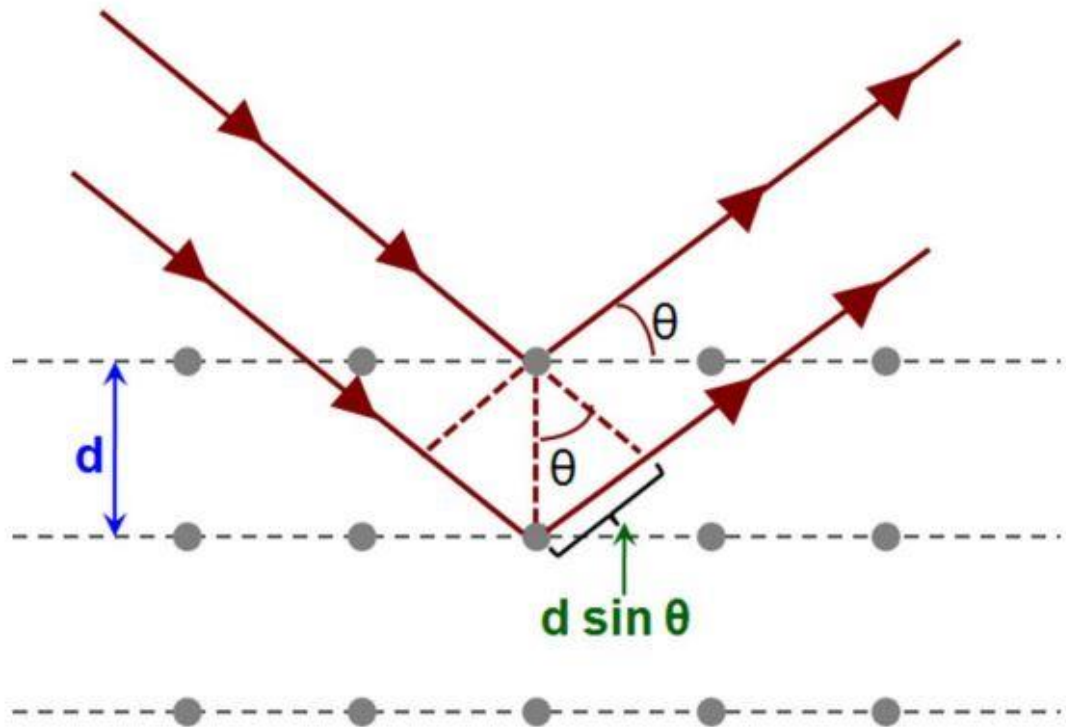


Figure 3.4. The grid represents a two-dimensional crystal lattice and a collection of imaginary planes. When the difference in the distance traveled ($2d \sin\theta$) equals an integral number of the wavelength ($n\lambda$), X-rays incident at an angle θ on the crystal cause coherent diffraction (in phase) [52].

3.3. Structure Parameters

3.3.1. Lattice constants

Lattice constants (a_o , c_o) are calculated for the tetragonal crystal structure in which it is ($a_o = b_o$, $a_o \neq c_o$) using the following equation [51]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a_o^2} + \frac{\ell^2}{c_o^2} \quad (3.2)$$

where (hkl) Miller's coefficients.

3.3.2. Crystallite size (D)

The size of crystallite (D) can be calculated by using the Scherrer's formula [53].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3.3)$$

D: Crystallite size (nm).

k : Shape factor Its value within the range (0.9 - 1) and depends on the shape of the grains.

λ : The wavelength of the X-rays falling on the target and its value is (1.54056 Å).

β : Full width at half maximum (FWHM) in radial units.

θ : Bragg's diffraction angle.

3.3.3. Texture coefficient (T_C)

The term “texture coefficient” is used to describe the prevailing trend for the crystal plane (hkl) in the polycrystalline thin films through the following equation:

$$T_C = \frac{I_{(hkl)}/I_{o(hkl)}}{N^{-1} \sum_N I_{(hkl)}/I_{o(hkl)}} \quad (3.4)$$

T_C : Texture coefficient.

N : Peaks count visible in X-ray diffraction.

$I_{(hkl)}$: Measured relative intensity of the plane (hkl).

$I_{o(hkl)}$: Intensity standard of the plane (hkl) taken from the card (ICDD).

If ($T_C > 1$), the material is monocrystalline, and the crystal growth of the planes is within this direction. But if the value of ($T_C < 1$), the material is polycrystalline with non-uniform directions. If the value of ($T_C = 1$), the material is a random composition [54].

3.3.4. Dislocation density (δ) and number of crystallites per unite area (N_0)

The intensity of the dislocations is the number of lines of dislocation that cross a unit area in that crystal. It represents the proportion of the total length of all lines of dislocation to the crystal size, and it calculated through the following relation [54]:

$$\delta = \frac{1}{D^2} \quad (3.5)$$

To calculate the number of crystals per unit area (N_0), use the following relation [54]:

$$N_0 = \frac{t}{D^3} \quad (3.6)$$

t : thickness of film.

3.4. Raman Spectroscopy

It is one of the techniques that give information of the phase of the material (crystalline, non-crystalline, mono-crystalline, and poly-crystalline). Raman name was come from the Indian physics scientist (Venkata Raman Chandrasckhra). Raman spectroscopy is used to detect vibration, rotary patterns and other vibrations in the system through an incident ray that includes the frequency of material as well as the frequency of the light.

When the photons fall on the material 99.9% of them are elastically scattered called (Rayleigh Scattering), when the incident photons frequency equal to the frequency of the scattering photons and the other photons inelastic scattering (Raman scattering) [55].

There are two types of Raman scattering: (Stokes scattering) when the photon loss energy, and (Anti-Stokes scattering) where the photon acquired the energy from the reactive material molecule with light. The relation in Raman spectroscopy is between Raman's intensity and Raman shift (cm^{-1}) and every spectrum peak is corresponding with Raman shift resulting from the falling light energy.

The (Rayleigh scattering) produces from the transitions that begin and end at the same level of oscillating energy, while (stokes scattering) is produced from the transitions starting from the ground level and ends at a higher level, and the (anti-stokes scattering) produces by the transitions from a higher energy level to a less energy level. So, the stokes transitions are more likely than the anti-stokes transitions because most molecular oscillation will be at the ground situation and as a result of stokes scattering is much stronger than anti-stokes scattering [56]. Figure 3.5. show Raman scattering and Rayleigh scattering.

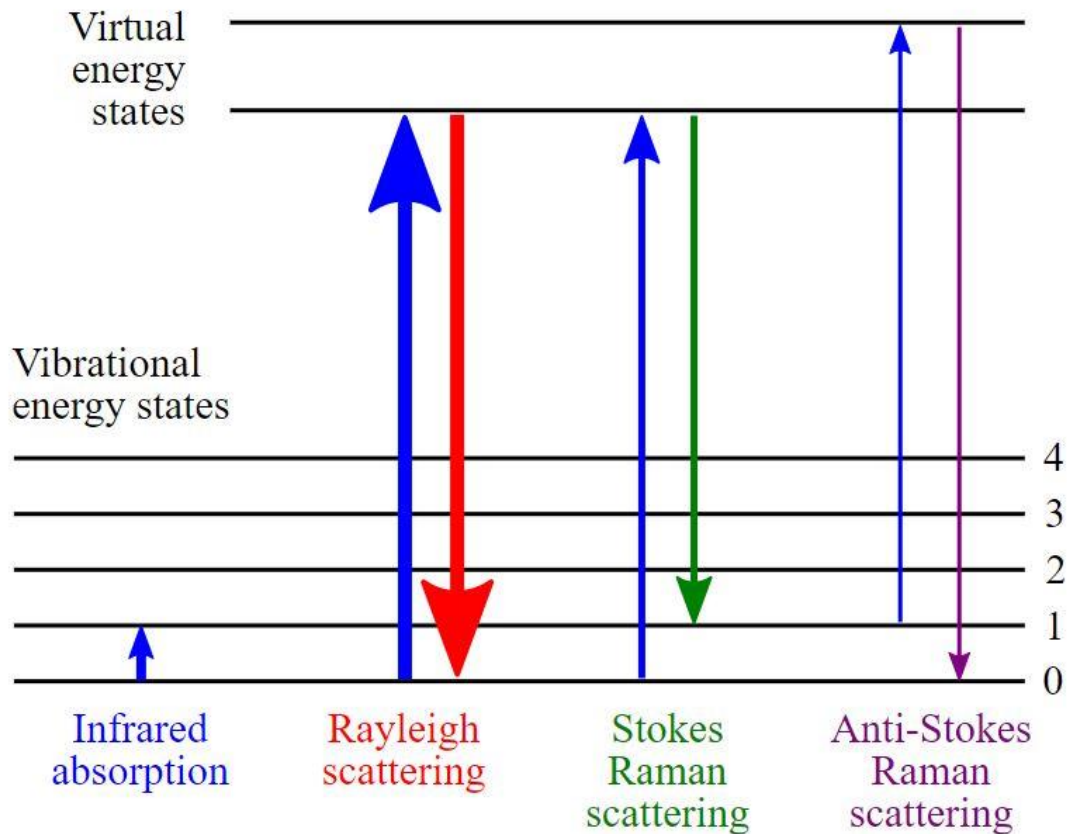


Figure 3.5. Raman scattering and Rayleigh scattering [57].

3.5. Field Emission Scanning Electron Microscopy (FESEM)

The field emission scanning electron microscope (FESEM) image the surface of the sample by scanning a point through it, using a high-energy beam of electrons. Electrons interact with atoms in the sample and produce various signals that contain information about surface topography, surface composition, and other properties such as electrical conductivity. There are two types of emission sources: the emitter by the thermal ionization method and the emitter by the field method. Emitter type is the main difference between a scanning electron microscope (SEM) and the field emitting scanning electron microscope (FESEM).

The emitter uses an electric current to heat the filament by thermal ionization, and the two most common materials used in the manufacture of the filament are tungsten (w) and lanthanum hexaboride (LaB6). When the heat is sufficient to overcome the work function of the filament material, the scanning electron escapes from the material. Thermal sources have a relatively low brightness, the evaporation of the cathode material and the thermal drift during the operation process made the (Field

Emission) method one of the ways to generate electrons to avoid these problems and obtain images with more accurate details. The field emission source (FES) is also called the cold cathode field emitter, as the filament does not heat up.

Electronic emission is achieved by placing the filament in a graded field of high electrical potential. The field emitting source is usually a tungsten wire.

Field emission sources are well combined with scanning electron microscopes (SEM) whose development has been supported by developments in secondary electron detection technology. Where the acceleration potential between the cathode and anode is within (0.5 – 30 kv), the device also requires a high air discharge of up to ($\sim 10^{-6}$ Pa) in the microscope column [58].

3.6. Optical Properties

Studying the optical properties of semiconductors provides us with much structure information of energy bands, electronic transitions type, and describes the characteristic properties that determine the interaction of light with material. When light falls on a material surface three processes may occur, these processes are absorption, reflection and transmission [59].

The details of the basic optical properties of materials lie inside the electromagnetic spectrum's visible part and are possible in the (UV and IR) regions. The total intensity of all cases of the incident ray hitting the surface (I_0) represents the sum of the intensity of absorption (I_A), reflectivity (I_R) and transmittance (I_T), as in the following equation [60]:

$$I_0 = I_A + I_R + I_T \quad (3.7)$$

Intensity can be defined as the photons number that striking a surface per unit area and time. If equation (3.7) is divided by the intensity of the incident ray, we will get the following form of the equation:

$$A + R + T = 1 \quad (3.8)$$

A : absorption, R : reflectivity, and T : transmittance.

It is impossible to have high absorbance, reflectivity and transmittance at the same time in the same material.

3.6.1. Fundamental absorption edge

The amount of rapid increase in the absorption rate when the energy gap is roughly same as absorbed radiation energy is represented by the “fundamental absorption edge”. It denotes the smallest energy difference between the valence band’s highest point and the conduction band’s lowest point in crystalline materials. The fundamental absorption edge in monocrystalline semiconductors is sharper than in polycrystalline semiconductors. The following absorption regions are divided into three regions, as shown in Figure 3.6., which shows the relationship between the energy of photon ($h\nu$) and absorption coefficient (α) [61].

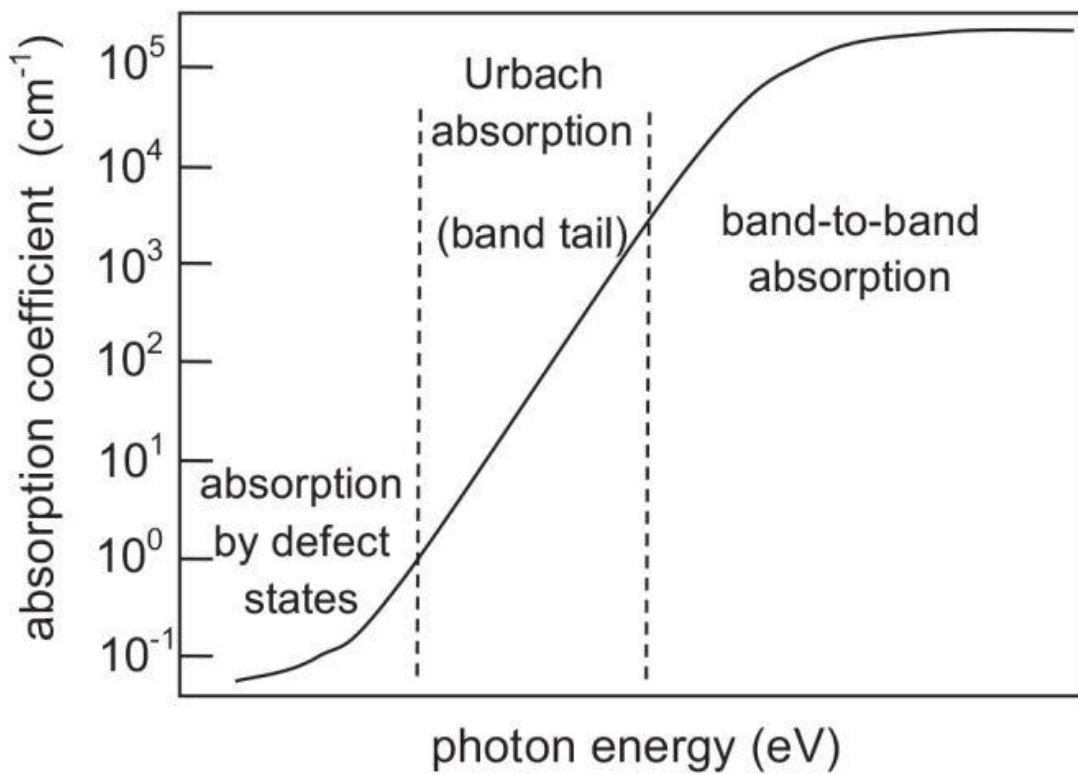


Figure 3.6. Absorption regions [61].

3.6.1.1. High absorption region

This region arises as a result of transitions between the extended valence band levels (V.B.) to the extended conduction band levels (C.B.), through it, the forbidden optical energy gap may could be identified, and the absorption coefficient (α) in this region is expressed by the following relation:

$$\alpha h\nu = P(h\nu - E_g)^r \quad (3.9)$$

P : a constant that is determined by the substance's nature.

$h\nu$: photon energy (eV).

E_g : optical energy gap.

r : the nature of the transitions determines this exponential coefficient.

3.6.1.2. Exponential absorption region

In this region the absorption coefficient (α) is within range ($1 < \alpha < 10^4 \text{ cm}^{-1}$) as shown in the Figure 3.6. Electronic transitions occur in this region between the local levels at the valence band's top to the conduction band's extended levels [62]. The edge of absorption increases exponentially, due to a progressive rise of a little electron volts in absorption, the absorption coefficient (α) in this region is expressed using the Urbach relation, which is represented by the following equation [63]:

$$\alpha = \alpha_o e^{h\nu/E_u} \quad (3.10)$$

α_o : proportionality constant.

E_u : the width of the tails in the local planes of the visual gap region (Urbach tails energy) and is equal to the reciprocal of the slope arising from plotting the graph between ($h\nu$) and ($\ln \alpha$).

3.6.1.3. Low absorption region

In this region the absorption coefficient (α) is very small ($\alpha < 1 \text{ cm}^{-1}$) and the absorption is weak. Electron transitions in this region are intersected between the local levels (tails) within the energy gap. Figure 3.6. shows the low absorption region.

3.6.2. Transmittance (T)

The transmittance is the proportion between the transmitted rays intensity (I_T) from the membrane to the rays intensity that falling on it (I_o), and it is given by the following relation [64]:

$$T = \frac{I_T}{I_o} \quad (3.11)$$

The transmittance is related with absorbance according to the following relation:

$$A = \log \frac{1}{T} \quad (3.12)$$

The semiconductor material when illuminated with a beam of light, part of the incident rays will be transmitted, and this light transmittance intensity depends largely on the incident photons energy and the semiconductor material properties [65].

3.6.3. Reflectance (R)

The reflectivity (R) is given in terms of the rays intensity that reflected from the film (I_R) to the incident rays intensity (I_o), as follows [66]:

$$R = \frac{I_R}{I_o} \quad (3.13)$$

As the reflectivity of the material depends on the material's extinction coefficient and refractive index, as shown [67]:

$$R = \frac{(n_o - 1)^2 + K_o^2}{(n_o + 1)^2 + K_o^2} \quad (3.14)$$

R: reflectivity, n_o : refractive index, K_o : extinction coefficient.

3.6.4. Absorbance (A)

It is the proportion between the absorbed rays intensity (I_A) through the film and the rays intensity falling on it (I_o), which is represented by the following equation:

$$A = \frac{I_A}{I_o} \quad (3.15)$$

A: absorbance, I_A : the intensity of the absorbed rays, I_o : the intensity of the incident rays. The absorbance could be expressed by the transmittance (T) and reflectivity (R), as follows [68]:

$$A = 1 - R - T \quad (3.16)$$

3.6.5. Electronic transitions

The electrons move to the conduction band through the energy gap after the interaction of the valence band electrons with the electromagnetic radiation falling on it, and absorption appears if the energy of the absorbed photon by the electron is greater or equal the energy of the forbidden gap ($h\nu \geq E_c - E_v$), Figure 3.7. shows

the types of electronic transitions that occur in semiconductors, and they are as follows [67]:

3.6.5.1. Direct transition

The direct transition occurs when the electron is perpendicular to the wave vector space to the conduction band from the valence band and for the wave vector values ($\Delta k = 0$), where the laws of conservation energy and momentum are fulfilled.

Direct transitions can be divided into two categories [62]:

Allowed direct transition: It occurs when the electron moves from the highest position at the valence band's top to the lowest position at the conduction band's bottom.

Forbidden direct transition: It occurs when the electron travels from the regions adjacent to the valence band's top to the regions near the conduction band's bottom.

The direct transitions energy gap is calculated by the following relation:

$$\alpha h\nu = B_o(h\nu - E_g^{opt})^r \quad (3.17)$$

B_o : a constant that is determined by the substance's nature.

r : an exponential factor that determines the nature of transition, for allowed direct transition ($r = 1/2$), and for forbidden direct transition ($r = 3/2$).

3.6.5.2. Indirect transitions

Transitions in which momentum of the crystal changes when the electron is transferred through the conduction and valence bands due to the change in the momentum of the transmitted electron, because the energy location of the valence band's top is far from the energy position of the bottom of the conduction band in the wave vector space. The transition is not vertical, and the vector value of the electron before and after the transition is not equal ($\Delta k \neq 0$). Therefore, the momentum of both the electron and the photon is not conserved, and the process takes place with the help of a third particle called the phonon, which achieves the conservation of momentum for the system. The phonon, which has a special energy (E_{ph}), gives the necessary momentum to the system, and the transition process from the (V. band) to the (C. band) takes place either by emission or absorption phonon, and it is of two types:

Allowed indirect transition: The transition is not perpendicular from the highest position at the valence band's top to the lowest position at the conduction band's bottom, with the change in wave vector's value ($\Delta k \neq 0$).

Forbidden indirect transition: This transition is also not vertical, but from the points adjacent to the valence band's highest point to the conduction band's lowest point, accompanied by change in value of the wave vector. The energy gap value for this type of transition can be computed using the equation below:

$$\alpha h\nu = B_1(h\nu - E_g^{opt} \pm E_{ph})^r \quad (3.18)$$

B_1 : constant depends on the type of material.

E_{ph} : phono energy.

r : an exponential parameter that specifies the type of transition, for allowed indirect transition ($r = 2$), and for forbidden indirect transition ($r = 3$).

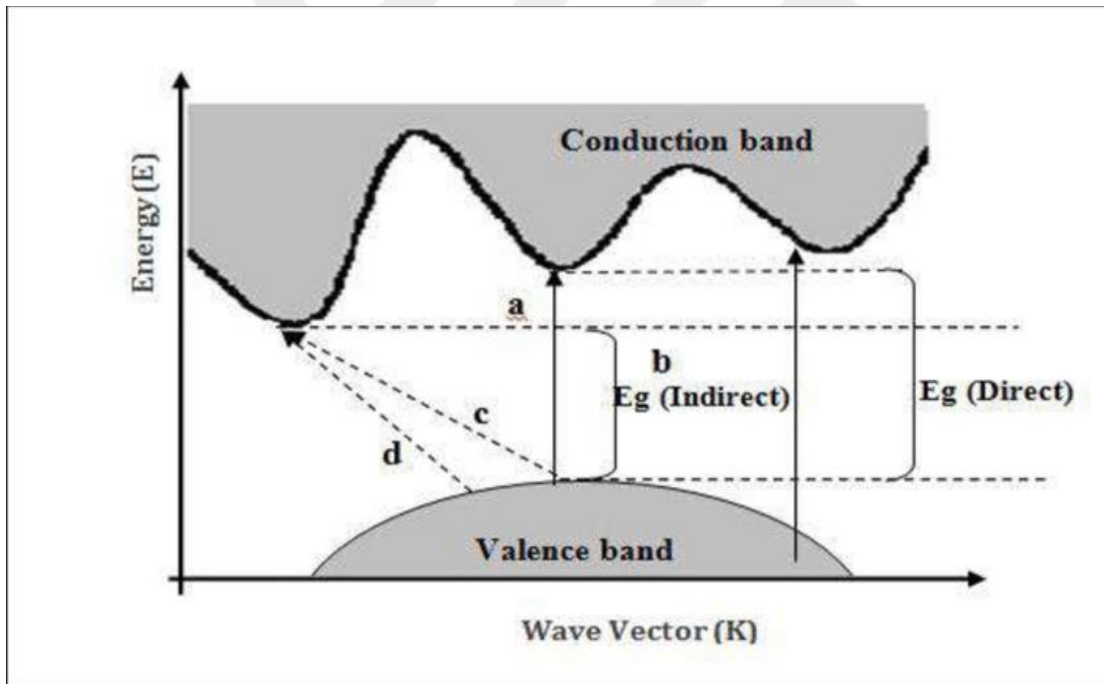


Figure 3.7. Types of electron transition, (a) allowed direct transition, (b) forbidden direct transition, (c) allowed indirect transition, (d) forbidden indirect transition [69].

3.6.6. Optical constants

3.6.6.1. Absorption coefficient (α)

The absorption coefficient is defined as the decrease in the energy of the incident radiation with respect to a unit distance in the direction of wave spread and it given by (cm^{-1}) [67]. When the energy of the incident photon is less than the value of the energy gap, the photon is transmitted, and the transmittance of films is given by the following relation [70]:

$$T = (1 - R)^2 e^{-\alpha t} \quad (3.19)$$

T : transmittance, R : reflectivity, t : thickness of film.

So, the equation (2.1) can be written as follow:

$$\ln \frac{I_t}{I_o} = -\alpha t \quad (3.20)$$

$$\alpha t = 2.303 \log \frac{I_t}{I_o} \quad (3.21)$$

Since ($\log I_t/I_o$) is the absorbance (A), we can write the equation (3.21) as follow [71]:

$$\alpha = 2.303 \frac{A}{t} \quad (3.22)$$

3.6.6.2. Refractive index (n_o)

The refractive index is defined as the ratio between the speed of an electromagnetic wave in a vacuum to its speed in a substance. The refractive index can be calculated from the following equation [72]:

$$n_o = \left[\left(\frac{1+R}{1-R} \right)^2 - (K_o^2 + 1) \right]^{1/2} + \frac{1+R}{1-R} \quad (3.23)$$

3.6.6.3. Extinction coefficient (K_o)

The extinction coefficient is the imaginary part of the complex refractive index, which is the exponential decay of the electromagnetic wave inside the material. It describes the amount of energy absorbed by the electrons of the material from the incident photons and it calculates by the following equation [73].

$$K_o = \frac{\alpha\lambda}{4\pi} \quad (3.24)$$

α : absorption coefficient, λ : wavelength of the incident light.

3.6.6.4. Dielectric constant (ϵ)

The ability of a material to polarize is known as the dielectric constant. It's the response of atoms of matter to different frequencies and with a complex behavior.

When the optical frequencies (represented by light waves) are the effect, the electronic polarization is dominant over the other types of polarizations, and the polarized charges of the medium (due to their interaction with the light) is usually described by the complex dielectric constant of the medium, and is symbolized by the symbol (ϵ) and given by the following equation [74]:

$$\epsilon = \epsilon_1 - i\epsilon_2 \quad (3.25)$$

ϵ : complex dielectric constant, ϵ_1 : real part of dielectric constant, ϵ_2 : imaginary part of dielectric constant.

Substituting the values of (ϵ) and (N), the equation becomes:

$$\epsilon_1 - i\epsilon_2 = (n_o - iK_o)^2 \quad (3.26)$$

We can write the real part and the imaginary part of the dielectric constant as follows:

$$\epsilon_1 = n_o^2 - K_o^2 \quad (3.27)$$

$$\epsilon_2 = 2n_oK_o \quad (3.28)$$

It is possible by equations 3.27 and 3.28 to calculate the dielectric constant in its real and imaginary parts for the prepared thin films.

3.7. Electrical Properties

The electrical properties of amorphous semiconductors differ from those of crystalline semiconductors due to different electronic transitions, the random material is characterized by the presence of a short-term arrangement in its composition, which leads to the emergence of local levels or tails at the conduction and valence band's kinetic edges, in addition to the presence of some cases near the middle of the energy gap [75]. While crystalline materials are characterized by the

presence of crystal grains and the effect of their limits and size on the movement of charge carriers, the grain limits of semiconducting compounds differ greatly from semiconducting elements in terms of the transfer of charge carriers due to the variation in the size of the grains. The electrical conductivity of semiconductors depends on temperature, and these materials behave opposite to that of conductive materials, as their resistance generally decreases with increasing temperature, so they are characterized by having a resistance with a negative thermal coefficient [76].

3.7.1. Hall Effect

The “Hall effect” is described as the difference in the distribution of current in a metal sheet due to a magnetic field, and this phenomenon is one of the important phenomena to know the type and density of charge carriers and the mobility of these carriers [77].

E.H.Hall used this phenomena for the first time in 1879 for the foil. Later, it became one of the methods adopted for studying the electrical properties of semiconductors. Hall effect depends on shining a magnetic field (B_z) to the semiconductor in perpendicular direction with the electric current flow direction (I_x) in it. The charge carriers tend to deviate sideways, causing the generation of a potential difference across the semiconductor in a direction vertical to both directions of the magnetic field and current, and it is called “Hall voltage” (V_H). It is accompanied by an electric field (E_H), as seen in the Figure 3.8. Hall coefficient (R_H) can be computed from the equation [78]:

$$R_H = \frac{V_H}{I_x} \frac{t}{B_z} \quad (3.29)$$

$\frac{V_H}{I_x}$: slope of the linear relation between Hall voltage and the outgoing current.

t : semiconductor thickness.

B_z : the magnitude of the applied magnetic field.

The (p-type) semiconductor has a positive hall coefficient, while the (n-type) semiconductor has a negative hall coefficient. Hall coefficient is expressed by the following relation [79]:

$$R_H = \pm \frac{\phi}{n_H e} \quad (3.30)$$

ϕ : scattering factor ($\phi \leq 1$), n_H : concentration of charge carriers.

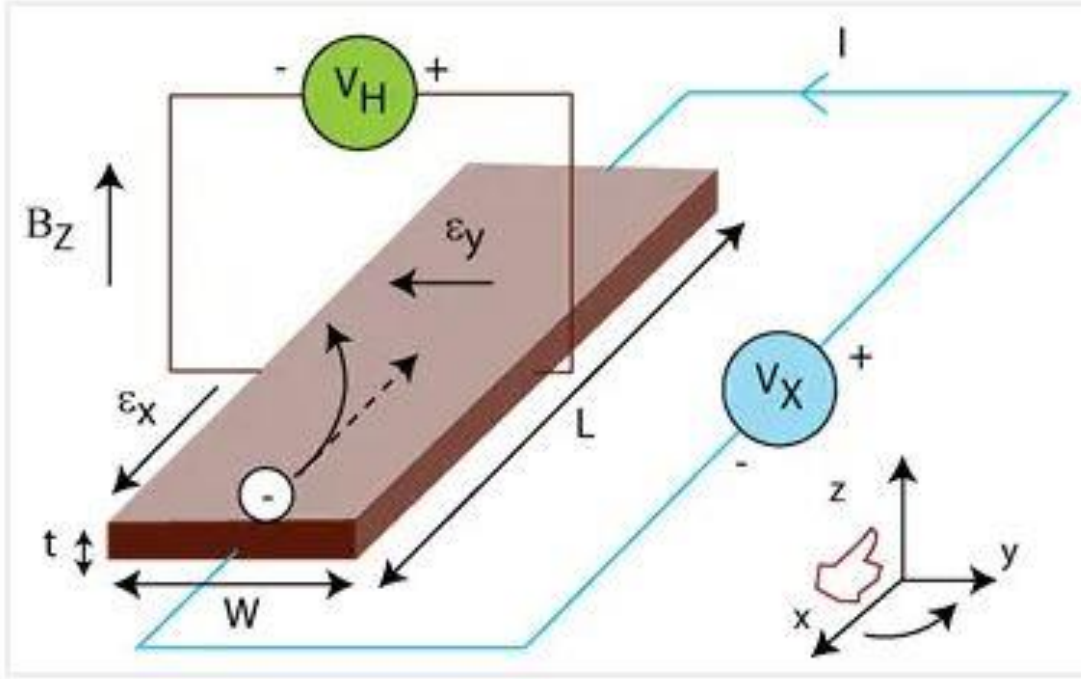


Figure 3.8. The basic configuration of the Hall phenomenon [80].

Therefore, the following equation is used to calculate the charge carrier concentration:

$$\left. \begin{aligned} n &= \frac{-1}{R_H e} & n \gg p \\ p &= \frac{1}{R_H e} & p \gg n \end{aligned} \right\} \quad (3.31)$$

From the conductivity (σ) and Hall's coefficient (R_H), Hall mobility (μ_H) can be found through the following equation:

$$\mu_H = \frac{\sigma}{n_H e} = \sigma |R_H| \quad (3.32)$$

4. EXPERIMENTAL DETAILS FOR (CZTS) FILMS

4.1. Introduction

Because the film preparation process has a substantial influence on thin film physical characteristics, synthesis thin film technologies are extremely important. In this chapter thin film fabrication of $\text{Cu}_2\text{ZnSnS}_4$, from solution preparation and substrate cleaning till film deposition is presented.

4.2. Preparation The Spray Solution

To prepare (CZTS) film, Copper chloride (CuCl_2) with molar mass (134.45g/mol), Zinc acetate dihydrate ($\text{C}_4\text{H}_{10}\text{O}_6\text{Zn}$) (219.5g/mol), Tin (II) chloride (SnCl_2) (189.6g/mol) and Thiourea ($\text{CH}_4\text{N}_2\text{S}$) (76.12g/mol) as a source of sulfur, dissolved by Ethanol ($\text{C}_2\text{H}_6\text{O}$) with pure water (H_2O) at room temperature.

The molar concentrations were used as follows, 0.2 molar of copper chloride, 0.1 molar of zinc acetate dihydrate, 0.1 molar of tin (II) chloride and 1 molar of thiourea. The concentration of sulfur ions (thiourea) is doubled more than once because a large amount of it will evaporate due to heating of the glass substrates during the final reaction of film growth, the formula $[\text{Cu}/(\text{Zn}+\text{Sn})]=1$ satisfies the equivalence formula for the compound (CZTS). The volume of the final solution was (50ml).

Weights were measured by using a sensitive balance scale, Figure 4.1a. In order to obtain the weight to be dissolved within the required standard, the following relation was used [81].

$$W_t = \frac{M \times V \times M_{wt}}{1000} \quad (4.1)$$

W_t : weight to dissolve (g).

M : molar concentration (mol/L).

V : solvent volume (ml).

M_{wt} : molecular weight of material (g/mol).

The metal salts are dissolved in its container with the volume of the solvent allocated to it by using magnetic stirrer, Figure 4.1b. Then the thiourea placed on it and mixed in one container using the magnetic mixer stirrer for 25 minutes to ensure its homogeneity and reach the state of complete dissolution. Then the solution is filtered by (0.45µm) filter, then the solution is left for an appropriate period to make sure that there are no sediments and to ensure that the materials are completely dissolved in the solvent. The final solution was transparent to yellow Figure 4.1c.

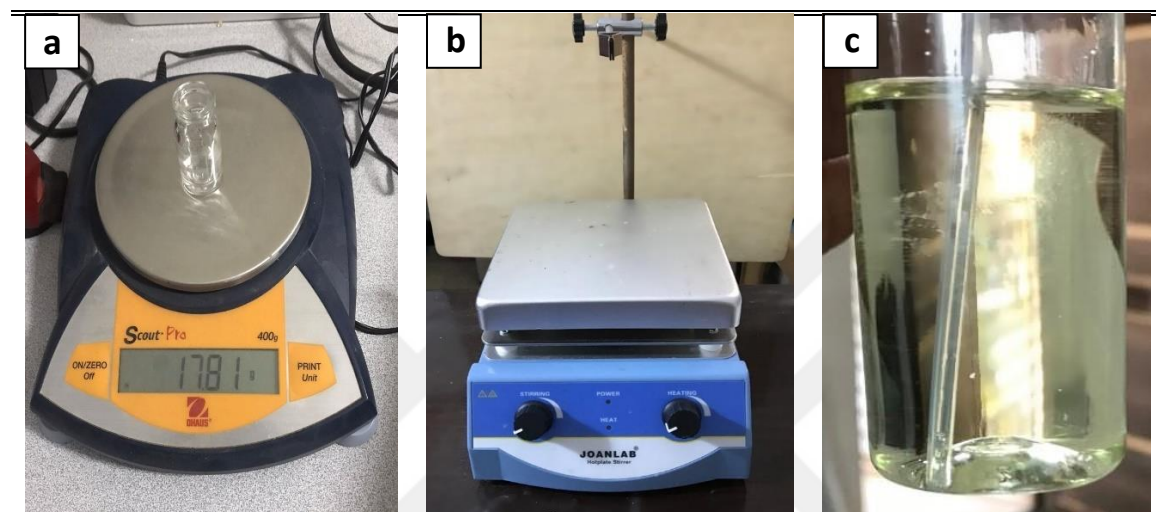


Figure 4.1. (a) sensitive balance scale, (b) magnetic stirrer, (c) CZTS solution.

4.3. Substrate's Preparation

The main task of the substrates in thin film technology is providing the mechanical support required for deposited layers, thin films can generally be deposited on a wide range of materials depending on the type of application and deposition method, such as glass, metals, ceramics, semiconductors and polymers. Glass is the most common substrate for CZTS films deposition, because it provides all the necessary specifications for the manufacture of ($\text{Cu}_2\text{ZnSnS}_4$) that using in solar cells, also it is an inexpensive and easy-to-cut and clean material.

Glass substrates have been cut with dimensions (2.5×2.5cm) and thickness (1mm). The substrates are carefully selected to ensure that they are free from scratches (associated with the cutting process) and any manufacturing defects. The substrates are washed well with distilled water to get rid of plankton of weather factors, then immersed with special forceps in acetone or ethanol of purity (99%) to ensure the removal of any greasy traces on the surface of the glass. Then picked up the

substrates by forceps and placed in a glass container containing distilled water to get rid of the acetone. Then put the bowl in the oven at 50°C for 15 minutes to dry it and make sure that it does not contain any moisture.

4.4. The Films Deposition

By using chemical spray pyrolysis, Figure 4.2. the solution was sprayed on glass substrates heated at (350°C) for (10 sec) and then left the samples for (1 min) until it returned to its original temperature, then resume spraying for several times depending on the thickness of the film to be prepared. During the spraying process, the samples move (spin) and regulate the amount of spray to obtain the best film uniformity. After spraying, the samples are left on the electric heater to allow the prepared films to complete the crystal growth process. Then it is left to cool gradually, avoiding sudden cooling that negatively affects to the films and substrates alike.

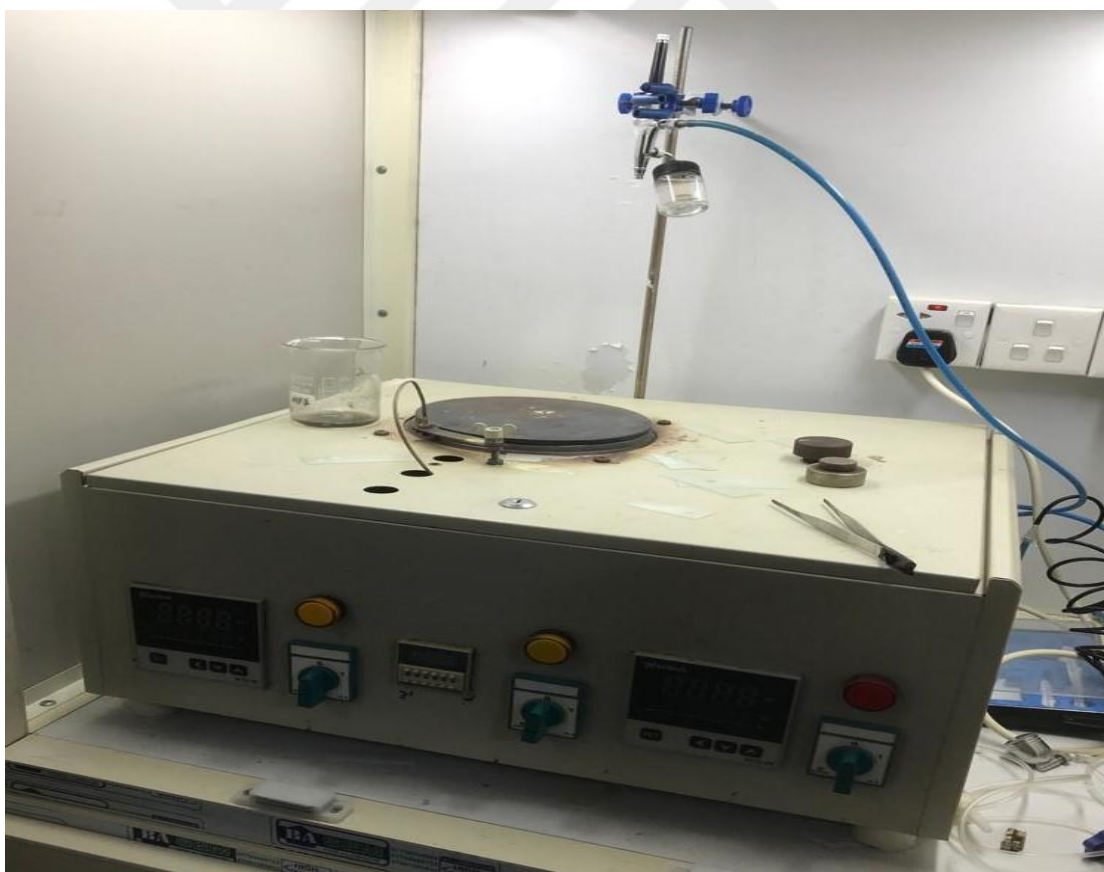


Figure 4.2. chemical spray pyrolysis device.

4.5. Structural Measurements

The results of the structural, optical and electrical measurements of (CZTS) films deposited with different thicknesses on glass substrates by using the chemical spray pyrolysis technique, will be presented and analyzed according to the theoretical principles that explain the behavior of this type of material, in order to know the effect of changing thickness on the physical properties of the formed (CZTS) films.

Table 4.1. shows the symbols of samples for current study.

Table 4.1. the symbols of samples for current study.

Sample's symbol	Thickness (μm)
S1	0.59
S2	1.25
S3	1.75
S4	2.1
S5	3.3

4.5.1. X-ray diffraction measurements

Figure 4.3. shows the results of the X-ray diffraction measurements CZTS thin films prepared at (350°C) with variable thicknesses. It is polycrystalline, with Tetragonal structure, Kesterite phase and in the dominant and preferred direction of growth (112). The sharpness of the peaks indicates the extent of crystallization of the prepared film material. The diffraction patterns showed clear and distinct peaks as shown in Table 4.2. these results almost correspond to the standard PDF card of international center for diffraction data (ICDD) with serial number (26-0575) Figure 4.4.

It is noticed from the results that increasing in film thickness causes to increases the number of peaks corresponding to the standard card with an increase in its intensity and accompanied by a decrease in full width at half maximum (FWHM), which leads to an increase in crystals size, and this confirms to increase the crystallization rate and reduction the crystal defects.

We can observe the appearance of some extra peaks in some of the films. The reason for this is due to the great susceptibility of copper and tin to formation of secondary

compounds accompanying the formation of the film. Some of them are classified among the most stable sulfur compounds, in addition to the tendency to form copper compounds due to its high presence.

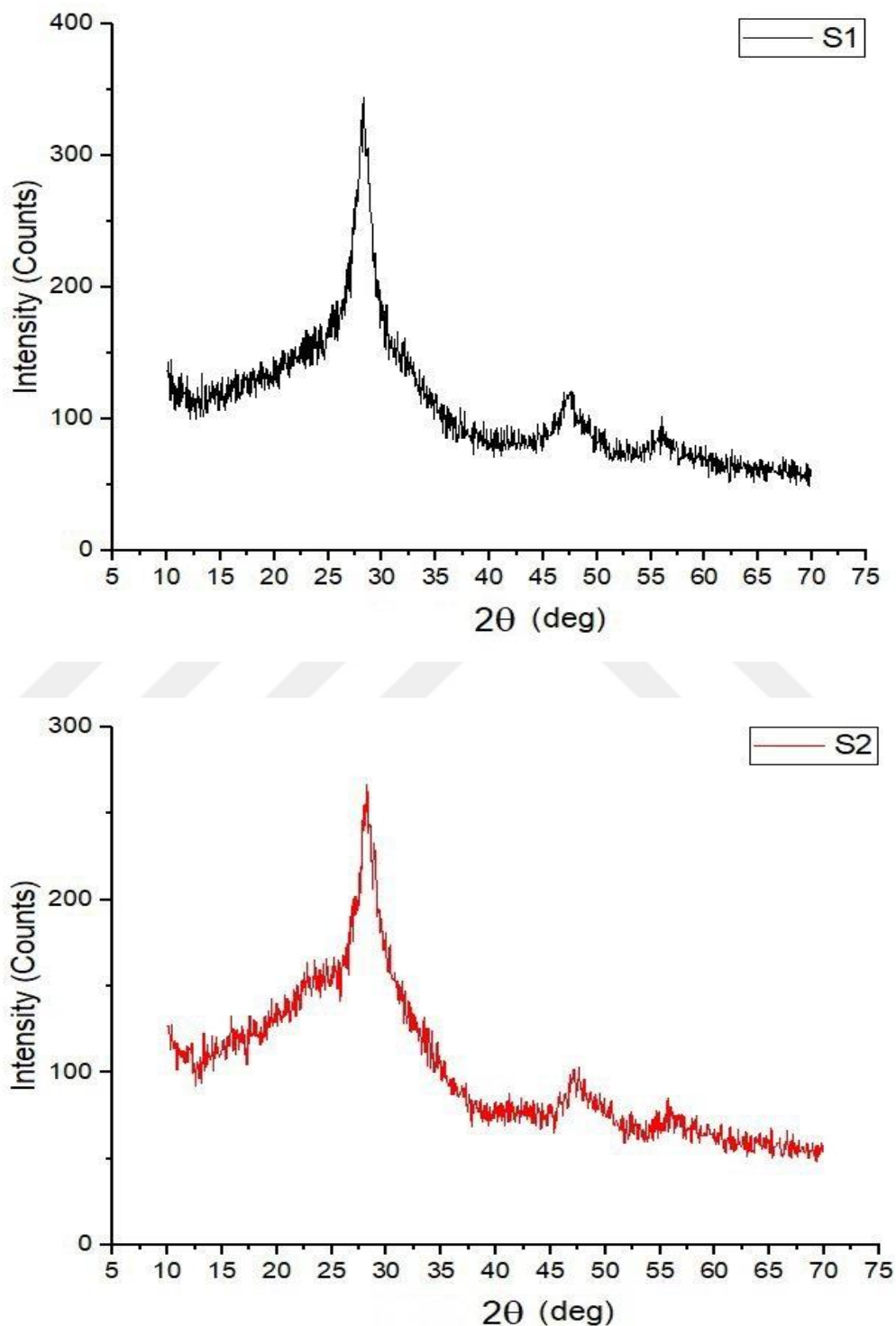


Figure 4.3. X-ray diffraction of S1, S2, S3, S4 and S5 samples.

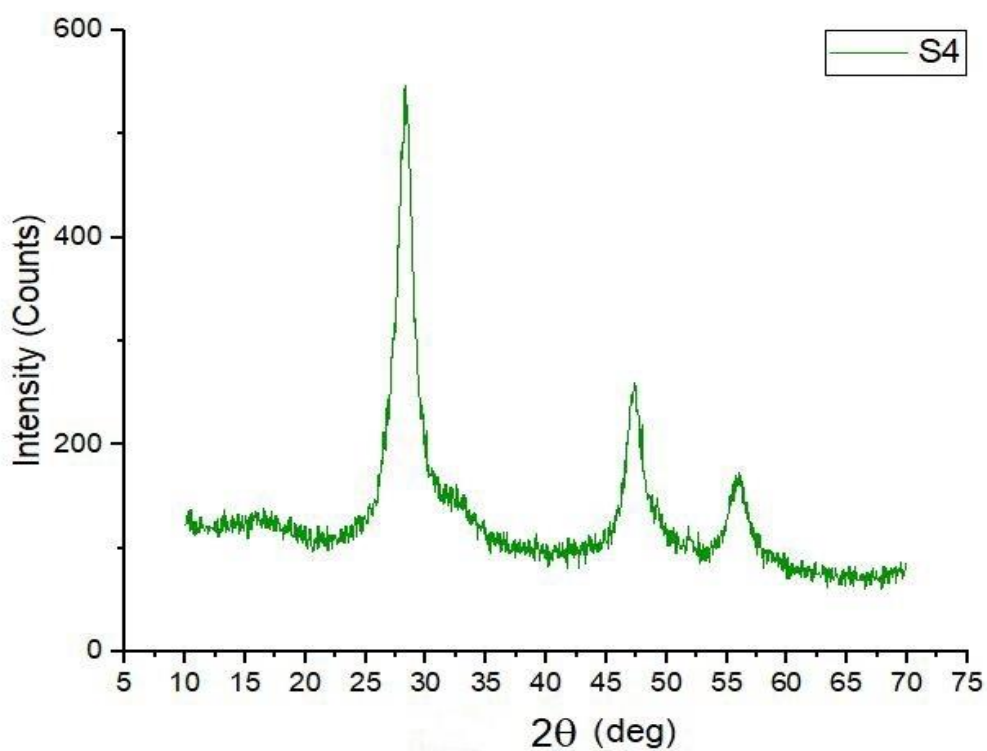
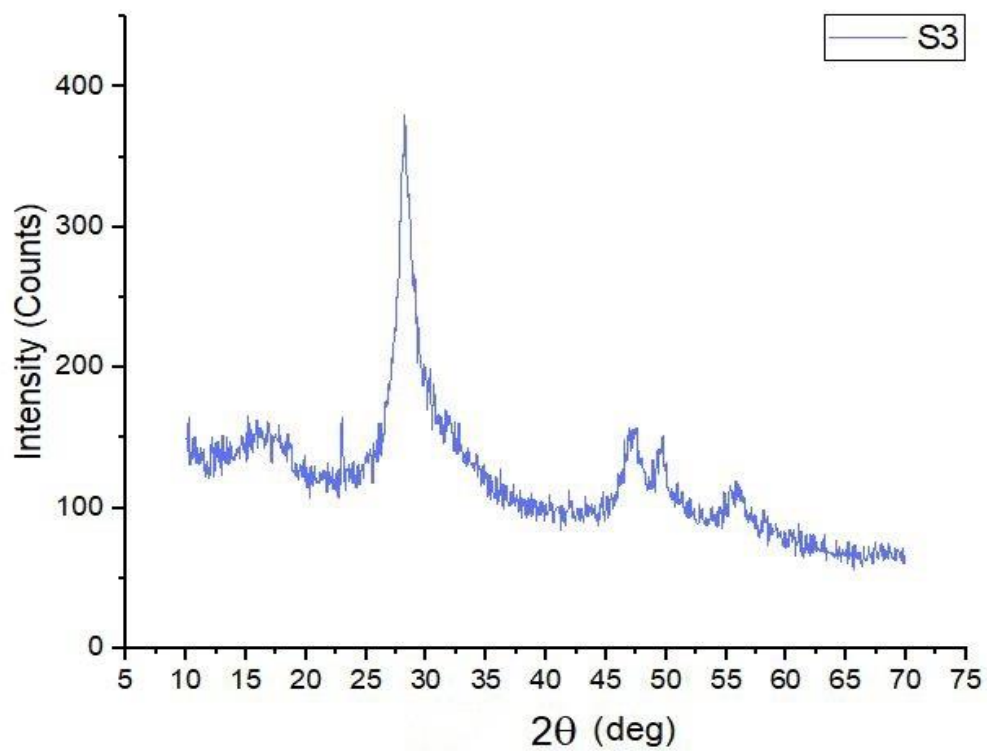


Figure 4.3. (Continued): X-ray diffraction of S1, S2, S3, S4 and S5 samples.

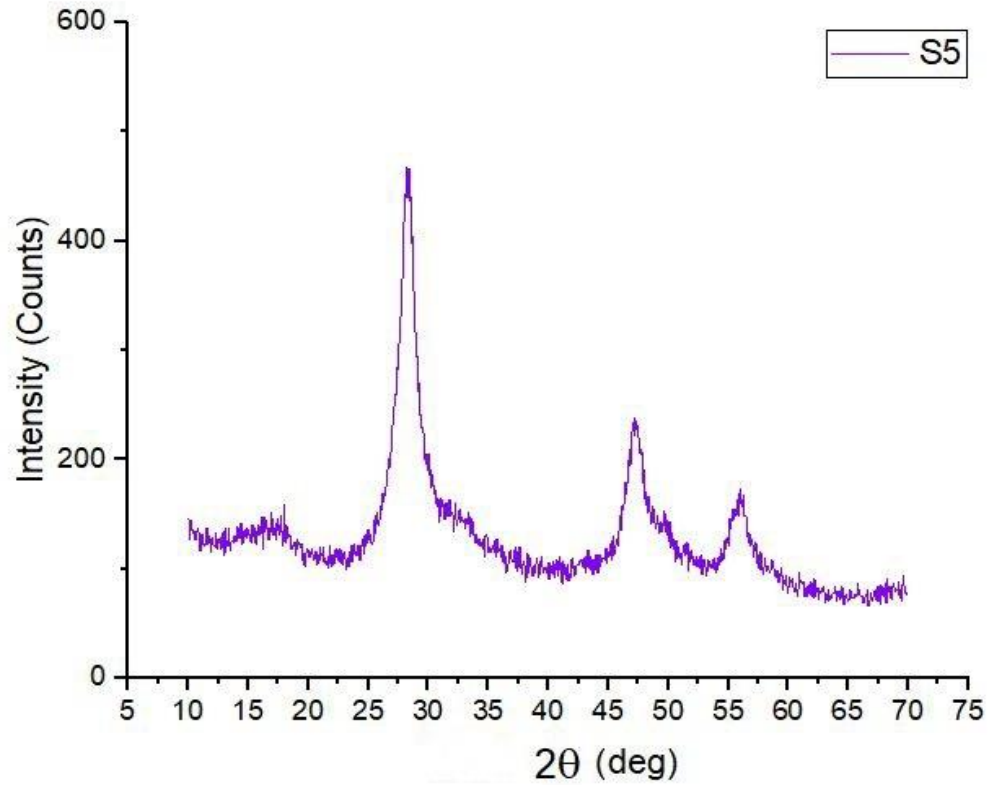


Figure 4.3. (Continued): X-ray diffraction of S1, S2, S3, S4 and S5 samples.

Table 4.2. Diffraction angles, Miller's coefficients, and values for the interlayer distances of S1, S2, S3, S4 and S5 CZTS films

Sample	2θ	hkl	$d(\text{\AA})$
S1	28.70	112	3.1080
S2	28.220	112	3.1597
S3	22.981, 28.619	110, 112	3.8668, 3.1166
S4	28.440, 47.300, 56.021	112, 220, 312	3.1358, 1.9202, 1.6402
S5	28.660, 47.240, 56.260	112, 220, 312	3.1122, 1.9225, 1.6338

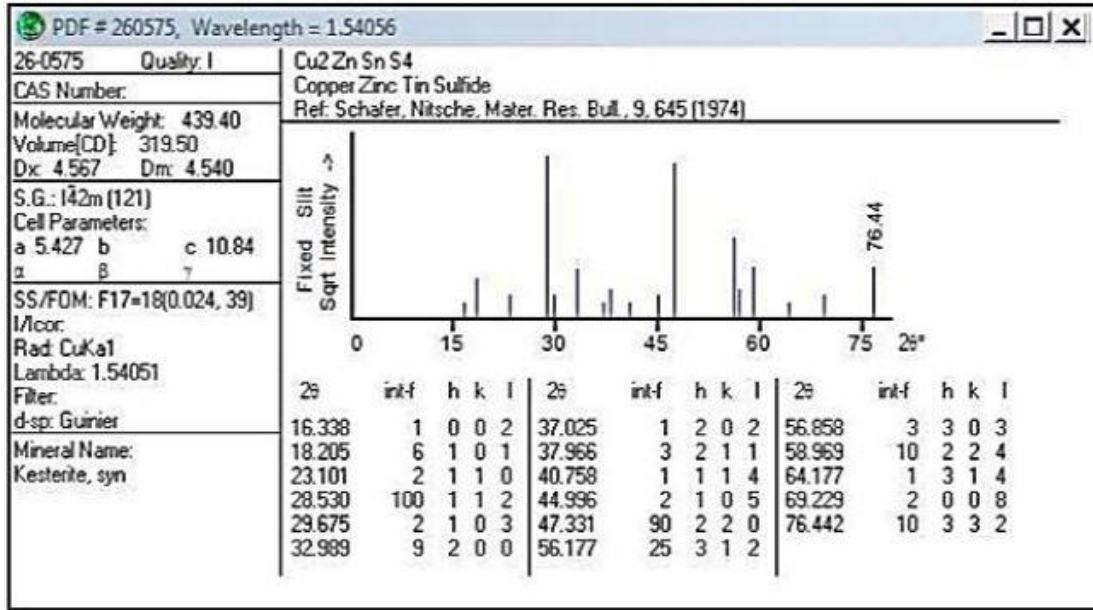


Figure 4.4. PDF card with serial number (26-0575).

4.5.1.1. Lattice constants and cell unit volume

The values of the lattice constants (a_0), (c_0) shown in Table 4.3. for the prepared CZTS thin films with tetragonal structure agree with the values of the standard PDF card (ICDD) (26-0575) for CZTS tetragonal compound. It was calculated by equation 3.2, depending on the interlayer spacing $d(\text{\AA})$ for the crystal planes calculated by equation 3.1, for the highest peak, that shown in Table 4.2.

Table 4.3. Lattice constants and cell unit volume for CZTS films.

Sample	Lattice constant ($\text{\AA}$)		$c_0/2a_0$	Unit cell volume ($\text{\AA}^3$)
	$a_0 = b_0$	c_0		
card 26-0575 (Cu ₂ ZnSnS ₄)	5.427	10.84	0.998	319.5
S3	5.46	10.56	0.97	314.81
S4	5.43	10.86	1	320.2
S5	5.43	10.62	0.98	313.12

The values of (a_0) were calculated for peaks at Miller's coefficients are (110) for the sample (S3), and (220) for the samples (S4 and S5), then the values of (c_0) were calculated, as for the samples (S1 and S2), they have only one clear peak at (112).

Note from the table that the unit cell size of the prepared thin films is smaller than the unit cell size measured for the standard PDF card, and this indicates that the unit cell suffered from pressure stress, except the unit cell size of the sample (S4) which is almost identical to the standard size.

4.5.1.2. Crystallites size

The crystalline size of the prepared thin films was calculated by using Scherrer's Formula (3.3) for the highest peak at the plane (112). The results show that increasing thickness lead to increase the crystals size and accompanied by a change in the full width at half maximum, Table 4.4.

4.5.1.3. Texture coefficient (T_c)

The values of the texture coefficient (T_c) for the prepared CZTS thin films were calculated by using equation (3.4), the results shown that the prepared CZTS thin films for (S1) at the plane (112) are less than one ($T_c < 1$), and this indicates that the prepared films are polycrystalline and there is more than one dominant orientation of growth, but for the other samples (S3, S4, and S5) ($T_c > 1$) that mean these prepared films has one dominant orientation (It has more crystallization than others). Table 4.4. shows the structural parameters of CZTS films at the dominant orientation (112).

4.5.1.4. Dislocation density (δ) and number of crystallites per unit area (N_o)

The values of the dislocation density and the number of crystals for CZTS thin films were calculated by equations 3.5 and 3.6 respectively, at the dominant and preferred growth orientation (112).

The results in Table 4.4, show that by increasing the thickness of the prepared films, the values of the dislocation density decreasing, and this indicates that the crystallization was increased.

We note that the highest value for the crystal size is match with the lowest value for the dislocation density. As for the number of crystals, it increases with the increase of thickness.

Table 4.4. crystallites size, texture coefficient, dislocation density and number of crystals for CZTS films at dominant orientation (112).

Sample	D (nm)	T_c	δ (cm ⁻²)	N_o (cm ⁻²)
S1	7.126	0.6	1.969×10^{12}	1.633×10^{14}
S2	8.420	1	1.41×10^{12}	2.097×10^{14}
S3	9.185	1.2	1.185×10^{12}	2.269×10^{14}
S4	9.222	3	1.176×10^{12}	2.689×10^{14}
S5	9.409	2.04	1.129×10^{12}	4.008×10^{14}

4.5.2. Raman spectrometer results

Raman spectroscopy was used as a suitable method for studying the appearance of compounds and studying their position depending on the phases, as small chemical changes can cause the Raman peak to be displaced.

The spectrum results showed several asymmetric peaks with shoulders. Figure 4.5. shows the drawings of the Raman spectroscopic analysis of the prepared (CZTS) films.

The main peak of all (CZTS) films appears clearly, accompanying this peak a few secondary peaks with lower intensity due to the (CZTS) component, also the height of the main peak changes with the change of thickness of the films.

The results of Raman spectroscopy are in complete agreement with the results of X-ray diffraction, and it supports the deposition of (CZTS) films in a pure form free of secondary phases with kesterite phase on glass substrates. Table 4.5. shows the results obtained through Raman spectroscopy.

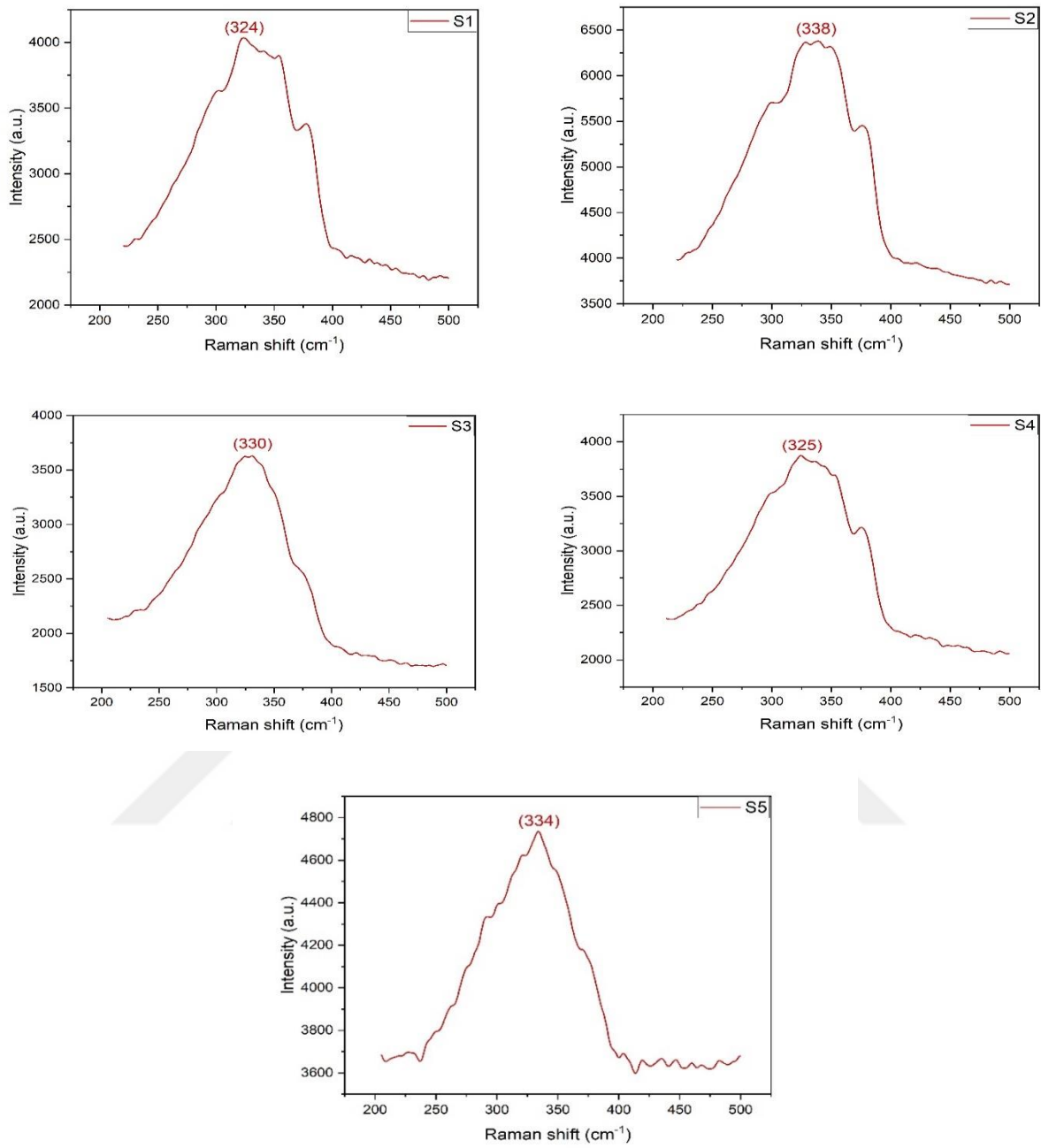


Figure 4.5. Raman spectroscopic analysis of the prepared (CZTS) films.

Table 4.5. The results obtained through Raman spectroscopy.

Sample	Center of peak (cm ⁻¹)
S1	324
S2	338
S3	330
S4	325
S5	334

4.5.3. Measurements of field emission scanning electron microscopy (FESEM)

The technique of field emission scanning electron microscopy (FESEM) was used to find out the surface nature of the prepared CZTS thin films, due to its high magnification and accuracy for the surfaces compound of materials.

Figures 4.6. show images with magnification forces for prepared CZTS thin films (S1, S2, S3, S4 and S5) sequentially.

It was found that the surface structure of the films was formed in beautiful shapes like intertwined twigs in nanoscale range, its ends have spherical, quadrilateral and other irregular shapes that vary in growth and increase in density with increase the thickness.

It is also noted that there are some voids and gaps resulting from the occurrence of secondary growth at the surface before the completion of the previous layer.

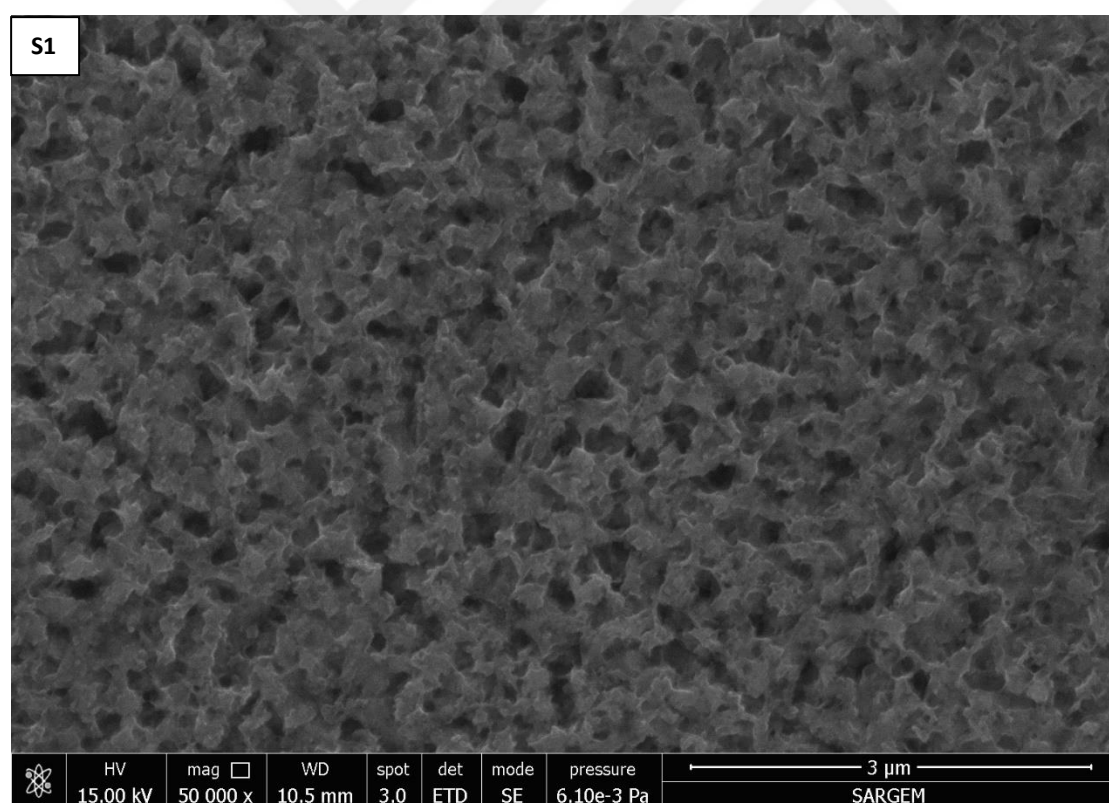


Figure 4.6. Images of (FESEM) for CZTS prepared films.

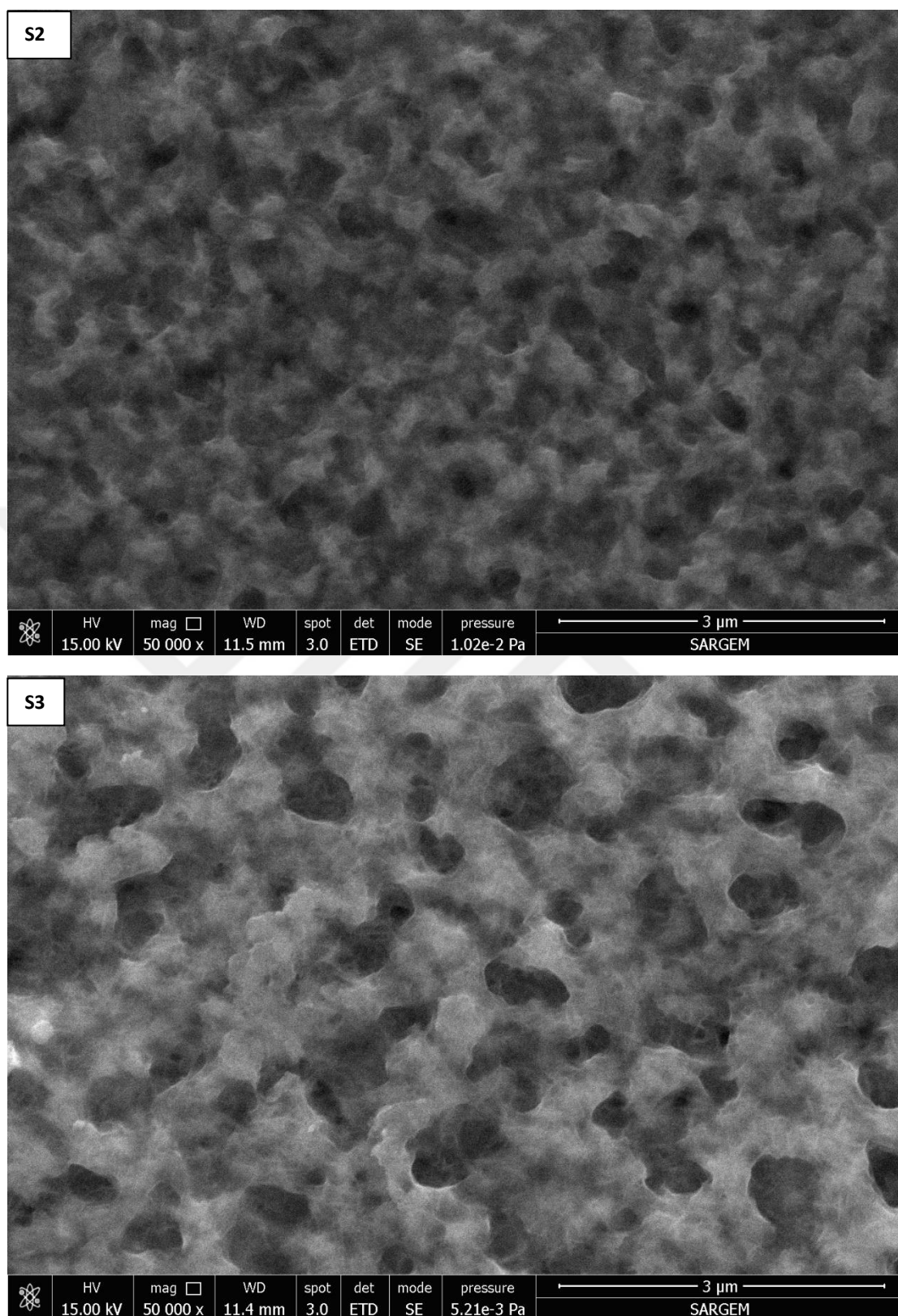


Figure 4.6. (Continued): Images of (FESEM) for CZTS prepared films.

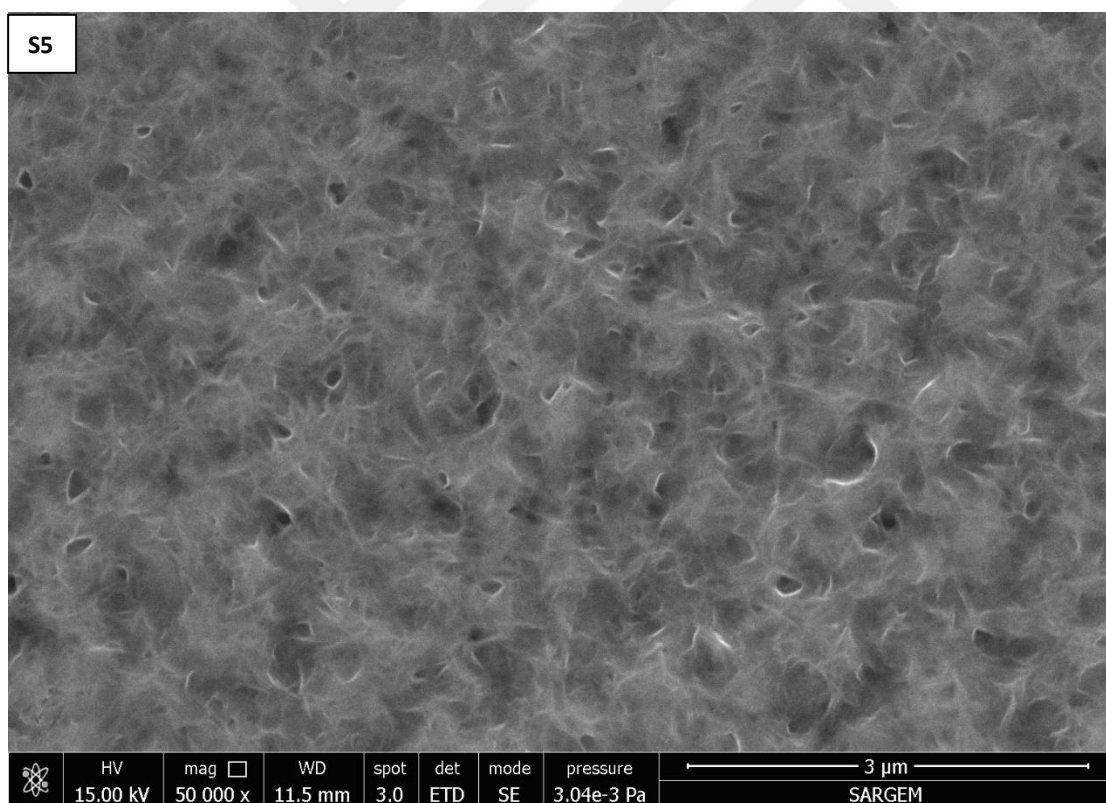
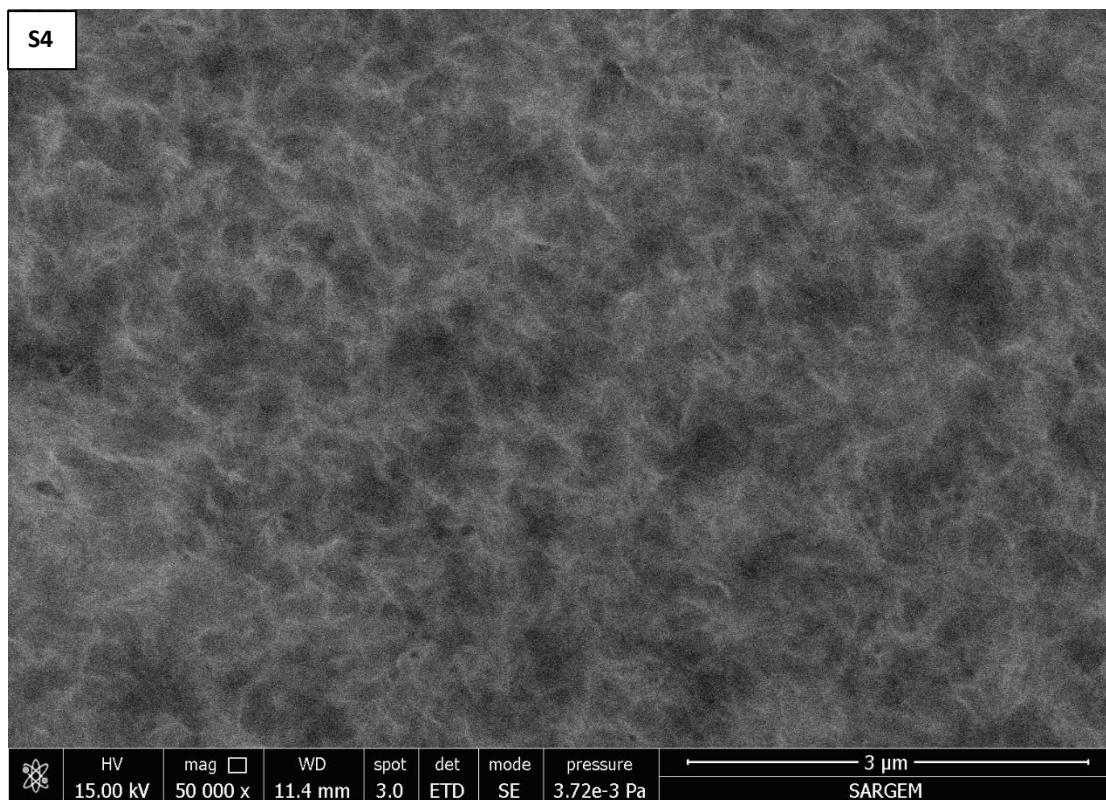


Figure 4.6. (Continued): Images of (FESEM) for CZTS prepared films.

4.6. Optical Measurements

The optical properties of prepared CZTS thin films at (350 °C) was detected by measuring the absorbance spectroscopy.

4.6.1. Absorbance

Figure 4.7. shows the absorbance of the prepared CZTS thin films at 400-800 nm range.

As the wavelength increases, the absorbance decreases, and at approximately (700 nm) the decrease is slow and almost stable for all the prepared films, due to the low energy of the incident photons and their inability to excite electrons from the valence band to the conduction band. We can also note that the relation between films thickness and absorbance is linear. As the film thickness increase the absorption increases linearly.

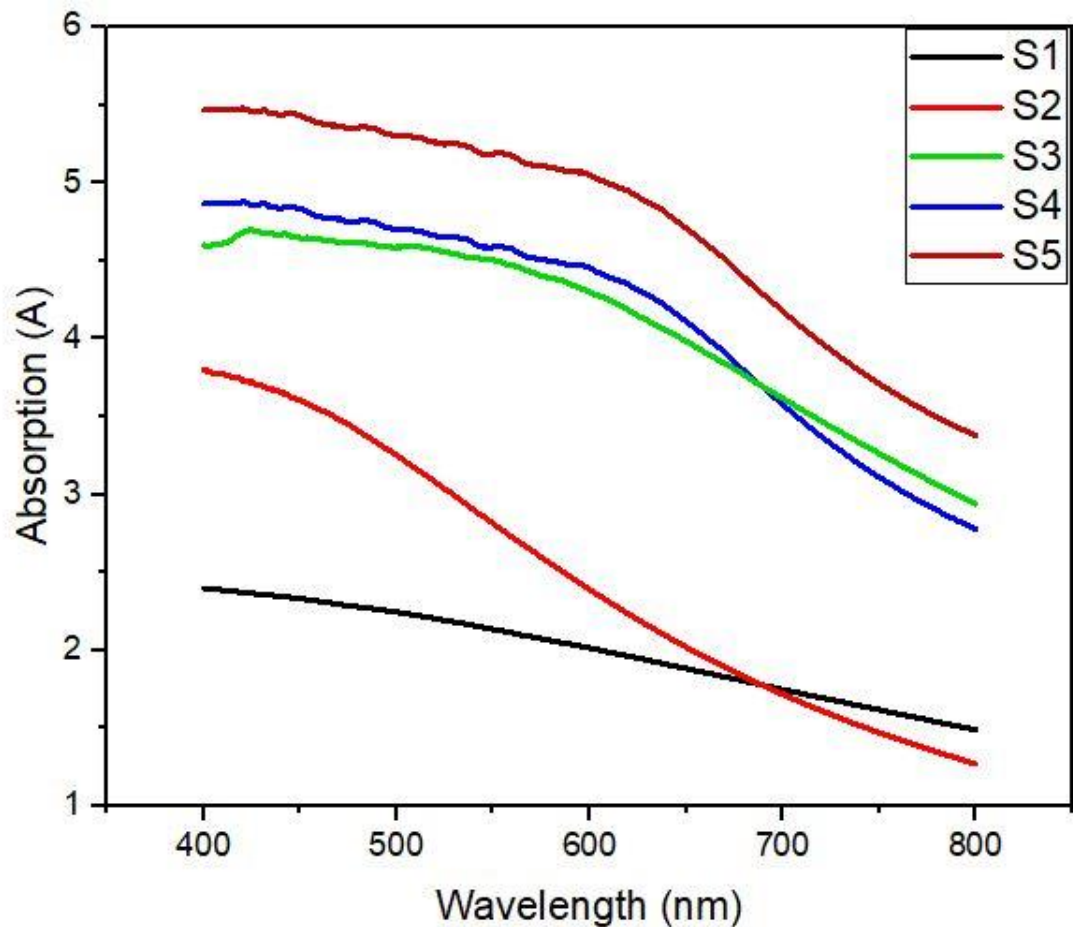


Figure 4.7. Absorbance for CZTS films.

4.6.2. Absorption coefficient (α)

The values of the absorbance coefficient for CZTS films were calculated using equation 3.22. Figure 4.8. shows that the curve of the absorption coefficient changes as indicates of the energy of incident photon for all prepared CZTS films.

The results show a slow change of the absorption coefficient (α) at low energies, then the values of the absorption coefficient rise near the basic absorption edge region. The values of the absorption coefficient of the prepared CZTS films are ($\alpha \geq 10^4$) at wavelengths (300 – 785 nm), and this indicates that the electronic transitions are direct transitions, and the prepared films have a direct energy gap.

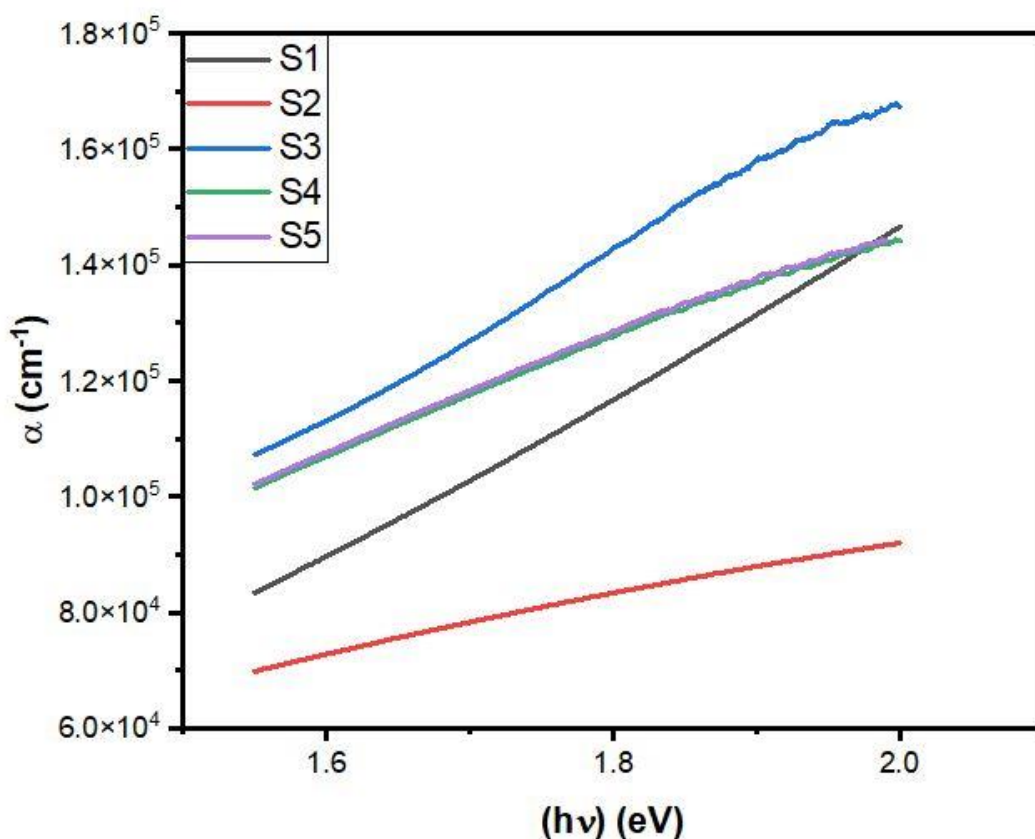


Figure 4.8. Absorption coefficient for CZTS films.

4.6.3. Energy gap (E_g)

The forbidden energy gap (E_g) was calculated for the direct electronic transitions of the prepared CZTS thin films by using equation 3.9 by drawing a graphic relation between the change of the values of $(\alpha h\nu)^2$ and the values of the energy of the incident photon ($h\nu$), and then drawing a straight line that passes through most of the

points beyond the main absorption edge, which cuts off the photon's energy axis at point $[(\alpha h\nu)^2 = 0]$. Figure 4.9. shows Tauc plots for prepared CZTS thin films.

It was found that the values of the energy gap (E_g) range between (1.56 to 1.72 eV), as shown in Table 4.6.

By increasing the thickness, the energy gap decreases for the prepared films, because the increase in thickness led to increase in the number of collisions between the photon and matter, and this leads to an increase in the number of electrons and holes, and then a decrease in the energy gap values.

Table 4.6. Energy gap for CZTS films

Sample	Energy gap (E_g) (eV)
S1	1.72
S2	1.71
S3	1.607
S4	1.57
S5	1.56

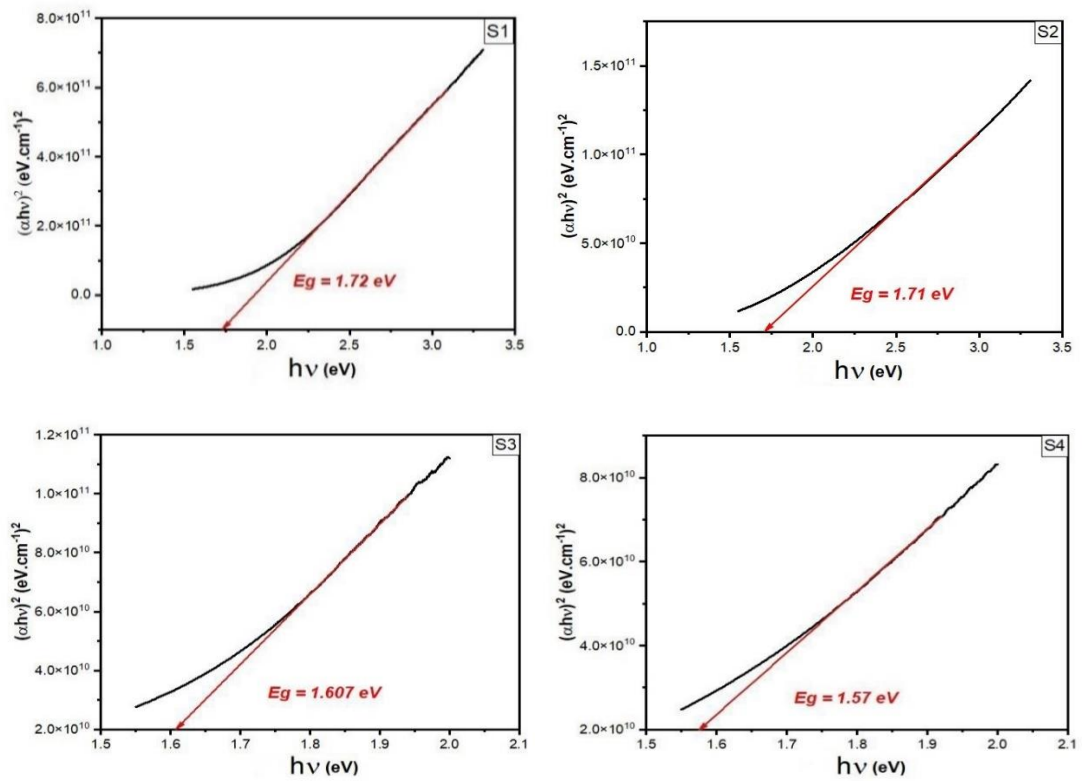


Figure 4.9. Tauc plots for energy gap of CZTS films.

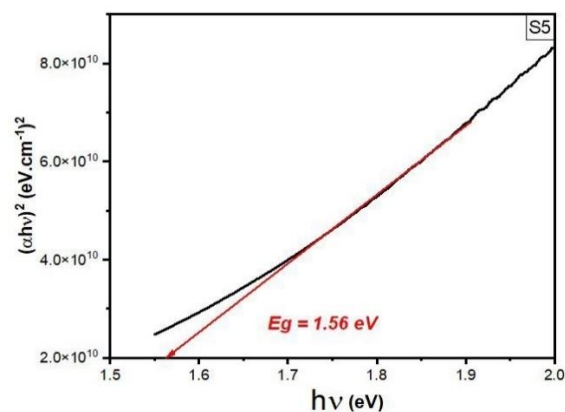


Figure 4.9. (Continued): Tauc plots for energy gap of CZTS films.

4.7. Electrical Measurements

The Hall Effect was measured to know the electrical properties of the prepared films as shown in Table 4.7. The conductivity of the prepared films was calculated using equation 3.32 and it was found that the values of conductivity [0.015, 0.016, 0.04, 0.069 ($\Omega.cm$)⁻¹] with high mobility for all samples.

Table 4.7. Hall coefficients of the prepared CZTS films.

Sample	ρ ($\Omega.cm$)	μ ($cm^2/V.s$)	R_H (cm^3/c)	σ ($\Omega.cm$) ⁻¹
S1	65.92	1.33	87.74	0.015
S2	72.14	1.94	140	0.016
S3	25.02	7.11	177	0.040
S4	16.89	30.5	515	0.069

5. CONCLUSION

CZTS thin films prepared by chemical spray pyrolysis technique with suitable properties to be an absorbent layer for solar cell applications.

The X-ray diffraction (XRD) results showed that the prepared films have a polycrystalline structure with kesterite phase of tetragonal texture and in the dominant orientation of growth (112). Increase in thickness increases the crystal size.

Raman spectrometer results showed the main peak of (CZTS) films appears clearly.

The results of the field emission scanning electron microscope (FESEM) showed shapes resembling a beautifully and homogeneously intertwined twigs.

Optical measurements showed that the energy gap decreases with increasing thickness and its value ranges between (1.56 – 1.72 eV), and the films have a high absorption coefficient and an allowed direct electronic transition.

Hall effect measurements showed that the prepared films are (p-type) materials. The conductivity and the mobility of the charged particles increased with increase in thickness. As the thickness increased from 0.59 to 3.3 μm , the conductivity increased from 0.015 to 0.069 $(\Omega.\text{cm})^{-1}$ and the mobility increased 1.33 to 30.5 $\text{cm}^2/\text{V.s}$ respectively.

The future work, fabrication of a solar cell by depositing an additional layer of cadmium sulfide (CdS) over the absorbent CZTS layer on silicon (Si) substrates n-type with silver electrodes.



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