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SÜLEYMAN DEMİREL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

PRODUCTION AND CHARACTERIZTION OF (CdZnS: Cu) NANOMATERIAL FOR X-RAY PHOTON DETECTION

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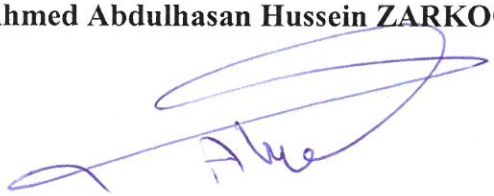
COMMITMENT

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Ahmed Abdulhasan Hussein ZARKOOSHI



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ABSTRACT

M.Sc. Thesis

PRODUCTION AND CHARACTERIZTION OF (CdZnS: Cu) NANOMATERIAL FOR X-RAY PHOTON DETECTION

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CdZnS thin film has been deposited on soda lime glass substrates by using the ultrasonic spray pyrolysis deposition technique. Cadmium acetate $Cd(CH3COO)_2.2H_2O$, cadmium chloride $CdCl_2$, zinc acetate $Zn(CH_3CO_2)_2.2H_2O$, zinc chloride $ZnCl_2$ and thiourea CH_4N_2S have been used to prepare precursor solution aiming the production of CdZnS, CdZnS: Cu thin films and CdZnS: Cu nanopowder. Cu doping of ternary material was done by adding copper sulfate $CuSO_{4.5}H_2O$ with 0.02 % atomic percentage. The deposition temperature is carried ranged around 275-175 °C respectively. Some of the samples have annealed for half an hour at 400 and 500 °C for pure CdZnS and Cu doped CdZnS: Cu thin films. Also, CdZnS: Cu nano powder have annealed at 200 and 300 °C by using an oven supplied with nitrogen gas and excess sulphur (Sulfurization). The effect of annealing has been investigated to study of the structural, morphological and electro-optical properties of each material by mean of XRD, SEM, EDS, and UV-Vis systems. XRD diffraction spectrum showed that the all the materials which have been produced are polycrystalline with cubic crystal structure. The crystal preferential orientation is (111) and the measurements showed that the average size of crystal is increased with increasing of annealing temperature for CdZnS thin film and for nanopowder whereas decreased for CdZnS: Cu thin film. SEM system showed the specific images for each sample regard with the materials are being used and EDS system showed that all components composed with closed chemical stoichiometry Cd+Zn/S=1: 1, Zn: Cd ratio is equal 3: 1 according the amount of molarity has been used for each component. The band gap values for all the materials CdZnS, CdZnS: Cu thin films and CdZnS: Cu nanopowder have been determined from UV-Vis measurements in the visible range of 300 - 1000 nm, and it is estimated to be ranged from 3.12, 3.01, 2.56 eV for CdZnS thin film and 2.51, 2.30 and 2.22 eV, for CdZnS: Cu thin film and 3.37 Ev for nanpowder CdZnS respectively. All the results are in agreement with the previous reported literature. Weak visible yellow light illumination has been noticed in CdZnS: Cu thin film for as grown under X-ray radiation but disappeared after the sample

annealed up to 400 °C due to the oxidization. However, the luminescence has been observed clearly for nano powder CdZnS: Cu until annealing up to 200 °C. Gamma ray measurement has been done by exposing of grown sample nano powder CdZnS: Cu. It shown low efficiency for luminescence light emitting due to the high activity of radioactive source.

Keywords: Nanomaterial, CdZnS: Cu, luminescence light, X-ray radiation

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ÖZET

Yüksek Lisans Tezi

X-IŞINI FOTONU ALGILAMAK İÇİN CdZnS: Cu NANOMALZEMELERİN ÜRETİMİ VE KARAKTERIZASYONU

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CdZnS ince filmi, ultrasonik sprey piroliz biriktirme tekniği ile soda kireç camı yüzeylerinde biriktirilmiştir. Kadmiyum asetat (Cd $(CH3COO)_2$.2H20), kadmiyum klorür $CdCl_2$, çinko asetat Zn $(CH3C0_2)_2$.2H20, çinko klorür ZnCl2 ve tioüre CH4N2S, CdZnS, CdZnS: Cu filmlerinin üretimini amaçlayan öncül çözeltiyi hazırlamak için kullanıldı. CdZnS: Cu nanopowder. Üçlü malzemenin Cu katkısı, 0.02 ile bakır sülfat (CuS04.5H20) ilave edilerek yapıldı. % atomik yüzde. Biriktirme sıcaklığı, sırasıyla 275 - 175 °C arasında değişmiştir. Numunelerin bazıları, saf CdZnS ve Cu katkılı CdZnS: Cu ince filmler için 400 °C'de ve 500 °C'de yarım saat tavlandı. Ayrıca, CdZnS: Cu nano tozu, azot gazı ve fazla sülfür (Sülfürizasyon) ile tedarik edilen bir fırın kullanılarak 200 ve 300 °C'de tavlanmıştır. Tavlamanın etkisi, her malzemenin yapısal, morfolojik ve elektro-optik özelliklerini XRD, SEM, EDS ve UV-Vis sistemleri üzerinden incelemek için araştırılmıştır. XRD kırınım spektrumu, üretilen tüm malzemelerin kübik kristal yapılı polikristal olduğunu göstermiştir. Kristal tercihli yönelimi (111) 'dir ve ölçümler, CdZnS ince filmi ve nanopowder için tavlama sıcaklığının artmasıyla kristalin ortalama büyüklüğünün arttığını, CdZnS: Cu ince filmi için azaldığını göstermiştir. SEM sistemi, kullanılan malzemelere göre her numune için özel görüntüler gösterdi ve EDS sistemi, kapalı kimyasal stokiyometri Cd + Zn / S = 1: 1, Zn: Cd oranının 3: 1'e eşit olduğunu gösteren tüm bileşenlerin kapalı olduğunu gösterdi. Her bileşen için molarite kullanılmıştır. CdZnS, CdZnS: Cu ince filmler ve CdZnS: Cu nanopowder malzemelerinin tümü için bant aralığı değerleri, 300 - 1000 nm'lik görünür aralıktaki UV-vis ölçümlerinden belirlendi ve 3.12, 3.01 ve 2.56 eV aralığında olduğu tahmin edildi, Sırasıyla 2.51, 2.30 ve 2.22 eV. Sonuçlar daha önce bildirilmiş olan literatür ile uyumludur. CdZnS: Cu ince filminde, X-ışını radyasyonu altında büyütüldüğü gibi zayıf görünür sarı ışık aydınlatması fark edildi, ancak oksidasyon nedeniyle 400 °C'ye kadar tavlandıktan sonra kayboldu. Bununla birlikte, ışıldama nano tozu CdZnS: Cu için 200 °C'ye kadar tavlanana kadar açıkça gözlenmiştir. Gama ışını ölçümü, yetiştirilen nano toz CdZnS: Cu numunelerinin açığa çıkarılmasıyla sağlanmıştır. Yüksek miktarda

radyoaktif kaynağın etkinliğinden dolayı ışık yayması için düşük verimlilik göstermiştir.

Anahtar Kelimeler: Nanomalzeme, CdZnS: Cu, lüminesans ışığı, X-ışını radyasyonu

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I dedicate this work to the souls of my parents and to my martyr brother **(MAJED),** my greatly gratitude to my wife who kept encouraging and supporting me to do my best to get my (M.Sc.) degree and my deep love to my daughters Maria and Fatimah and my deep thanks to all my family individuals for their praying for me.

Ahmed Abdulhasan Hussein ZARKOOSHI
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LIST OF SYMBOLS AND ABBREVIATION

A	Absorbance
B	Proportionality constant
D	Grain size
d	Lattice spacing
EDS	Energy Dispersive Analysis
E_g	Band gap energy
eV	Electron –volt
H	Planck constant (6.62×10^{-34} J.S)
hkl	Miller-Indices
hν	Photon energy
I	Transmitted beam
I_0	Fallen beam
M	Molarities
n	Value of exponent denotes the nature of the transition
SEM	Scanning Electron Microscope
T	Transmittance
t	Thickness of thin film
UV-Vis	Ultraviolet–visible spectrophotometer
USP	Ultrasonic spray pyrolysis system
XRD	X-ray diffraction
α	Absorption coefficient
β	Full Width at half Maximum
ε	Internal micro strain
θ	Bragg angle
λ	Wavelength
ν	Frequency

1. INTRODUCTION

1.1. Overview

Nanotechnology science is studying the basic principle of atoms which its dimension around 100 nanometers. This material can be generated through rearranging the atoms inside the lattice by chemical reaction to obtain new materials with nanometer scale, and then, it can be used in different application such as the production of semiconductor material (thin film) as well as in the medical field, agriculture, industrial and scientific research etc. (Bruus, 2004).

Thin films it is one of nanotechnology application, it can be defined as a layer or several layers of atoms that are not more than one micron. They can be deposited on the soda lime glass, quartz, silicon, aluminum, etc. substrates according the nature of material and the field which can be used(Lofgran, 2013).

Working in the field of thin film started in the middle of the nineteenth century specifically in 1852 through the scientists Bunsen and Grove by using chemical interaction. Over many years, the scientists tried to develop the technique of preparation of thin films until it reached advanced stages as we see now in our life. Actually this subject contributed effectively to the study of semiconductors materials to understand the physical and chemical properties to be a key role in the manufacture of solar cell systems and electronic devices such as capacitors, transistors, resistors and photoelectric detectors (Seshan, 2002).

Nanomaterial CdZnS is belong group compound II-VI, it has optical band gap energy ranged between 1.5-3.7 eV, which make it be attracted by many scientists, and demonstrated having optical absorption coefficient properties where just 1μm thickness can absorbs 99 % of the incoming radiation. In that case it used in the solar cell application and photoluminescence devices such as

luminescence dosimeter and scintillation detectors (Rajathiet et al., 2013; West and Kearfott, 2015).

CdZnS thin film can be prepared by different deposition techniques, such as the chemical bath deposition (CBD), physical vacuum deposition technique (PVD) and ultrasonic spray pyrolysis (USP). In our study USP technique has been used, because it is a simple, flexible and cost-efficient thin film deposition system.

In this work nano material and thin film form of CdZnS have been prepared with and without Cu metal doping through using copper sulfate ($CuSO_4.5H_2O$). The aim of Cu doping was to create inter band states (extra energy levels in the band gap) to enhance the electro optical efficiency and used as an activator inside the CdZnS material. In this work, annealing and Cu doping effect on CdZnS thin film have been investigated in the view of electro-optical and structural properties.

1.2. The Aim of Study

The aim of this thesis, is the fabrication of Cadmium Zinc Sulfur (CdZnS) and copper doping to them by Ultrasonic Spray Pyrolysis (**USP**) deposition technique and investigate whether this material can be used for X-ray florescence, even in the luminescence dosimeter application as a basic scintillation material, through take the advantage from the emission properties (luminescence phenomena), when photons of X –ray interacting with the electrons of material, and determine the best condition for this material that possibly can work without getting a negative impact. Sample has been exposed with gamma radioactive sources, to investigate whether it can be possible for gamma ray photon. This works includes the main objectives as given below:

- The deposition technique of Ultrasonic Spray Pyrolysis.
- Nano material fabrication thin film /nanopowder.
- Thin film structural characterization.

- X-ray luminescence.
- Thin film optical characterization.
- Gamma ray measurements.

1.3. Literature Survey

There are a lot of works relating with CdS-ZnS(Selvan et al., 2016) and CdZnS, because of their beneficial electro optical properties. G. Selvan studied the effect of precursor aging on the properties of CdZnS thin film. Fabrication of thin film was made from fresh and 4 days aged solutions. CdZnS thin films were prepared by using a perfume atomizer through spray pyrolysis technique from solutions 0.05M for cadmium chloride $CdCl_2$ and thiourea $[SC(NH_2)_2]$ and then dissolved in 50 ml of deionized water. The results showed that, CdZnS thin film which prepared by aged solution displayed better physical properties.

(Baykul and Orhan, 2010) they deposited CdZnS thin film on by using spray pyrolysis technique, and they used the parameters as fallow: 0.05 M for $CdCl_2$, ZnCl2 and NH_2CSNH_2 solutions respectively and glass substrate temperature was at 260 °C. All the materials were dissolved in the de-ionizing water in the separate beakers. The surface roughness of the CdZnS thin film was about 50nm, and the grain size ranged between 100- 760 nm.

(Asogwa, 2010) prepared CdZnS thin film by chemical bath deposition, the source for Cd^{2+} was cadmium chloride ($CdCl_2$), the source for $Zn2^{+}$ was Zinc sulphate ($ZnSO_4$), and thiourea $[(NH_2)_2CS]$ as a source for sulphide ions (S^{2-}), suitable parameters were used as 3 molality of 1M $CdCl_2$, 2 molality of 1M $ZnSO_4$, 5 molality of 1M thiourea and 35 molality of distilled water put in that order into a 50 ml beaker. The result showed that, the band gap ranged between 2.10 – 2.30 eV which it could be used in the solar cell application.

(Rajathi, and Sankarasubramanian, 2012) used chemical deposition by spray pyrolysis technique to study the properties of CdZnS thin film. Suitable

parameters for this experiment have been done such as 0.5 M for $ZnCl_2$, 0.5 M for $CdCl_2$ and 0.5 for thiourea. She found that the maximum and minimum optical transmittance ranged between 80% - 20 % respectively, the result showed that the band gap was ranged between 3.3 - 3.5 eV which can be used in the solar cell application and sensors.

(Selvan and Abuback, 2016), used (Cl-doped) ternary CdZnS thin film to study the effect of chlorine doping on the structural, morphological, optical and electrical properties of CdZnS thin film. They were used 0.05 M for cadmium chloride, [$CdCl_2$.$2H_2O$], thiourea [$Sc(NH_2)_2$] respectively and 0.06 M of zinc chloride [$ZnCl_2.6H_2O$] to prepare CdZnS thin film. Cl doping was achieved by adding NaCl (sodium chloride) in the CdZnS thin film with different concentration. The results showed that, Cl doping decreased the band gap and resistivity that confirm Cl doping might be suitable for enhancing the physical properties of CdZnS thin film.

(Kumar et al., 2011), studied the effect of concentration of ethylenediamine teraacetic acid on the photoluminescence behavior of CdZnS thin films. The preparation of CdZnS thin film has been done by using CdCl, ZnCl and thiourea with distilled water, and 0.32 M of $CdCl_2$, 0.34 M of $ZnCl_2$, NH_4Cl and NH_2-CS-NH_2 was used, respectively, as a precursor solution parameter for this experiment. The results showed the photoluminescence emission is enhanced with increased of (EDTA) concentration.

(Kamaruddin and Yusoff, 2017), deposited CdZnS thin film for low cost deposition conditions. They studied surface and morphological properties of CdZnS thin films which deposited by under atmospheric pressure metal organic chemical vapor deposition technique. They set sulfur source 1 M, $CdCl_2$ 0.5 M and $ZnCl_2$ 0.5 M as precursor solutions parameters. The results showed the average grain size was 96.16 nm which obtained by annealing at the temperature 440 °C.

(Verma and Thakur, 2015), used chemical deposition by spray pyrolysis technique to study the structural, morphological and optical properties of nanocrystalline thin film CdZnS. The aqueous solutions of $CdCl_2$ 0.1 M and NH_2CSNH_2 0.1 M were mixed in the ratio 1: 2 of $ZnCl_2$. Concentration of Cd in spray solution was kept stable while the amount of Zn was different to obtain a series of $Cd_{1-x}Zn_xS$ films. The results showed that doping of Zn concentration did not effect on the morphological properties of CdZnS thin film, and SEM measurements showed that the particle size is increased with annealing temperature.

(Balakumari and Elangovan, 2013), were caring out the fabrication and characterization of CdZnS thin film by chemical bath deposition. They used soda lime glass which were cleaned with acetone and distilled water and used as a substrate. The suitable parameters were; 0.05 M of $CdCl_2$, 0.02 M of $ZnCl_2$, NH_4Cl and 0.4 mol of $CS(NH_2)_2$ dissolved into 100 ml of distilled water, processing of the deposition cared out for 45 minutes. The results showed that the average of particle size is < 10 nm, and they found that optical transmittance is around 85% under optimized condition.

(Raji and Sanjeeviraja, 2005), deposited CdS thin film by spray pyrolysis technique to study thermal and structural properties. 0.5 M of thiourea, 0.5 M for $CdCl_2$ were used as a precursor solution parameter. They also prepared CdS thin film and used several concentrations of cadmium chloride and thiourea; 0.125 M, 0.25 M and 0.375 M, respectively. The annealing temperature ranged between 300 °C- 500 °C. The study showed that, thermal diffusivity and conductivity properties are increased with thickness of layer and the size of particles.

(Kumar and Saravanakumar, 2011), studied the effect of annealing on the surface and band gap of CdZnS thin films. They used chemical bath deposition technique, $ZnCl_2$, $CdCl_2$, and $NH_2–CS–NH_2$ were used as sources of Cd^{+2}, Zn^{+2} and S^{-2} ions respectively, the appropriate parameters which used in this study 0.25M

of $CdCl_2$, 0.25 M of $ZnCl_2$, 0.2 M of NH_4Cl and 0.3 M of $NH_2–CS–NH_2$ it used as stoke solution, the solution has been mixed together in the 100 ml beaker. The results showed that the crystalline is improved with increase of annealing temperature, and band gap values were ranged between 2.27–3.25 eV.

(Sharma and Patidar, 2006), measured the structural properties and optical bad gaps of $Cd_{1-x}Zn_xS$ (x=4 and 6) nano materials by using solution of $CdCl_2$ and $ZnCl_2$ (1 M) mixed in proper ratio by magnetic stirrer for 20 min, and produced H_2S gas through heating thiourea and passed inside the solution and then filtered the precipitate and dried under atmosphere. After drying the precipitate it was crushed to obtain the fine powder by using grinding mortar, the material prepared and characterized by XRD system and measured the average of crystal size by using Scherrer equation, they found that an optical band gape has been measured by Tauc plot formula it was estimated 3.4 eV.

(Yakoubi et al., 2016), studied the aqueous synthesis of Cu-doped CdZnS powder form quantum dots with controlled and efficient photoluminescence. They demonstrated that the photoluminescence (PL) of the Cu-doped CdZnS and the nanocrystals could be tuned in the visible spectrum through the chemical stoichiometric ratio of Cd/Zn, tuning the particle size and by optimization of the experimental parameters such as Cd/Zn ratio, reaction time, and PH value.

(Azizi and Dizaji, 2016), studied Structural and optical properties of $Cd_{1-x}Zn_xS$ (x = 0, 0.4, 0.8 and 1) thin films prepared using the precursor obtained from microwave irradiation processes, they used Cadmium acetate, zinc acetate, and thioacetamide to produce CdZnS powder by using by microwave radiation reaction, ethylene glycol was used as a solvent solution, they dissolved cadmium acetate and zinc acetate in the ethylene glycol under stirring at room temperature and separately dissolved thioacetamide in the ethylene glycol and then added to the solution which contain cadmium acetate and zinc acetate drop by drop, the final solution was exposed to the microwave radiation and they dried by oven at 80 °C for 48 hours. They obtained CdZnS powder form to

deposited CdZnS thin film by using thermal evaporation technique to study the structural properties of the thin film. They demonstrated that increasing of Zn ions in CdS the phase can changed from the hexagonal structural to the cubic structural.

1.4. Group Compounds (II-Vi) and Some of Their Applications

Group compound (II-VI) considered greatly important by many scientists. It has widely direct energy band gap ranged between ultraviolet light to the infrared light zone, and it is formed by metals from the group (II) like Zinc (Zn), Cadmium (Cd) and Mercury (Hg) with metals from group VI (chalcogen) such as Oxygen (O), Sulfur (S), Selenium (Se) and Tellurium (Te), for example CdS, CdTe and CdSe or ZnS, ZnO and ZnSe. Its characterized having wideband energy ranged between 1.5-3.7 eV, and principally the crystallize compound is hexagonal type (wurtzite) and cubic type (zinc blend) or multiple phases compound between both of them, where in the room temperature the formation state of (II-VI) group is belong zinc-blend, and in the high temperature is that wurtzite (Shadia, 2015).

The most interesting property belong this group the crystal can be grown under vapor and liquid phase. Also its optical absorption and emission coefficient properties is very high so in this case just 1μm thickness can absorbs 99% of radiation with energy higher than band gap. Therefore it is very suitable for the optical devices and solar cell application (Shadia, 2015)(Huang, 2013).

1.5. Cadmium Zinc Sulfide (CdZnS)

CdZnS ternary material can be grown on the clean soda lime glass substrates by ultrasonic spray pyrolysis technique, where specific molarity belongs each element has been chosen to satisfy the aimed chemical stoichiometry Cd+Zn/S equal to 1: 1, and the ratio between Zn/Cd is equal to 3: 1. In this section, we

will explain in detail about the chemical and physical properties for each element as follow:

1.5.1. Cadmium (Cd)

Cadmium is a rare metal element occurs naturally with low concentration in the crust of earth. The atomic number of Cd is 48 which belong to group (II) of periodic table. It considered as a secondary produce for melting of major metals like copper, zinc and gold. The physical and chemical properties of cadmium are given as follows (Sharma et al., 2015).

1. Silver white color
2. Volumetric mass 8.6 g/cm^3,
3. Molar mass 112.41 g/mole
4. Melting point 321 °C
5. Boiling point 765 °C
6. The conductivity property is very high which make it to use in the battery industrial.

1.5.2. Zinc (Zn)

Zinc is inorganic substance occurs on the earth and doesn't occur free in the nature but as in the form of zinc oxide, zinc silicate and zinc carbonate. It is found in different concentration in the rocks and as a result from the volcanic eruption. The atomic number is 30 and it belongs group (II) of periodic table. In fact, it plays main role in the human life also in termed essential nutrients (Frassinetti and Bronzetti, 2006). The chemical and physical properties of zinc as follows:

1. Silver–gray color
2. Volumetric mass 7.14 g/cm^3

3. Molar mass 65.37 g/mole
4. Melting point 419.58 °C
5. Boiling point 907 °C

1.5.3. Sulfur

Sulfur is a chemical element whose symbol is **S** and with atomic number 16. It is available in the nature under normal situation. It has a brightness yellow color. Sulfur is occurring in the layers of earth's surface specifically occurs in the vicinity of volcanoes where released from volcanoes as a gas. After cooling down to room temperature, it turns to a solid state with beautiful yellow color deposited on the edge of volcano (Maeda and Tanaka, 2011).

Chemical and physical properties of Sulfur are as follow;

1. Sulfur reacts with all elements except noble gases, tellurium, platinum, iridium and gold
2. Burns in blue inflame with form of sulfur dioxide and oxidized in the humid air
3. There are three types of isotope belong sulfur S_{32}, S_{33}, S_{34} and S_{36}.
4. Melting point is 115.21 °C

Annealing by sulfurization process is an important factor which used to control the elements composition, due to its ability to improve the crystallinity and keeps the material preventing the oxidization. Sulphurization of thin film with high rate temperature of 580 °C can improve the grain size also improving the crystallinity but over than 600 °C this process causes deteriorate the structure and generate amorphous film on the surface. Also, at low level sulfurization temperature the absorbance shifted to the near of infrared wavelength. For the conductivity properties increasing of sulfurization able to decrease the resistivity and electro optical can be enhanced (Mkawi and Ibrahim, 2015). With

regard to optical properties absorption coefficient can be increased with sulfurization temperature (Maeda et al., 2011).

1.6. Doping Mechanism

Doping mechanism is adding a little impurity material to the pure semiconductor material to enhance its electro-optical properties or structure. For example; the conductivity, if the number of electron or hole in the valance or conducting band is very little which makes the conductivity properties very low unless increasing the temperature, and in the same time it is not desirable just depending on annealing to increase the conductivity. So, in that case, doping method can be used to improve the conductivity or optical properties for some materials (Zhou & Qiu, 2019).

Doping method is playing an important role during the growth of semiconductor materials, by adding an extra energy level in the band gap which helps the electron to transfer from the valance band to conducting band, as well as creates a trap of electrons, recombining between the electron and the hole can be happen during their movement inside the crystal and by this way emitting photoluminescence. In our study, to prepare and growth CdZnS: Cu nanomaterial copper sulfate ($CuSO_4$-$5H_2O$) was used as a doping material as a source of copper ions.

1.7. Application of CdZnS Thin Film

Using semiconductors materials in solar cell application is more desirable and useful as a renewable energy in the worldwide. Because, these facilities do not cost the country more budget like electricity stations which commonly found in our life. CdS is an n type semiconductor material whose band gap energy is 2.42 eV. It has been made to be suitable for the CdTe and $CuInSe_2$ thin film in the solar cell (Figure 1.1) or photovoltaic system application. Actually just 0.1 μm of CdS can absorbs just 36% of incoming solar radiation with energy more than

2.42 eV due to the large value of its band gap. Therefore, CdZnS material can be used instead of CdS to increase the photocurrent by providing more harnessed electrons by smaller band gap. CdZnS materials can be used with another materials like $CuIn_xGa_{1-x}Se_2$ or($CuInS_2Se_1)_2$ to be more useful material for the fabrication of p-n heterojunctions (Lee et al., 2003).

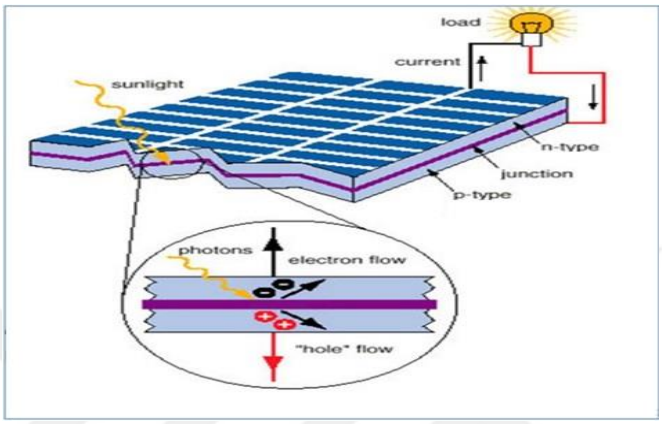


Figure 1.1. Solar cell system schematic representation (Velauthapillai, 2017)

In fact the development of nanoparticles science can lead CdZnS semiconductor material and related ternary could be a suitable compound for blue laser diode application due its high of optical density, as well as the florescence value belong this material is playing a main role in different field such industrial sector and medical physics (Huang, 2013).

On the other hand, CdZnS thin film is involving in the optoelectronic application technology by designing devices which can convert the electrical signals to the light signal and vice versa. In fact, this technology includes variant of devices for example fiber optic communication, different types of diodes, remote sensing and medical diagnostic hardware. Furthermore, CdZnS ternary material it is suitable compound for blue laser diode, X-ray florescence analysis, photo detector, used for thin-film transistors (TFTs), luminescence dosimeter, gamma ray detector as a scintillation material (Kumar et al.,2011b; Lee et al., 2003; Ravangave and Mahewar, 2015; Raviprakash et al., 2009).

1.8. Inorganic Luminescence Materials

Definition of luminescence phenomena is emission of light by the material when absorbing some external energy. Luminescence can be used in different application which is summarized in Table 1.1. The external excitation energy can be provided by several methods:

1. Photoluminescence: the process of excitation is coming from the light photon such as UV or laser.
2. Cathode luminescence: the excitation is generated by electron beams.
3. Radio luminescence: the process of excitation is coming from interaction of X-ray or gamma-ray photons with the atoms of the material.
4. Thermo- luminescence: the process of excitation generated from applying thermal energy to the material.

Scintillation phenomena: the same phenomena of radio-luminescence. But, this technique can be used to detect the photon pulse which is generated from interaction of X-ray or gamma-ray photons with the matter (Leverenz and Seitz, 1939; West and Kearfott, 2015).

In general, the luminescent system generally includes a host lattice and a luminescent center, called "*activator*". The host lattice allowed to the radiation source to pass through it for excitation process, and the activator will absorb the extra energy to be transferred from the ground state to the excited sate and then return to the ground state by emitting "a luminescence light". For some material, the activator doesn't absorb the excitation energy, and this extra energy can be absorbed by other ions called sensitizer and subsequently transfer to the activator ions as shown in the Figure 1.2.

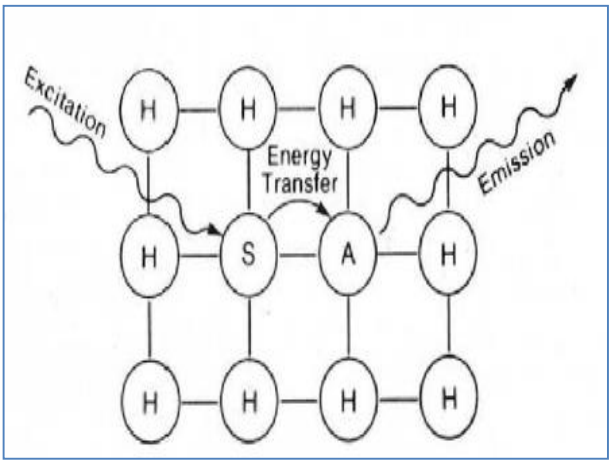


Figure 1.2. Diagram represents the role of activator (A) doped in the host lattice (Deluca, 2009)

Basically, pure material could not exhibit this phenomenon unless doping with doped material should be added to the ternary material CdZnS in order to take the role of activator ions, and that it will introduce an extra energy level by creating `traps` inside the band gap energy to help the electron transferring from the valance band to the conduction band. In our study, we added copper sulfate ($CuSO_4.5H_2O$) as an activator ions for source of Cu to the host material CdZnS (Kenneth et al.,2002).

Table 1.1.Classification of luminescence and their applications

No	Phenomenon	Applications
1	Photoluminescence (PL)	fluorescent lamps phototherapy lamps highlighting paints and inks
2	Radio -luminescence	X-ray screen and scintillation detectors
3	Cathode luminescence	TV screens
4	Thermo- luminescence	dosimetry of ionizing radiation personnel monitoring environmental monitoring

2. MATERIAL AND METHOD

In this chapter, the deposition method and the characterization system will be explained in details

2.1. Ultrasonic Spray Pyrolysis Technique

Ultrasonic Spray Pyrolysis (USP) technique is a method being very commonly used in the scientific research field to produce thick film, thin film and nano-powder Nowadays, USP is very popular technique. Because; it is very simple usage, low cost, and does not need specific ambiance requirements. Also this technique can be used for producing multi-layer thin film also. Spray pyrolysis technique has been employed for several years in the glass manufacturing and solar cell production (Eygi et al .,2016 ; Perednis and Gauckler, 2005; Rane and Patil, 2012; Ravangave et al., 2015).

Basically, USP system includes an atomizer, and an ultrasonic frequency generator system to generate short wavelength for atomizing the solution, controllable substrate heater, nitrogen gas generator for pressurizing the solution and for making the deposition being homogeneous.

There are some researchers used this technique and published their studies like (Parameshwari and Gopalakrishna, 2017). He studied the influence of Zn content on the structural properties of $Cd_{1-x}Zn_xS$ from the XRD spectra, and he observed that the band gap of the $Cd_{1-x}Zn_xS$ thin films depends on the Zn composition in the solution (Deokate et al., 2009). They measured the characterization of the thin film by X-ray diffraction (XRD), SEM, optical absorption and Hall effect techniques. The XRD studies reveal that films are of polycrystalline $CdIn_2O_4$ with cubic structure and the crystalline increases appreciably after annealing (Rajathi et al., 2012). Their results showed that the mean grain size of the CdZnS thin film calculated from the XRD data lies between 50 and 250 nm, and the influence of substrate temperature on the

sheet resistance and resistivity of the CdZnS films has been studied and reported.

In this technique, thin film produced by inject of reactive substance, where nitrogen gas was used to help the deposition going in harmony. Therefore, the material will be transferred to the vapor chamber, and then the vapor which resulted from the reactive substance will be collected on the substrate by ultrasonic waves as shown in the Figure 2.1.

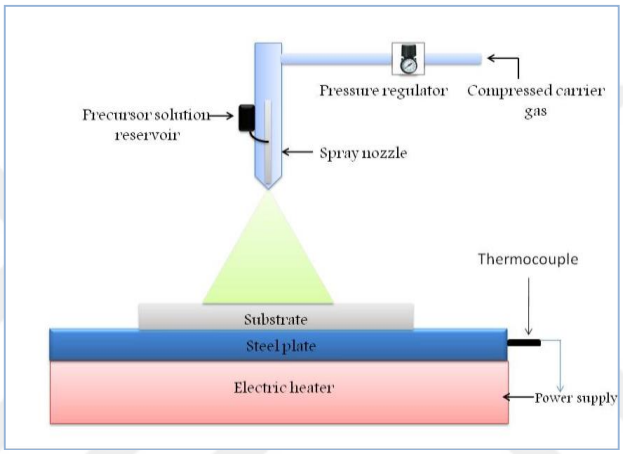


Figure 2.1. Schematic representation of ultrasonic spray pyrolysis system (USP)

2.2. Influence of Parameters on the Thin Film Properties

Ultrasonic spray pyrolysis deposition method involves spraying the precursor solution onto heated substrate to produce a structure as disk shape by thermal decomposition. The shape and size of this disk is depending on the volume of droplet, substrate temperature, height of the nozzle, flow rate of the solution and applied frequency. At the same time, deposited thin film can be composed by collecting of the metal salt which converted to metal oxide on the heated substrate.

In this section, the influence of the main USP parameters on the structure and the electro optical properties of the deposited thin film have been defined as given below:

2.2.1. Effect of substrate temperature

The temperature of the substrate is very important parameter to defining the morphology and electro-optical properties of thin film. In fact, the morphology and structure of the thin film can be transferred to various shape and crystallography due to the effect of thermal energy by increasing the substrate temperature. Behind these changes in electro-optical properties of the thin film it can also effect on the adherence of the material to the substrate (Oh and Bang, 2007).

2.2.2. Precursor solution

Precursor solution it is the second factor, which can affect the properties of the thin film such as the concentration of chemical elements, kind of salt and the type of solvent. All these factors effective on the physical and chemical properties of thin film. Therefore it can change the structural and electro-optical properties of the films by changing the composition of constituent elements.

2.2.3. Shape of the atomization nozzle

The effect of the nozzle shape has been noticed and studied for many years. The main idea is to understand the process of deposition condition, and which kind of atomizing shape is perfect for the appropriate deposition condition. Actually, the shape of atomization is also affecting the structural properties of the thin film. To determine the quality of material whether thin film, thick film or powder, the flow rate of the solution and also changing the angle and the shape of the nozzle can be controlled.

2.3. Advantage of Ultrasonic Spray Pyrolysis Deposition Technique

It is extremely easy to prepare a thin film by USP technique with wide area deposition, free of ambiance controlling and other beneficial flexibility of the deposition conditions as follow;

1. USP technique doesn't need high quality substrate which make it commonly used in the industrial application like functional glass manufacturing.
2. Thickness of thin film can be easily arranged by changing the parameters of the deposition.
3. Substrate temperature which can be applied in between RT-500 °C makes it easy to produce a thin film by thermal decomposition of the constituent material.
4. It is easy to produce multi-layer thin film by changing the composition of solution through spray operation (Kozhukharov & Tchaoushev, 2013).

2.4. Characterization of the Deposited Materials

2.4.1. Topographical characterization by scanning electron microscope measurement (SEM)

It is a kind of microscopes where it displays the images of sample under duty by scanning the surface of material via the electron beam. The principle of action is the interaction between the electron and the surface atoms, then presents different signals containing morphological information on the surface of the material and its elemental component by means of Energy Dispersive Spectroscopy (EDS).

The electron microscope can obtain an image with a high-resolution reaching to more than 1 nm where very small size of the matter can be observed. It has the ability of operation in various environmental situation, whether in cases of high vacuum or low vacuum by applying humidity. The most common measurement that the electron microscope scanning carry out is detection the secondary electrons were emitted from excited surface atoms by the electron beam, and the number of secondary electrons depends on the condition of matter itself and also topography (Castle JE. and Zhdan, 1997).

2.4.2. Structural characterization by X-ray diffraction (XRD)

X-ray diffraction system is used for many issues as below:

- This system is used to define the structural properties of the matter whether it is crystalline, polycrystalline or amorphous.
- Measure the average distance between the crystal layers of material
- Determine the orientation of crystal by detecting the peaks which producing from the X-ray beam falling at the atomic layers and its diffraction in an angle (θ)
- Measuring the lattice constant by applying Bragg diffraction equation (Raviprakash et al., 2009).

$$n\lambda = 2d\sin\theta \qquad (2.1)$$

where; λ: X-ray wave length; d: the distance between the layers of atoms; and θ: is the Bragg angle which is represented in Fig 2.2.

- Measuring the numbers and grain size by Scherrer equation (Alkhayatt, 2015).

$$D = 0.9\,\lambda \setminus \beta\cos\theta \qquad (2.2)$$

where; D: grain size, λ: Wave length, β: full width at half maximum (FWHM).

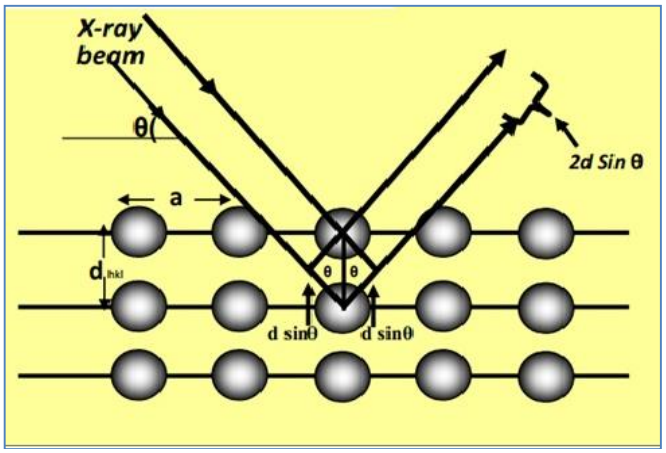


Figure 2.2. Layers of atoms and Bragg law diffraction

2.4.3. Electro-optical characterization of the material

- Electro-optical effect is the changing the physical properties of matter where interacting with electromagnetic field or photon. It can change the shape, position and the stability of the molecules inside the matter.
- In the semiconductor materials, the valence band (v.b) is filled with electrons where the conduction band is empty (c.b). The electrons couldn't cross the forbidden band gap unless applying enough energy. For example; in the case of photon energy which is equal or greater than the band gap energy ($h\nu \geq E_g$), the valance band electrons absorbs the photons energy and exited to the conduction band, and electrical conduction will be produced by this way.
- If the value of photon energy ($h\nu$) lower than the band gap ($h\nu < E_g$), the photons cannot be absorbed, and the electrons transition doesn't happen. Conductivity can be manipulated by doping material which is added to the structure of the material.
- If the photons energy is the same value of band gap ($h\nu = E_g$), electrons transition (conductivity) will be produced. This level is named as threshold energy, and the absorption of the photons is provided. All this mechanism is showed in Figure 2.3 (Omar, 1994; Zones, 2004).

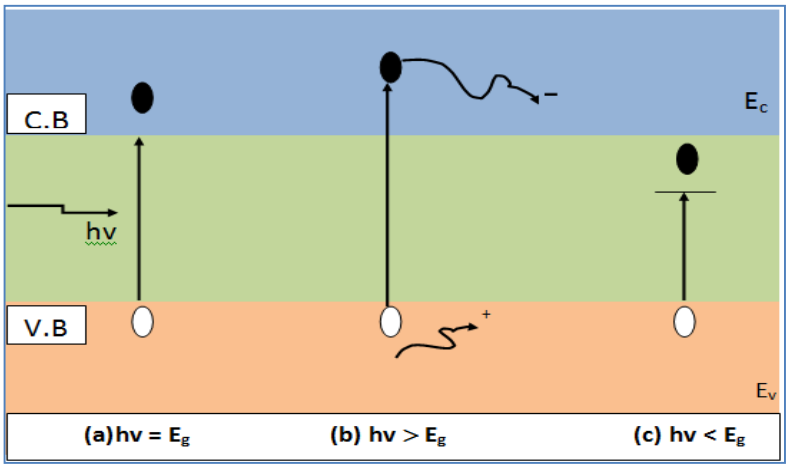


Figure 2.3. Absorption of photon for different energy level

2.4.3.1. Transmittance measurement

It is the ratio between the light beams transmitted by the material to the incoming beam. It is given by the law as below (Omar, 1994).

$$T = I / I_0 \quad (2.3)$$

Where; T: Transmittance, I: transmitted beam and I_0: incoming beam

2.4.3.2. Absorbance measurement

It is the ratio between the absorbed beams into the semiconductor material to the incoming beam. It is given by the law as fellow (Omar, 1994).

$$A = I_A / I_0 \quad (2.4)$$

where; A: absorbance, I_A: absorbed beam, I_0: incoming beam

2.4.3.3. Absorption coefficient

Absorption coefficient takes the main place in thin film measurements, regarding with photoelectric devices and solar cell applications. It differs depending on the type and the structure of semiconductor, and gives the information about electro optical properties of materials.

The definition of absorption coefficient is a measurement of absorption under electromagnetic radiation when it passes through semiconductor material. Actually three optical process can be occurred during the electromagnetic beam interaction with the thin film materials (reflecting, transmitting and absorbing) as shown in the Figure 2.4. Absorption coefficient can be obtained from Lambert Law (Omar, 1994).

$$I = I_0 e^{-\alpha t} \quad (2.5)$$

$$\alpha = 2.303 \, A\backslash t \quad (2.6)$$

where; α: Absorption coefficient with unit (cm^{-1}) and t: thickness of the substrate with unit cm.

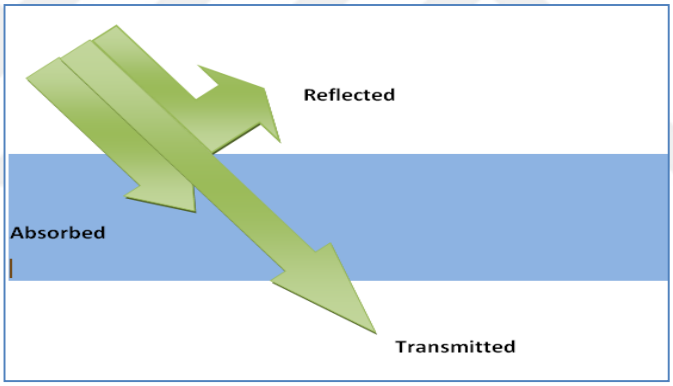


Figure 2.4. Optical processes in the thin film; reflection, absorption and transmission

2.4.3.4. Optical band gap energy

It represents the minimum energy required for the electrons to pass from the top of valence band to the bottom of conduction band. The value of optical energy band gap is changing depending on the nature of the material, temperature and the method which been used in the thin film deposition. Also, it can be increased or decreased if doping substance added to the semiconductor material. Optical energy band gap can be obtained by the equation (Baykul and Balcioglu, 2000);

$$\alpha h\nu = B\,(h\nu - E_g)^n \qquad (2.7)$$

n: the value of the exponent n denotes the nature of the transition (direct or indirect transition)

B = proportionality constant

h = Planck constant (~ 6.63×10^{-34} J.s)

ν = frequency

E_g = band gap energy

3. RESULTS AND DISCUSSION

3.1. Introduction

In this chapter, to define the structural, topographical, elemental composition and electro-optical properties of thin films and nanomaterials, which were produced by ultrasonic pyrolysis spray technique, X-ray diffraction system (XRD), scanning electron microscopy (SEM), Energy Dispersive Spectroscopy system (EDX) and UV-Vis spectrometer characterization system were used, respectively. To investigate the luminescence light phenomena of these nanomaterials, the samples were exposed to X-ray photons.

Three materials have been produced regarding with CdZnS; the first was CdZnS thin film, where $CdCl_2$ and $ZnCl_2$ and thiourea (CH_4N_2S). CdZnS thin film was used as a starting material, and considered as a reference. Second material was CdZnS: Cu thin film which same starting material was used, as well as doped with the copper in atomic percentage of 0.02 at% by using copper sulfate ($CuSO_4.5H_2O$) as a defect material to add an extra energy level inside the band gap as an activator for luminescence effect.

Third material was CdZnS: Cu nanopowder; in this case we used cadmium acetate, zinc acetate and thiourea with same molarity. There were details belongs to the previous materials regarding with its chemical and physical properties, deposition condition and their possibility of emitting the photon (luminescence) under X-ray photons irradiation because of the quantum confinement effect of the nano structures.

3.2. Substrate Preparing

Firstly, glass substrate has been prepared by cutting the soda lime glass in dimension 2×2 cm^2. All glass substrate was cleaned with pure water, ethanol, and acetone and afterward dried with nitrogen gas, actually cleaning the substrate considered as an important point to growth the qualified thin film and

to increase the adherence of films to the glass surface. Glasses should be cleaned accurately before the deposition. This is a usually processing which were used for each thin film deposition processes.

3.3. Optimization of Deposition System

After preparing the glass substrates, the optimization of deposition system (USP) should be done like; the nozzle distance, exhaust velocity of the deposition ambient and applying the substrate temperature on the stage step by step until reaching the temperature which suitable for pyrolysis during the deposition.

The Sono-tek Flexi coat ultrasonic spray pyrolysis deposition system was used to deposit the thin films with a nitrogen gas supplier. The USP deposition parameters were listed as; nitrogen pressure = 2.5 $kg.cm^{-2}$, substrate to nozzle distance = 12 cm, solution flow rate = 0.5 ml/minute.

Figure 3.1. Sonotek Flexi Coat Ultrasonic spray pyrolysis system

3.4. CdZnS Thin Film Production

The precursor solution has been prepared before the deposition which containing; $CdCl_2$, $ZnCl_2$ and thiourea, and the all calculations about the molarity for each component were conducted accurately. The appropriate weight for each element has been measured by a sensitive electronic balance device (Model; Sartorius Group 2004).

We prepared the precursor solution by dissolving each compound separately in distilled water and mixed together by magnetic stirrer (Model; Dlab2018). At first 0.3 M of $ZnCl_2$ dissolved in 20 ml of distilled water and after 10 minutes, added to the solution two drops of HCl acid to prevent the oxychloride, and then dissolved 0.6 M of thiourea in 10 ml and added to $ZnCl_2$ solution. Afterward, dissolved 0.1 M of $CdCl_2$ in 20 ml added and ten mixed all the solutions together by magnetic stirring for two hours at 80 °C until being homogenous solution.

For USP deposition; the set temperature of substrate was 300 °C and the real substrate surface temperature was 275 °C, which measured with a laser thermometer. The nozzle to substrate distance was 12 cm, and solution flow rate fixed to be 0.5 ml/min. After thin film deposition, some samples have been annealed under sulphur ambiance at 400 °C and 500 °C, respectively.

3.4.1. X-ray diffraction measurements of CdZnS thin film

Measurements have been done by X-ray diffraction (XRD) system under room temperature. The diffraction patterns recorded for CdZnS thin film on glass substrate for as grown and annealed samples, and given in Figure 3.2. As it can be seen, all the peaks matching with CdZnS and polycrystalline in nature. The main diffraction peaks of cubic structured CdZnS thin film for as grown and annealed films at 400 °C and 500 °C, are sited at 2θ values of 28.62°, 28.72°, and 28.28°, respectively. This main peak is attributed (111) planes as a preferred orientation. As mentioned in the section (2.4.2), the Scherer's equation (Eq. 2.1.)

has been applied to calculate the average size of the crystal, as shown in Table 3.1.

Table 3.1. Average of crystal size of CdZnS thin film

Sample	Peak position for (111)	FWHM (rad)	Average of crystal size (nm)
As grown	28.62°	0.784	88.94
Annealed at 400 °C	28.72°	0.735	94.78
Annealed at 500 C°	28.28°	0.692	101.09

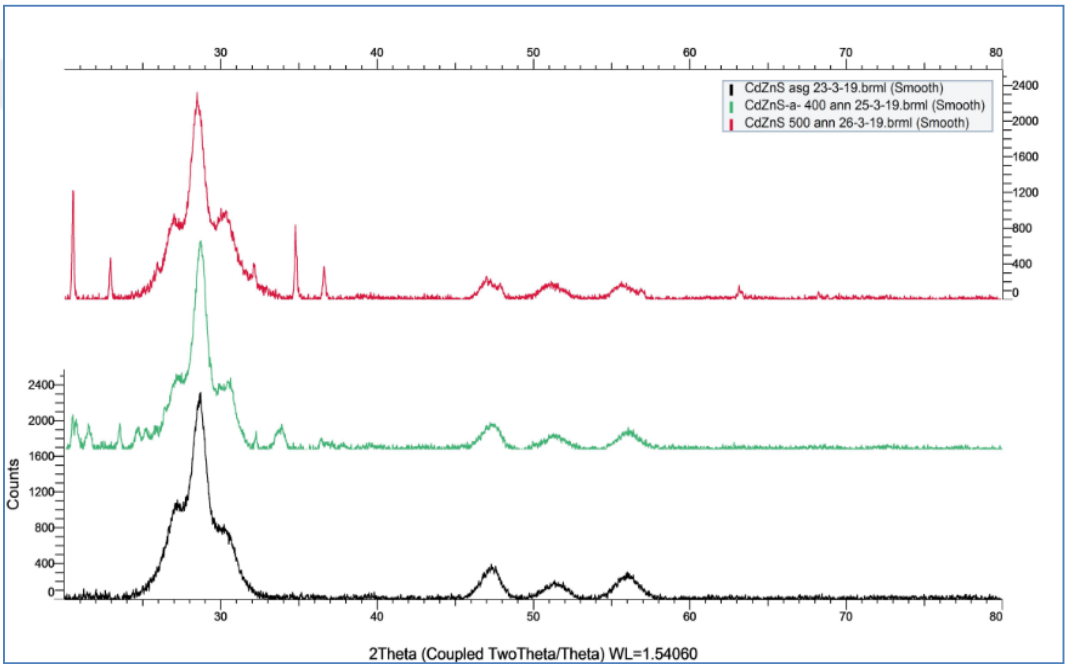


Figure 3.2. XRD patterns of CdZnS for as grown, 400 °C and 500 °C

Table 3.1 shows; increasing of grain size with increasing of annealing temperature, that can be associated with reduction of grain boundary and the deformation inside the lattice (Hossain et al., 2013a; T. Prem Kumar et al., 2011c).

Figure 3.2 also showed the improving of intensity of peaks with increasing of annealing temperature, due to thermal energy helps the atoms to take its suitable position inside the lattice. Although, there are extra small peaks that

might be associated with zinc oxide crystal phase (Goswami et al.,2018; Zakria et al., 2015).

3.4.2. SEM measurements of CdZnS thin film

Morphology and elemental analyses of the film surface examined by FEI Quanta FEG 250 Scanning Electron Microscope (SEM), which attached an EDS (EDAX) system. Surface morphology measurements have been done by SEM and given in Figure 3.3. as follows; a, b and c represent the images of CdZnS thin film for as grown, annealed 400 °C and annealed 500 °C, respectively. The Figures (3.4), (3.5) and (3.6) represents the spectrums of CdZnS thin film for as grown, and annealed at 400 °C and 500 °C respectively.

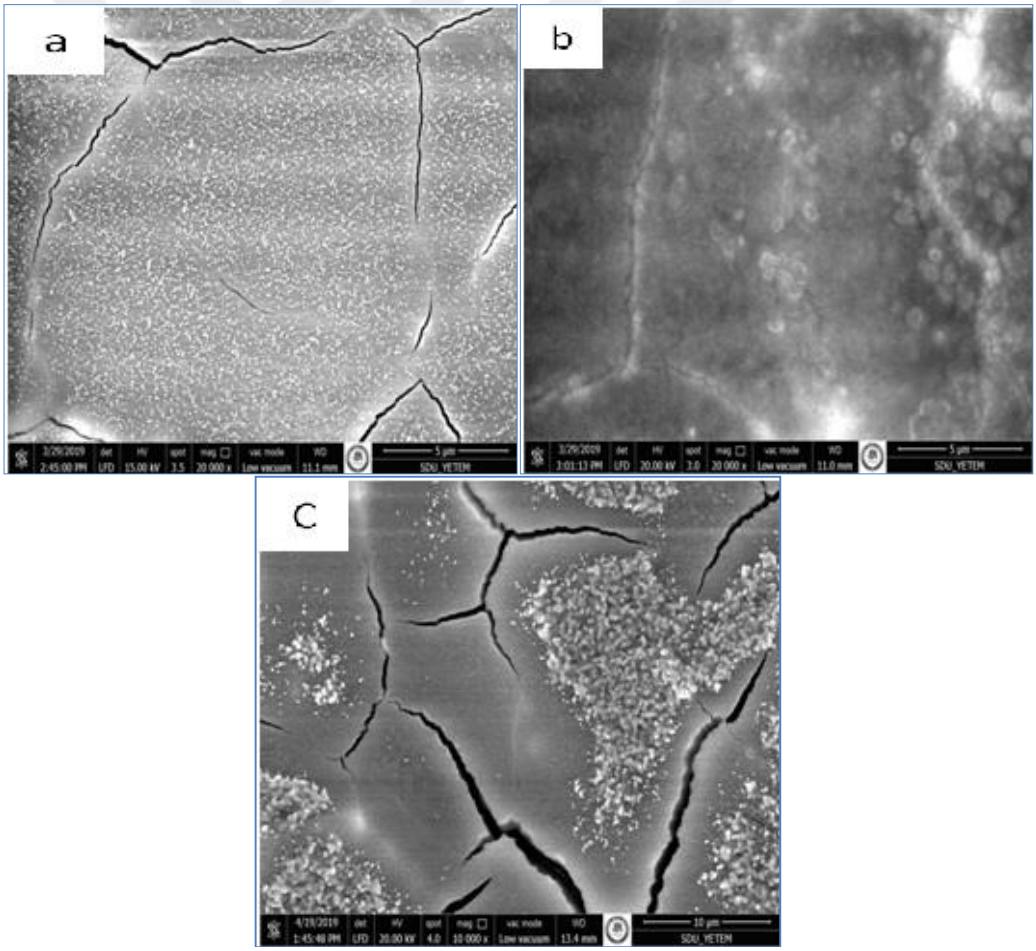


Figure 3.3. SEM image of CdZnS thin film for a) as grown, b) annealed at 400 °C and c) at 500 °C

The morphology of CdZnS thin film surface through SEM system showed that the samples converted to varied shape beginning from grown sample it shows smooth surface covered with a little bit of cracks, afterward, when annealed to 400 °C the morphological surface improved, and the cracks tended to close with each other to be homogenized and smooth, and when annealed to the 500 °C the surface slightly disrupted again, while noticed large cracks due to the effect of thermal energy on the particles of material (Hossain et al., 2013a; Rasool et al., 2019).

3.4.3. EDS measurements of CdZnS thin film

Energy dispersive spectroscopy system (EDS) is followed by SEM measurements. It was used to determine of elemental composition of the CdZnS thin film for as grown, 400 °C and 500 °C annealed films, respectively. Table 3.2 shows the atomic percentage for each component. It displays how much the components have been homogenized or not according the starting precursor solution composition.

Table 3.2. EDS analysis of chemical components for CdZnS thin film as grown, 400 °C and 500 °C

Samples	S	Cd	Zn	Zn/Cd	Zn+Cd/S
As grown	50.43	10.34	40.23	3.89	1.02
Annealing 400 °C	51.09	10.07	38.13	3.78	0.94
Annealing 500 C°	51.19	11.36	37.91	3.33	0.96

Table 3.2 shows that all the elemental compositions for as grown and annealed samples are proximate with each other, and demonstrated that, the deposition of the precursor solution on the glass substrate has been done in acceptable homogeneity. All the compounds are proximately closed to be composed with chemical stoichiometry of Cd+Zn/S equal to 1: 1, and the ratio between Zn/Cd is close to 3: 1.

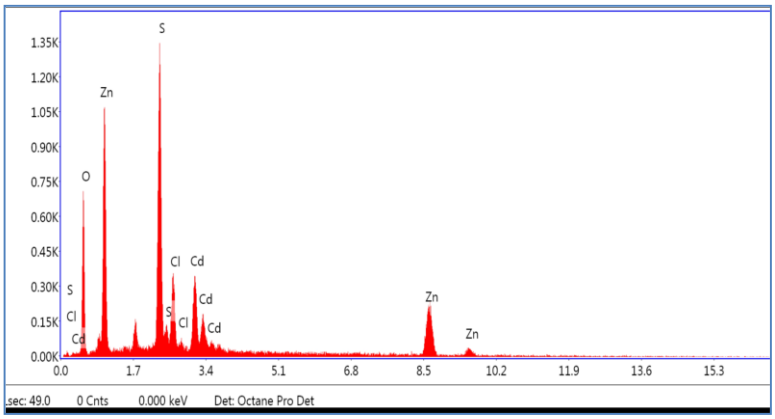


Figure 3.4. EDS spectrum image of as grown CdZnS thin film

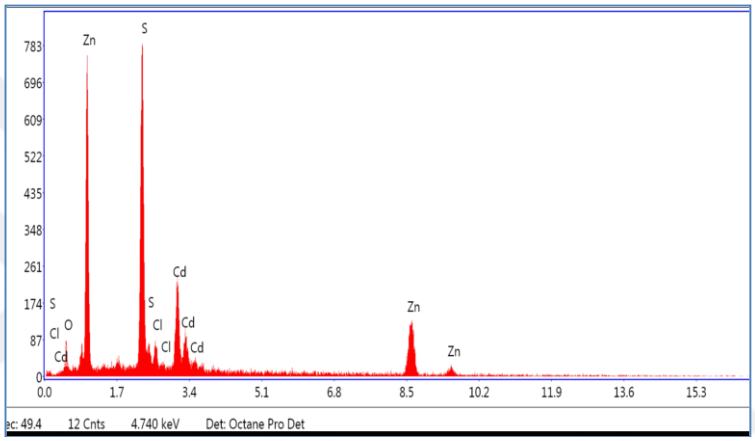


Figure 3.5. EDS spectrum image of CdZnS thin film for the sample annealed at 400 °C

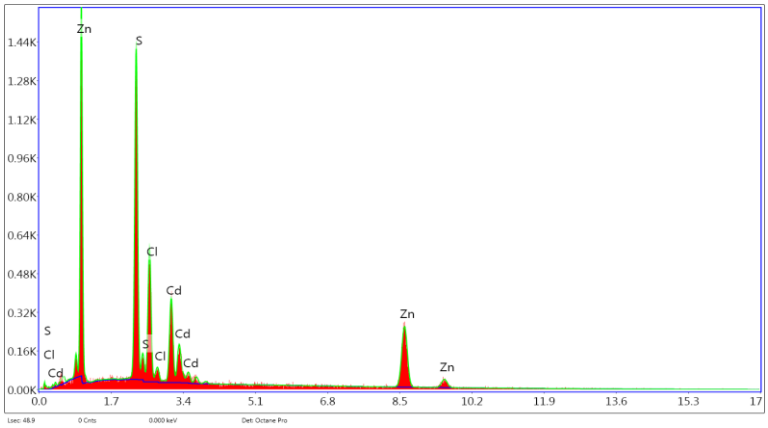


Figure 3.6. EDS spectrum image of CdZnS thin film for the sample annealed at 500 °C

3.4.4. UV-Vis measurements of CdZnS thin film

Absorption spectra of CdZnS thin film for as grown and annealed sample were recorded by using spectrophotometer at room temperature in the wavelength ranged from 300 nm to 1000 nm and shown in the Figure 3.7. Energy band gap has been approximated with the help of absorption spectra and by using Tauc equation (Eq. 2.7) as mentioned in the section 2.4.3.4.

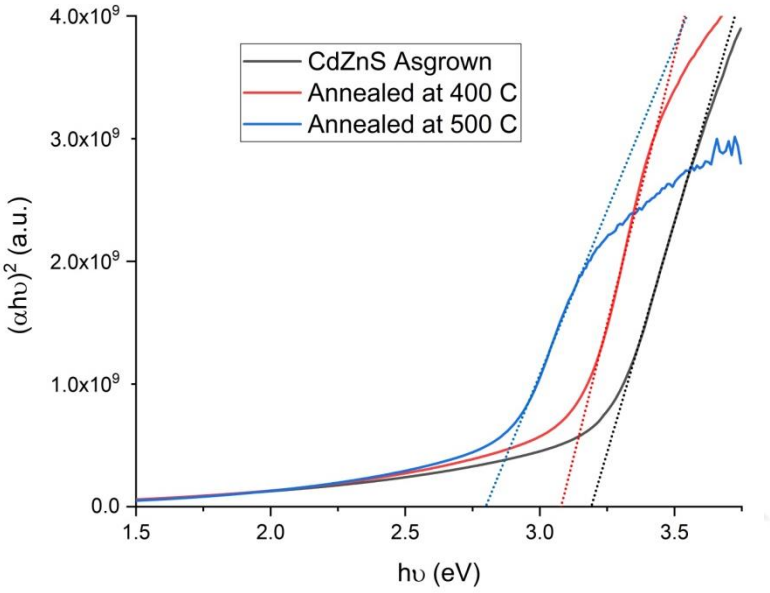


Figure 3.7. Energy band gap determination of CdZnS thin film

The Figure 3.7 shown that an absorption edge is shifted to the red region, which exhibited lower absorption in the longer wavelength, and optical band gap value decreased from 3.12, 3.01, to 2.56 eV for as grown, annealed sample at 400 °C and annealed sample at 500 °C, respectively. The decreasing of band gap values arises from increasing of gain size as it seen in the Table 3.1 and quantum confinement which taking place in the crystal. These results in agreement with the reported literatures (Azizi, 2014; Hossain et al., 2013; Lee et al., 2003).

3.5. CdZnS: Cu Thin Film Production

CdZnS: Cu thin films were deposited by using the same materials, and the molarity were been used in the previous production as well as added in 0.02 at% of copper sulfate $CuSO_4.5H_2O$ to the precursor solution as doping material to add an extra energy level (activation center) inside the band gap.

All the parameters regarding of deposition condition for previous production are the same when the CdZnS: Cu thin film has been produced.

3.5.1. X-ray diffraction measurements of CdZnS: Cu thin film

Measurements have been done by X-ray diffraction (XRD) system under room temperature. The diffraction recorded for CdZnS: Cu thin film on glass substrate for as grown and annealed samples were shown in Figure 3.8. As it can be seen all the peaks matching with CdZnS: Cu and polycrystalline in nature. The major diffraction peaks of cubic structured CdZnS: Cu thin film for as grown, annealing at 400 °C and 500 °C are found at 2θ values of 28.39°, 28.21°, and 27.92°, respectively. Attributed (111) plane is the preferred for crystallographic orientation in all films. Also, as mentioned in the section 2.4.2, Scherer's equation (Eq. 2.1.) has been used to calculate the average of crystal size and results are collected in Table 3.3.

Table 3.3. Average of crystal size for CdZnS: Cu thin film for each sample

Sample	Peak position for (111) lattice	FWHM (rad)	Average of crystal size (nm)
As grown	28.39°	3.515	19.88
Annealed 400 °C	28.21°	3.084	22.69
Annealed 500 °C	27.92°	3.352	20.94

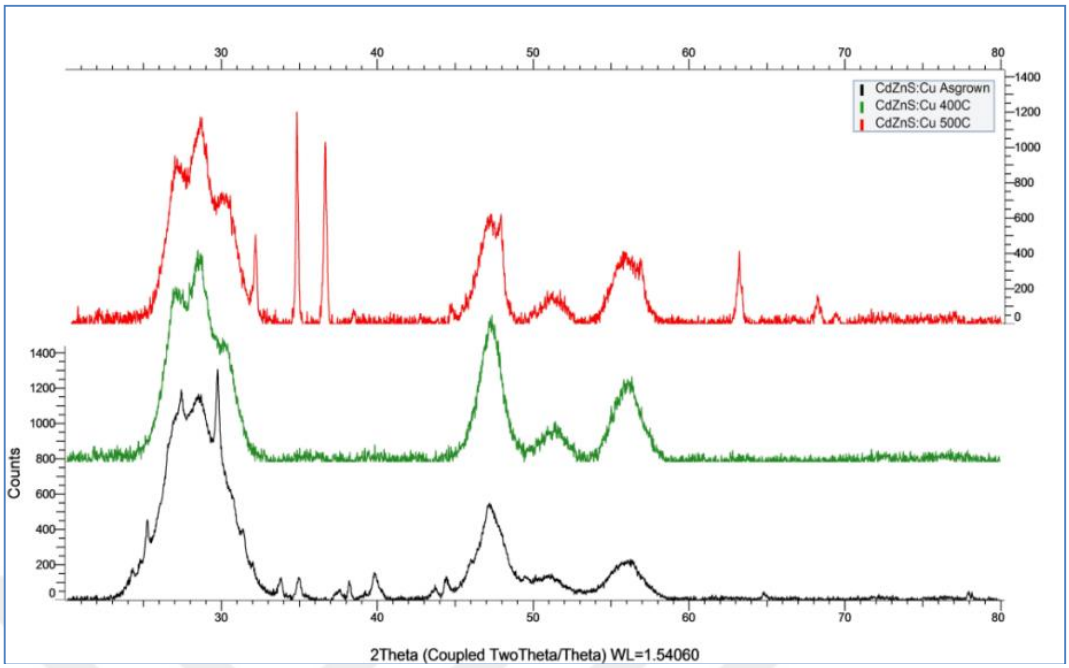


Figure 3.8. XRD patterns of CdZnS: Cu thin film for as grown, at 400 °C, and 500 °C annealing temperature

The Table 3.3 shows that the average of grain size is disrupted after annealing up 500 °C due to the effect of oxidization on the structural properties of thin film. The oxygen atoms makes the ZnO phase creation, and reduce the grain size of the films (Ison et al., 2009).

Fig 3.8. shows that, the intensity of peaks did not improve very well after annealing up 400 °C, due to associated with zinc oxide which generated inside the film structure. ZnO try to create its own crystal structure within the host material. Therefore, the diffraction of the incoming X-ray photons on the atomic levels (for both the host and the doped atoms), will not be in the same phase, that is in agreement with reported literature (Figueiredo et al., 2008; Lui et al., 2006).

For as grown thin film sample, week luminescence light has been noticed under X-ray photons interaction. But, this luminescence has been disappeared, when annealed up 400 °C. Because of the effect of oxidization, which makes degradation of photo luminescent intensity (Kathuria and Ramrakhiani, 2014).

3.5.2. SEM measurements of CdZnS: Cu thin film

The morphology and elemental analyses of the film surface examined by Scanning Electron Microscope (FEI - SEM) which attached an EDAX EDS system. The Figures 3.9 (a, b and c) represent images of CdZnS: Cu thin film for as grown, annealed at 400 C°, and 500 C°, respectively. The Figures 3.10, 3.11, and 3.12 represents, the EDS spectrums of CdZnS for each thin film samples, respectively.

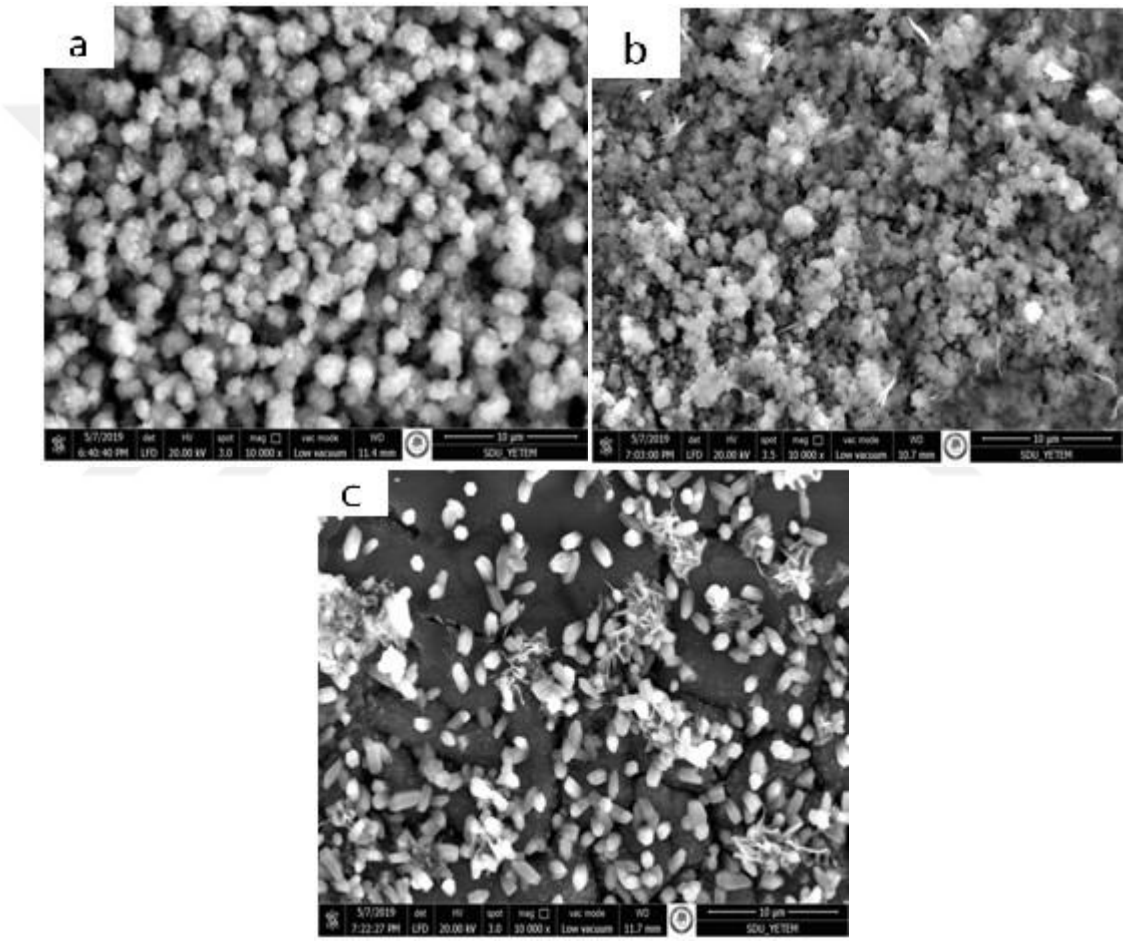


Figure 3.9. SEM image of CdZnS: Cu thin film for a) as grown, b) annealed at 400 °C and c) at 500 °C

The morphology of CdZnS: Cu thin film surface through SEM system showed that the surface of grown sample covered with cluster particles. The particle size around 128 nm and for annealed sample at 400 °C the size of cluster particle slightly decreased to be around 100 nm due to effect of high

temperature. Afterward, when annealed up to 500 °C, the surface disrupted to be converted from the cluster shape to the seed particles rich with zinc oxide compound as well as some cracks has been noticed. This is an evidence of thermal energy effect on the particles of material (Hossain et al., 2013a; Rasool et al., 2019).

3.5.3. EDS measurements of CdZnS: Cu thin film

Energy dispersive spectroscopy system (EDS) has been used to determine the compositional elements for CdZnS: Cu thin film, and to exhibit how much the compounds matched together on the films according the amount of molarity were been used. Table 3.4 shown the atomic percentage for each compound for different annealing temperatures.

Table 3.4. EDS analysis of chemical components for CdZnS: Cu thin film as grown, at 400 °C and 500 °C

Samples	S	Cd	Zn	Zn/Cd	Zn+Cd/S	Cu
As grown	30.54	7.78	30.60	3.93	1.25	0.36
Annealing 400 °C	31.86	8.97	32.19	3.58	1.29	0.45
Annealing 500 C°	33.32	8.10	35.94	4.43	1.32	0.37

Table 3.4 shows that all the elemental compositions for as grown sample and annealed 400 °C are proximately closed to be composed with chemical stoichiometry of Cd+Zn/S, and equal to 1: 1. Also, the ratio between Zn/Cd is proximately equal to 3: 1. After annealing up to 500 °C, the surface of materials effected by the thermal energy which caused disruptive effect on surface and break the homogeneity of elemental distribution in the structure of the material. Because of this, the zinc concentrations are enriched which can be seen in the EDS results. The concentration of copper ions shown a little amount due to a few grams has been used of copper sulfate not exceeding 0.00294 grams for 0.02 at%. However, the results of XRD, SEM and EDS are in agreement with each other.

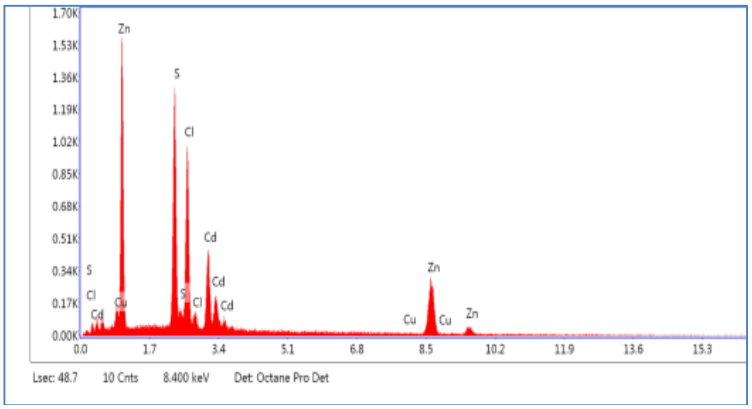


Figure 3.10. EDS spectrum image of as grown CdZnS: Cu thin film

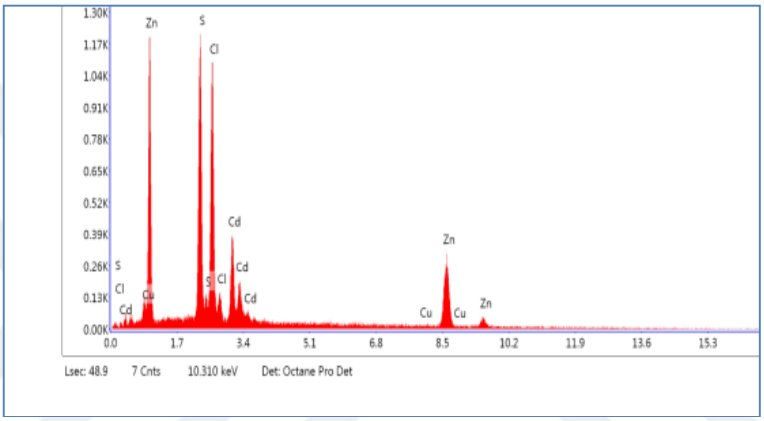


Figure 3.11. EDS spectrum image of CdZnS: Cu thin film for the sample annealed at 400 °C

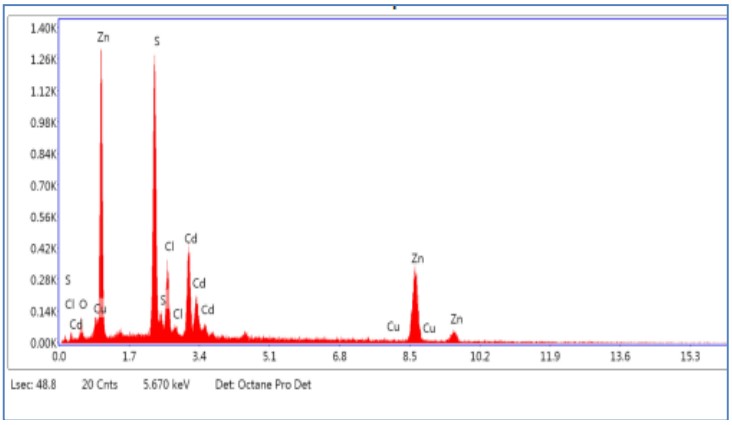


Figure 3.12. EDS spectrum image of CdZnS: Cu thin film for the sample annealed at 500 °C

3.5.4. UV-Vis measurement of CdZnS: Cu thin film.

Absorption spectra of CdZnS: Cu thin film was recorded by using spectrophotometer at room temperature in the wavelength ranged from 300 nm to 1000 nm. Energy band gap has been measured with the help of absorption spectra and by using Tauc relation (Eq. 2.7), as shown in Figure 3.13.

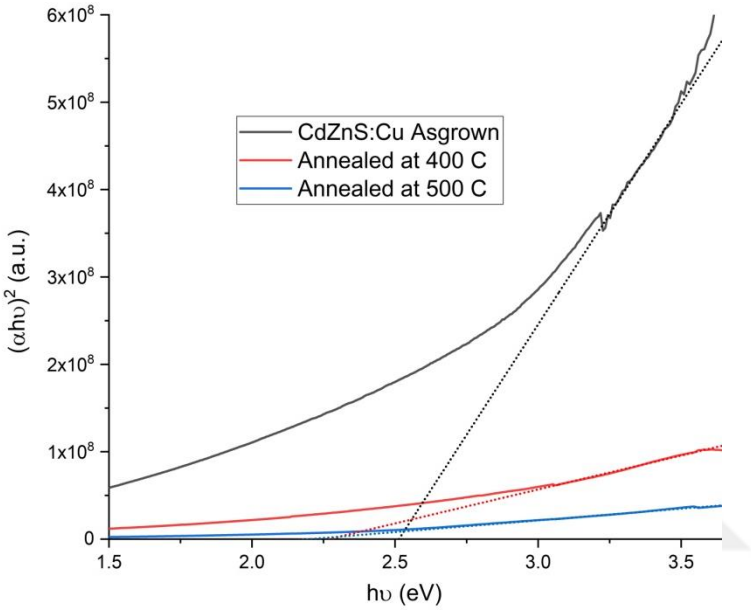


Figure 3.13. UV-Vis spectrum of CdZnS: Cu thin film for energy band gap determination

From the UV-Vis measurement, it could be clarified the effect of Cu doping on the absorption spectrum. In fact, doping of copper ions makes increasing of absorption values of thin film in short wavelength region. The band gap values of thin films for as grown and annealed at 500 C° decreased from 2.51 to 2.22 eV, that because an extra energy levels which generated from copper doping in the thin film and having an extra phase of CuO_2 after oxidization which has lower band gap (around 2.00 eV) causing a shift toward to lower band gap energies. However, this is in agreement with XRD, SEM and EDS measurements and literature reported familiar results for the different deposition condition (Figueiredo et al., 2008; Serin et al., 2005 ; Johan et al., 2011).

3.6. 3.6. CdZnS: Cu Nanopowder Production

According the results of previous thin film productions and by taking into consideration the effect of annealing on the chemical and physical properties of the material, different materials have been used to investigate the luminescence properties of the CdZnS in different method. 0.1 M of cadmium acetate dehydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$), 0.3M of zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$), 0.4M of thiourea (CH_4N_2S), and 0.02 at. % of copper ions from copper sulfate ($CuSO_4.5H_2O$) were used to prepare the precursor solution.

The solution solved in 50 ml of deionized water and mixed together for 2 hours by magnetic stirrer at the temperature of 80 °C and 600 rpm rotation. The glass substrates were cleaned by ethanol, methanol, acetone, and ethanol and then dried by nitrogen gas, respectively. Other optimization parameters were applied as; nitrogen gas pressure; 2.5 kg cm^{-2}, substrate to nozzle distance; 12 cm, solution flow rate; 0.5 ml/minute. The deposited materials were in nanopowder form. They have been annealed at 200 °C and 300 °C, respectively by the oven for 30 minutes under nitrogen gas atmosphere to improve the crystallinity.

3.6.1. X-ray diffraction measurements of CdZnS: Cu nanopowder

The XRD patterns of CdZnS: Cu nanopowder on glass substrate were recorded for as grown and annealed samples for 200 °C and 300 °C, respectively, and given in Figure 3.14. All the peaks matching with CdZnS structure with PDF: 01-079-7040 library number which is in cubic structure and polycrystalline in nature. The main diffraction peak for as grown and annealed at 200 °C and 300 °C CdZnS: Cu nanopowder are found at $2\theta = 27.922°$ which is attributed (111) as a preferred for crystallographic orientation. Scherer's equation (Eq. 2.1.) has been applied to calculate the average size of the CdZnS: Cu nanopowder crystallite for as grown and annealed at 200 °C and 300 °C are given in Table 3.5

Table 3.5. The average crystal size of CdZnS: Cu nanopowder

Sample	Peak position for (111) lattice	FWHM (rad)	Average of crystal size (nm)
As grown	27.922°	3.906	17.970
Annealed 200 C°	27.922°	3.829	18.332
Annealed 300 C°	27.922°	3.691	19.017

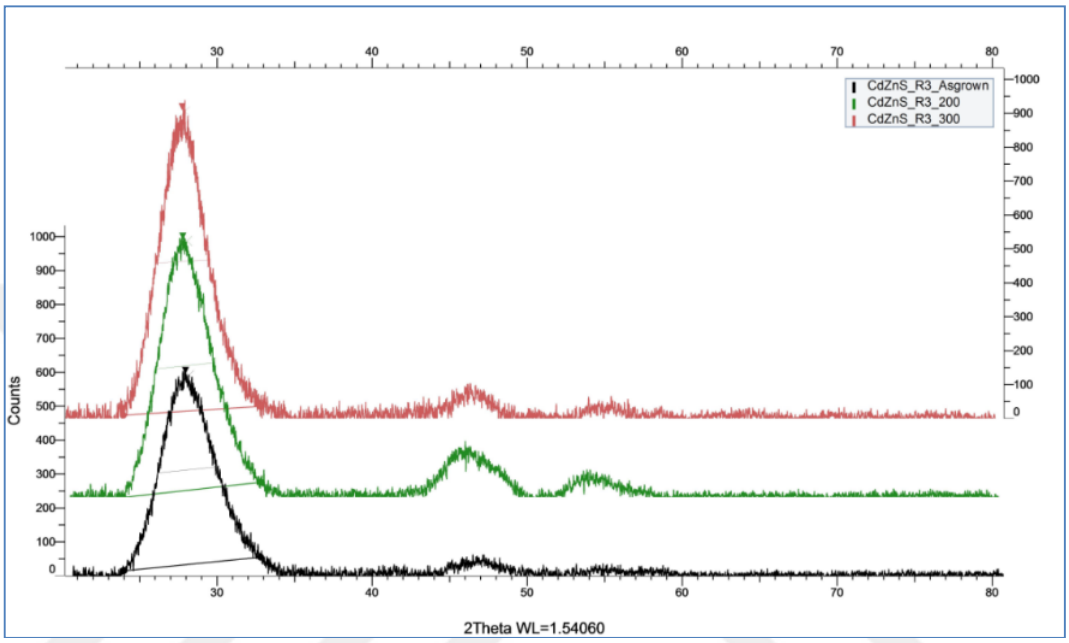


Figure 3.14. XRD patterns of CdZnS: Cu nanopowder for as grown, 200 °C, and 300 C° annealing temperature

Table 3.5. shows the increasing of the grain size with increasing of annealing temperature, which can be associated with reduction of grain boundary and elimination of the deformation inside lattice (Kumar et al., 2011).

It is was observed that the crystallinity was improved after annealing up to 200 °C, because the thermal energy which supplied through annealing process helps the atoms to move to the correct position (Goswami et al., 2018; Zakria et al., 2015).

The lattice spacing (d-values) were calculated by using Bragg diffraction equation and compared with the values of CdZnS: Cu nanopowder related library file number PDF: 01-079-7040. The elicited values are in agreement with the standard values with 3.19 Å.

It can be seen in Figure 3.15, shiny yellowish luminescence light has been observed for the as grown and annealed at 200 °C CdZnS powders. This luminescence has been disappeared when the material annealed up to 300 °C The luminescence intensity is decreased with increasing of annealing temperature and disappeared completely. It might be attributed that, due to the oxidation of activator ions (here Cu ions) is the main cause of the degradation of the photo luminescent intensity. However, increasing the annealing temperature leads to deplete of radiative level of activator (Kathuria and Ramrakhiani, 2014; Manh and Thuy, 2013).

Figure 3.15. CdZnS nano powder luminescence light under illumination of X-ray photons

3.6.2. SEM results of CdZnS: Cu nanopowder

Figures 3.16 (a,b and c) represents the surface morphology of the CdZnS: Cu nanopowder for as grown, annealed at 200 °C and 300 °C, respectively. As grown and annealed at 200 °C samples exhibit small nanoparticles covered on the surface of material and their size ranging in between 50 to 145 nm. When the sample annealed up to 300 °C, these nano particles were converted to bulk structures which were located together in some parts on the surface. This is

obviously the effect of annealing on the physical properties of material (Hossain et al., 2013a; Rasool et al., 2019).

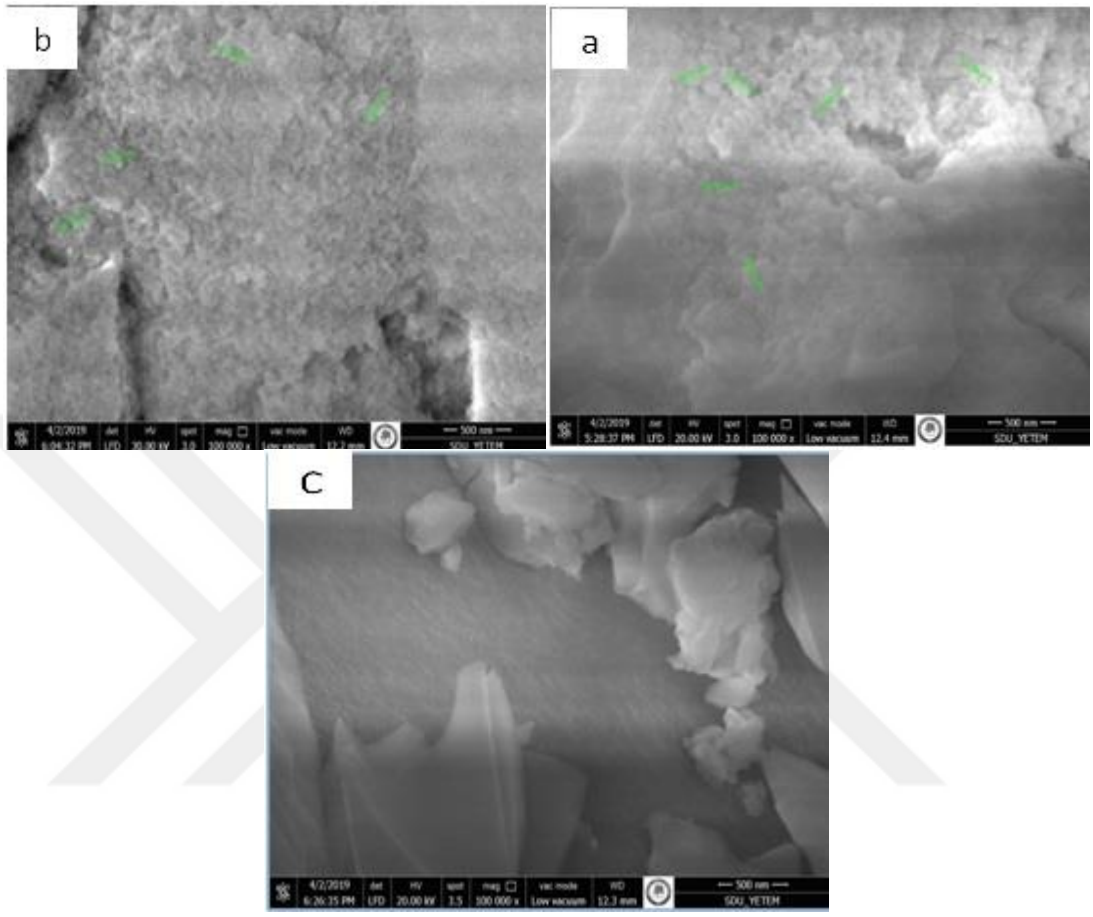


Figure 3.16. SEM image of nanopowder CdZnS: Cu for a) as grown, b) annealed at 200 °C and c) at 300 °C

3.6.3. EDS measurement of nanopowder CdZnS: Cu

Energy dispersive spectroscopy system has been used to determine the elemental compositional of the nano powder form CdZnS: Cu for as grown, annealing at 200 °C and 300 °C, respectively. The Figures 3.17, 3.18 and 3.19 represents the elemental spectrums for each sample, respectively. Also, the Table 3.6 shows that, all the atomic percentage of compounds for each sample are proximately closed together which demonstrate that the precursor solution was prepared in acceptable homogeneity. It was noticed, also, the sample annealed at 300 °C was slightly zinc enriched.

All the elements are closed with chemical stoichiometry of the precursor solution (Cd+Zn/S =1: 1), and the ratio of Zn: Cd = 3: 1 according to the amount of molarity, which has been used for production of CdZnS: Cu nanopowder.

Table 3.6. EDS analysis of chemical components for CdZnS: Cu nanopowder as grown, annealed at 200 °C and 300 °C

Samples	S	Cd	Zn	Zn/Cd	Zn+Cd/S	Cu
As grown	52.05	11.17	36.44	3.26	0.91	0.41
Annealing 200 C°	51.28	11.07	37.22	3.36	0.94	0.43
Annealing 300 C°	49.49	10.16	39.49	3.88	1.003	0.40

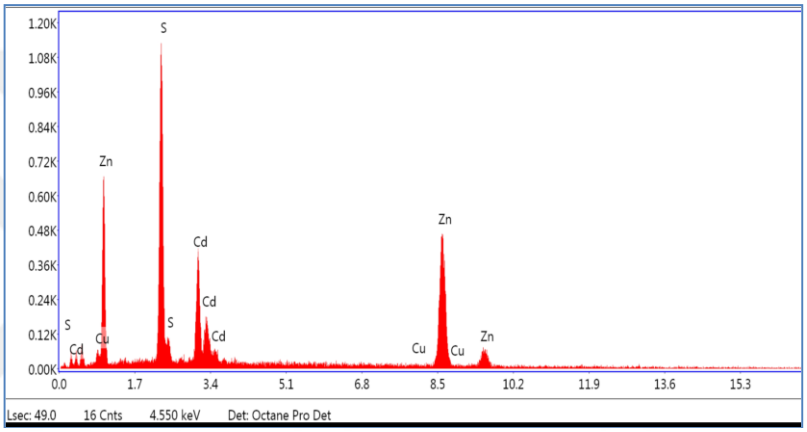


Figure 3.17. EDS spectrum image of as grown CdZnS: Cu nanopowder

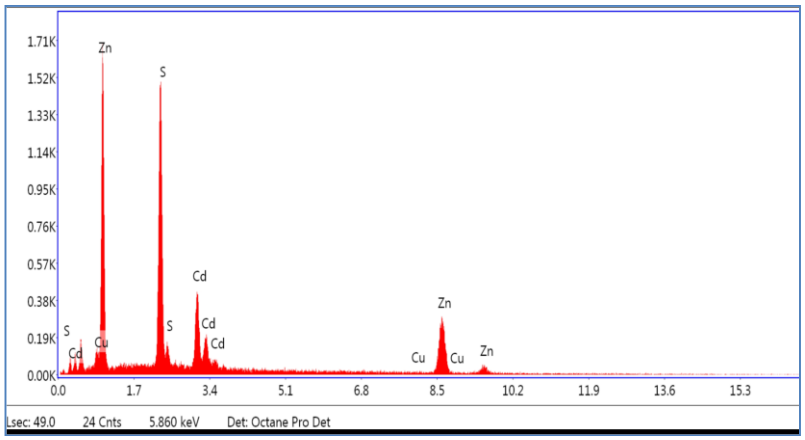


Figure 3.18. EDS spectrum image of nanopowder CdZnS: Cu for sample annealed at 200 °C

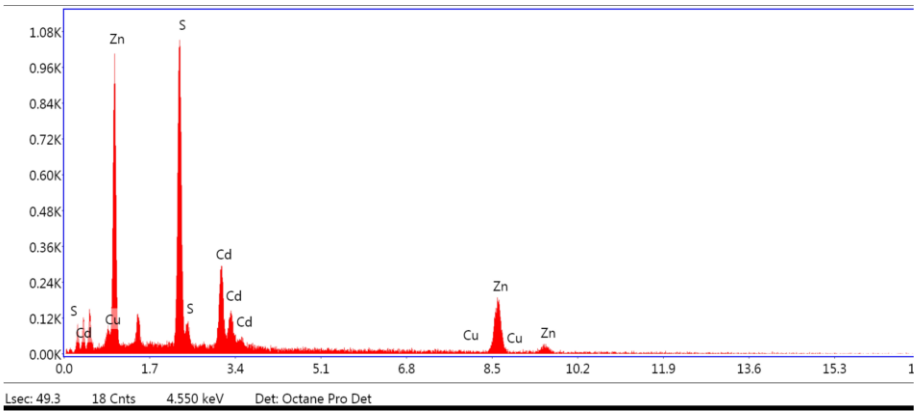


Figure 3.19. EDS spectrum image of nanopowder CdZnS: Cu for sample annealed at 300 °C

3.6.4. UV-Vis measurements of nanopowder CdZnS: Cu

Energy band gap has been measured and calculated from precursor solution of CdZnS: Cu. Because it is difficult to apply for the nanopowder. Optical absorption spectra of CdZnS: Cu precursor solution was recorded by using spectrophotometer at room temperature in the visible wavelength ranged from 300 to 1000 nm and shown in Figure 3.20. The absorption was occurred in the blue region which below 330 nm wavelength. Energy band gap has been also calculated with the help of absorption spectra by using Tauc relation (Eq. 2.7).

Optical energy band gap value estimated to be 3.76 eV. This result is in agreement with the literature for CdZnS which deposited by different techniques and conditions.

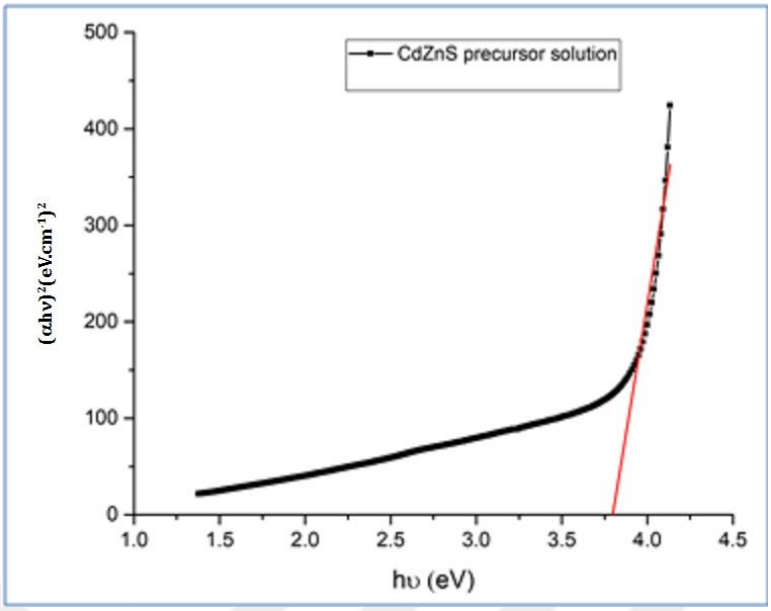


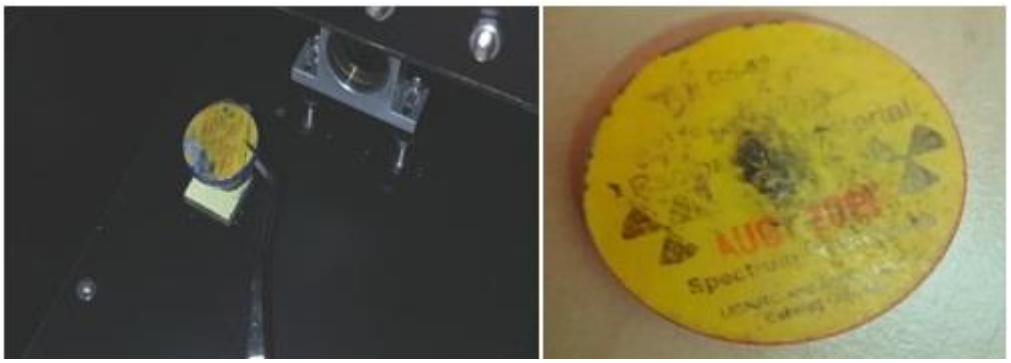
Figure 3.20. Energy band gap determination of CdZnS: Cu precursor solution

3.6.5. Gamma - ray measurements of nanomaterial CdZnS: Cu

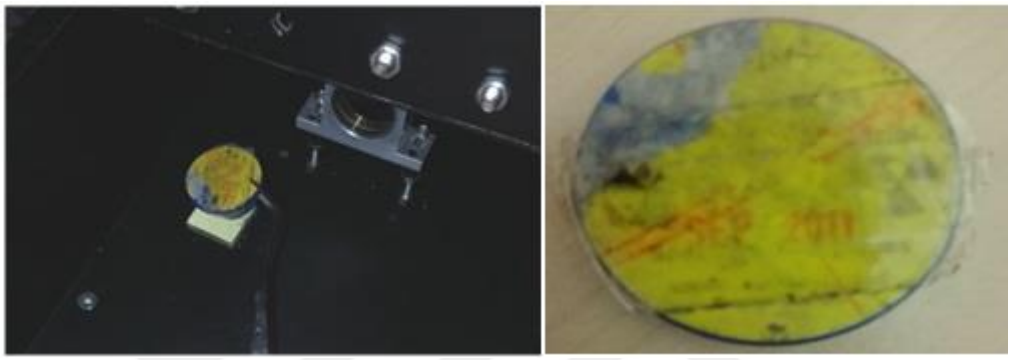
Gamma-ray measurements have been done, by exposing the nanomaterial CdZnS: Cu, as grown sample to the radioactive sources with specific activity as it shown in Table 3.7and Figures 3.21 (a and b), to investigate about the luminescence light, and to determine whether this material has a the potential for gamma-ray photon responding or not.

Table 3.7. Measurements of gamma ray sources

No	Source	Energy (KeV)
1	Cobalt (Co-60)	1333 1173
2	Cesium (Cs-137)	662



a)



b)

Figure 3.21. Images of a) Cobalt-60 and b) Cesium137 radioactive sources

Figure 3.21 showed that, the luminescence light not been observed clearly after exposed nanomaterial CdZnS: Cu sample to the gamma ray radioactive sources cobalt and cesium. This reason can be explained, that the high activity belong both cobalt and cesium as it seen in that Table 3.7 makes the probability of photons energy absorption by electrons very difficult to emitting photon in the visible range that possibly penetrate the material. Suitable thickness of crystal scintillation material shows large absorption efficiency, and take place main role to give a chance for interacting the electrons with the photon of gamma ray it should be (at least 1mm) whereas nanomaterial CdZnS: Cu is low efficiency for absorption of high energy of gamma ray photons due to it has small density proximately 3 μm, this is in agreement with literature reported (Grujić et al., 2013; Akkurt et al.,2014; Salgado et al., 2012).

4. CONCLUSION

The main goal of this work was to produce CdZnS nano material and thin films for X-ray photon detection by different deposition techniques. Pure CdZnS thin films as a reference sample, Cu doped CdZnS: Cu thin films, and CdZnS: Cu nanopowder were deposited to investigate the luminescence light emitting during X-ray photons illumination. Interaction of X-rays with atoms of CdZnS: Cu material cause the excitation process and recombination of this electrons create visible light photons.

CdZnS (un doped) thin film:

XRD measurement has been used to study the structural properties of the material and the measurements show that the material has polycrystalline in nature, cubic structure and the crystal preferential orientation is (111) for grown and annealed samples at 400 °C and 500 °C. The calculation shows that, the average size of the crystal is increased with the increasing of annealing temperature because of reduction of deformation and increasing the grain size, also increasing annealing temperature improved intensity of XRD peaks. SEM measurements showed that, as grown film has smooth surface with a little bit of crakes, and for the sample surface which annealed at 400 °C the cracks closed with each other, and for the sample annealed at 500 °C the surface got disruptive due to oxidization effect.

EDS measurement showed that, all the compounds are proximately composed with chemical stoichiometry (Cd+Zn/S =1: 1), with the ratio of Zn: Cd = 3: 1 according to the amount of molarity was been used.

UV-vis measurements showed that, the absorption was occurred in the blue region which exhibited lower absorption in the longer wavelength and band gap values ranged in between 3.01 - 3.12 eV for as grown and annealed samples, respectively. This demonstrates that, the band gap is increased with increasing

annealing temperature, and it is in agreement with the previous reported literature.

Cu doped CdZnS: Cu thin film:

XRD measurements show that the thin film has polycrystalline in nature, cubic structure, the crystal preferential orientation is (111) for asgrown and annealed samples at 400 °C and 500 C°, respectively. A weak luminescence light has been noticed under X-ray photons illuminations for grown sample and then disappeared when annealed up 400 °C due to effect of oxidization on the activator ions (copper ions). Because of the same reason intensity of peaks did not improved very well after annealing up 500 °C and the material got disruptive which effected on the average of grain size, where the oxidization effect on the average size of crystal.

SEM system measurements showed that the surface of material covered with cluster particles, and their size was around 128 nm for as grown sample and annealed sample at 400 °C, after annealing at 500 °C. The shape of surface has been changed to be covered with small beads rich in zinc compound due to the effect of thermal energy, which can be changed the physical properties of the material.

EDS measurements showed that all the compounds are proximately composed with chemical stoichiometry (Cd+Zn/S =1: 1), and the ratio of Zn: Cd = 3: 1 according to the amount of molarity which has been used. It was noticed also for sample annealed at 500 °C that rich in zinc compound due to effect of thermal energy changed the vertical homogeneity of the film, However, XRD, SEM and EDS measurements are in agreement with each other. UV-Vis measurements showed that the material has a band gap ranged in between 2.50 - 2.35 eV. It was observed that, band gap values are decreased with increasing of annealing temperature, due to the effect of copper oxide structure which generated inside the main structure of CdZnS thin film. This result is in agreements with previous reported literature.

CdZnS: Cu nanopowder:

According to the results obtained from the previous thin film productions, and the effect of annealing temperature on the chemical and physical properties of material, deposition substrate temperature was set at 175 °C. XRD measurements show that the nanopowder CdZnS: Cu has a polycrystalline in nature, cubic structure, the crystal preferential orientation is (111) for as grown and annealed samples at 200 °C and 300 °C, respectively. Clear luminescence light has been noticed for as grown samples and annealed at 200 °C. The intensity of luminescence has been disappeared when annealing reached at 300 °C which demonstrates us the luminescence efficiency of nanomaterial CdZnS: Cu is decreased at high temperature, due to the oxidation. However, intensity XRD peaks were improved with increasing of annealing temperature, also the average of grain size has been increased.

SEM measurements showed that the surface has nano particles whose size ranged around 145 nm for as grown samples and annealed at 200 °C and then converted to the bulks shape after 300 °C due to the effect the thermal energy.

EDS measurements showed that all the compounds are proximately close to chemical stoichiometry with (Cd+Zn/S =1: 1), and the ratio with Zn: Cd=3: 1 according to the amount of molarity were been used for each element, which exhibit that the precursor solution has been deposited on the glass substrate in aimed ratio.

UV-vis measurements for precursor solution of CdZnS: Cu has been done, because it was difficult to do it for powder form. The measurements showed that the absorption was occurred in the blue region which below 330 nm wavelength and band gap value calculated as 3.76 eV for nanopowder CdZnS: Cu

Finally, gamma ray measurement has been done by exposing the grown sample of nanomaterial CdZnS: Cu to the radioactive sources type Cobalt Co-60 and Cesium Cs-137 and showed low efficiency for responding to the gamma ray

photon and the luminescence light never been observed clearly, due to the high activity belong the sources, this can be clarified that nanomaterial CdZnS: Cu is suitable for low energy for at 8 keV.

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