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Thermal Annealing Effect on Optical and Electrical Properties of Zinc Selenide (ZnSe) Thin Films

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Abstract: The impact factor of ZnSe thin films in an aqueous solution of zinc acetate and hydrazine hydrate (HH) using the non-toxic complexing agent EDTA along with the films were annealed at 200, 300, and 400°C. This research aimed to employed XRD analysis, optical measurements, and electrical resistivity measurements to study the ZnSe thin films, respectively. The use of these complementary techniques allowed for a compressive understanding of the effect of annealing on the physical properties of the films. The ZnSe thin films are annealed in an oven at various temperatures which are characterized by structural and optical properties. An increase in annealing temperature distorted the nanocrystillinity and made the ZnSe thin films amorphous. The variation of resistivity indicates the semiconducting nature of the thin film. The electrical resistivity of the films decreases with increasing annealing temperature. In this study, the Band gap of ZnSe decreases from 2.8eV to 2.65eV with the increase in temperature and decreases for as-deposited to 2.5eV. As a result of this research ZnSe is used for certain applications, it has been widely utilized in various optoelectronic devices such as thin film solar cells, green-blue light emitting diodes, lasers, photo-luminescent, and electro-luminescent devices.

Keywords: Chemical Bath Deposition, ZnSe Thin Film, Band Gap, Solar Cells

1. General Introduction

The physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source and it is very expensive than the chemical deposition technique, whereas chemical deposition techniques are very cheaper than physical deposition which depends on a certain specific reaction [4]. Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. A thin film is defined as a low-dimensional material created by condensing, one-by-one atomic/molecular/ionic species of matter [26]. Chemical bath deposition techniques have proven to be useful and important deposition techniques for the synthesis of various functional metal chalcogenide devices [5]. Due to their role in the fabrication of electronic devices semiconductors are an important part of our lives.

1.1. Semiconductors

Semiconductors have made possible the advent of integrated circuitry that has revolutionized the electronics and computer industries [4]. The two general classifications of semiconductors are the elemental semiconductor materials, found in-group IV of the periodic table, and the compound semiconductor materials, most of which are formed from special combinations of group III and group V elements [6]. In addition, Semiconductors can be grouped into intrinsic and extrinsic Semiconductors (Figure 1). An intrinsic semiconductor is a material with no impurity atoms present in the crystal. An extrinsic semiconductor is defined as a semiconductor in which controlled amounts of specific doping effects or impurity atoms have been added [7].

Recently, the group II-VI compounds semiconductor thin film (e.g. CdS, ZnS, CdSe, ZnSe) have received intensive attention due to their application in thin film solar cells, optical coatings, optoelectronics devices, and light-emitting diodes [19]. This paper will focus on one of the most important compound semiconductor materials, ZnSe. Zinc Selenide (ZnSe) is a relatively wide direct band gap (2.7eV) group II-VI compound semiconductor. Zinc Selenide (ZnSe) is a metal chalcogenide semiconductor [21].

1.2. Compound Semiconductor

According to the findings of the research [8, 25] compound semiconductor is a semiconductor made from two or more elements of group III and V of the periodic table (such as GaAs) that have properties very similar to their group IV counterparts (table 1). While the large band gap II-VI compound semiconductors are important materials for the fabrication of infrared detectors [17].

Table 1. *Chemical properties of Zinc Selenied [11].*

Chemical Formula	ZnSe
Molecular Weight	144.35
Group	Zinc-12 and Selenium-16
Crystal structure	Cubic

1.3. General Properties and Application of Zinc Selenide (ZnSe)

Zinc selenide is a light yellow binary solid compound that rarely occurs in nature (table 2). As shown (tables 3 and 4) the thermal and mechanical properties of Zinc Selenide is chemically inert and highly pure material largely found in the mineral satellite [24].

Table 2. *Electrical properties of Zinc Selenide [11].*

Dielectric constant	9.2
Band gap	2.7ev
Electronic mobility	540cm2/vs
Hole mobility	28cm2/vs

Table 3. *Thermal properties of Zinc Selenide [11].*

Heat of formation	422 KJ/mol
Thermal expansion coefficient	720 μm/m°C
Specific heat capacity	0.339 J/g°C
Thermal conductivity	0.339 J/g°C

Table 4. *Mechanical properties of Zinc Selenide [11].*

Melting point	1517°C
Density	5.42 g/cm^3
Young's modulus	67.2 Gpa
Bulk modulus	40 Gpa
Poisons ratio	0.28

1.4. Annealing of the Thin Films

Annealing is the heat treatment of materials at elevator temperature aimed at investigating or improving their properties [9].

1.5. Research Objectives

1.5.1. General Objective

The General objective of this work is to study thermal annealing effect on physical properties of ZnSe thin films prepared by chemical bath deposition technique.

1.5.2. Specific Objective

1) To synthesize ZnSe thin films by using chemical bath deposition technique.
2) To anneal the thin films at different temperature.
3) To investigate the effect of annealing on structural, optical and electrical properties of ZnSe thin films.

1.6. Justification of the Research

Semiconductor devices have revolutionized the way we work and live. One reason why semiconductors have become the choice material for the electronics industry is the existence of highly sophisticated growth techniques [16]. These attributes have made them so attractive to researchers and technologists. Microstructures of thin films have been observed to differ from the bulk material of similar composition and can vary depending on the growth conditions. In the last decade, ZnS thin film much attention has been focused on the synthesis of group II-VI semiconductor materials due to their important applications in catalysis, optical devices, and magnetic field for large area deposition of the compound semiconductor produced by CBD. But recently ZnSe is one of the substitutes other than ZnS, having better lattice parameter conformity, non-toxicity, and a good conduction band that may transfer the high energy photons to the absorber layer of the solar cells [12]. Due to these, the authors were interested to investigate the effect of annealing with different temperatures such as 200°C, 300°C, and 400°C on ZnSe thin films at the reported conditions. As far as the author's knowledge there was no similar report. This research presents the definition of thin films, the application of thin films, and the review of the literature on Chemical Bath Deposited ZnSe thin films.

2. Review of Related Literature on Chemically Deposited ZnSe Thin Films

Many researchers have reported that there is an appreciable shift of band head with the size of ZnSe when the particle size changes from bulk to nanosize (Figure 2). According Ikhioya I. Lucky1 et al. [14] synthesized ZnSe thin films by CBD method and they revealed that the films are amorphous also analyzed the deposition of ZnSe and HgSe thin films by the chemical bath deposition technique [8, 15]. According to Cullity, D. [11] the result revealed the presence of some small nanocrystalline particles in the reaction. Maney researchers studied zinc selenide thin films by using the reducing environment in the chemical growth [4, 18, 22]. Chemical bath deposition of zinc selenide (ZnSe) thin films as a mixture of non-toxic complexing agent trisodium citrate (Na_3-citrate) were analyzed by the research [1, 4].

3. Methodology

This chapter briefly discussed the basic principle of CBD and concepts of solubility products, experimental procedures, reaction mechanisms, and thin film deposition techniques.

3.1. Thin Film Deposition Techniques

Thin films can deposit on a substrate by thermal growth or by vapor deposition. Deposition technology is well regarded as the major key to the creation of devices such as computers since microelectronic solid-state devices are all based on material structures created by thin film deposition [2]. The chemical bath deposition (CBD) method is the one because it does not require sophisticated instrumentation [7]. It is relatively cheap, simple to handle, convenient for large-area deposition, and capable of yielding good-quality thin films. In the present work, the researcher focused on the chemical bath deposited technique, which is used for the preparation of ZnSe thin films (Figure 4). The influences of annealing on the properties are in demand for a better understanding and improvement of the properties of ZnSe (Figure 3).

3.2. Chemical Bath Deposition Technique

The CBD works on the principle of the controlled precipitation of the desired compound from a solution of its constituents (Fisher, and Visoly, 2003). The precipitation is observed in solution only when the ionic product exceeds the solubility product. Even though there are four ways by which the growth of the thin films in the CBD technique can proceed simple ion-by-ion mechanism, Simple cluster (Hydroxide) mechanism, Complex decomposition ion-by-ion mechanism, and Complex decomposition cluster mechanism [1]. This deposition technique is mostly used for the preparation of metal chalcogenide thin films (Chanrdamohan et al., 2004). When an X-ray beam hits the atom, electrons of that atom will oscillate in the frequency of the beam [9, 21]. The variations of electrical resistivity of the as-deposited and annealed ZnSe films with temperature were examined by using a four-point probe technique. The electrical resistivity of the films has been determined by using the following relation [13].

The concentration of complexing metal ion decreases with increases in the complexing ion concentration. According to [18] the rate of reaction and precipitation is reduced, resulting in a larger thickness of the thin film reaction chemicals are mainly used the concentration of complexing metal ions.

3.3. Materials Used

To synthesize, ZnSe thin film the experimenter used the following materials. Water distilling apparatus used to distill water (Figure 1). A table stand was used to settle materials and chemicals on it. Distilling water was used as a solvent in all experiments, a PH reading instrument was used to record the PH of the solution, a Hot plate (heater) was used to heat the solution, a Magnetic stirrer was used to stir the solution, and Ordinary glass substrates in different size were used to film deposit on it, Thermometer was used to record the temperature of the solution, Beakers with different size were used to measure the amount chemicals, Electronic beam balance was used to measure the number of masses (Figure 1).

a b

Figure 1. *(a) purchased commercial chemicals and (b) Oven Furnace observed in physics laboratory class.*

4. Result and Discussion

In this research the results and discussions on the reaction mechanisms for ZnSe thin film deposition, Optical characterization, and structural characterization. We summarized the result of this research in (table 5) below.

Table 5. *The summary of experimental detail for the synthesis of Zinc Selenied (ZnSe).*

Sample preparation	Zinc Acetate	Hydrazine	EDTA	Distilled Water	Sodium Selenosulphate	Total volume
As deposited	7ml	4.2ml	5.6ml	44.2ml	14ml	75ml
Annealed at 200°C	7ml	4.2ml	5.6ml	44.2ml	14ml	75ml
Annealed at 300°C	7ml	4.3ml	5.69ml	45.2ml	14.2ml	76.39ml
Annealed at 400°C	8ml	4.8ml	5ml	44.2ml	15ml	77ml

4.1. Reaction Mechanism for ZnSe Thin Film Deposition

ZnSe deposition occurs when ionic products of Zn^{2+} and Se^{2-} ions exceed the solubility product of ZnSe (Figure 2). A strong reducing agent such as ammonia (NH3) is required to deposit ZnSe from selenosulphate baths [20, 27]. The ammonia presumably reduces the selenosulphate to give a high enough Se^{2-} ion concentration to allow ZnSe to form (Figure 2).

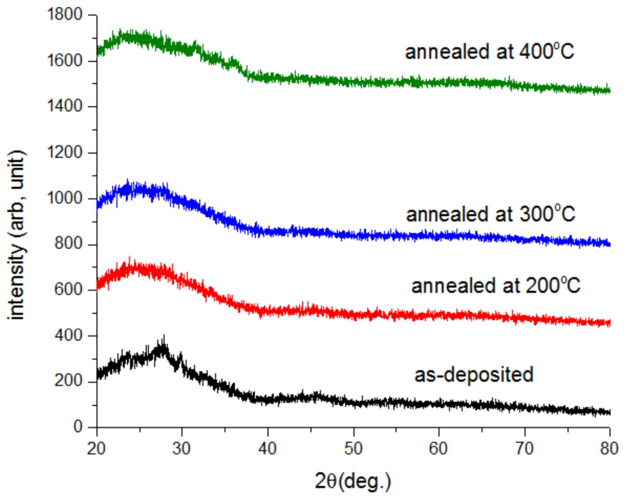


Figure 2. *XRD result for ZnSe thin films with deposited and annealed at different temperature.*

4.2. X-ray Diffraction Analysis

According to Fisher, B. and Visoly, I. [13] the X-ray diffraction studies were made with diffract meter using radiation (λ=1.5406 Å, with 40 KV and 30 mA). The various structural parameters such as lattice constant, crystal size, and strain have been evaluated (Figure 3). The data were collected over a 2θ range of 200- 800. This implied that annealing has decomposed the nanocrystalline as deposited (Figure 3). It was observed that as-deposited and annealed at 673K have the highest absorption than annealed at a temperature of 200°C and 300°C but have low transmission.

4.3. Optical Absorption Studies

The most remarkable property of the optical absorption spectrum is its sensitivity to the size of the nano regime [3]. We observed the optical characterization, films without annealing present an optical band gap of 2.5 eV, and after annealing treatment, the band gap of the films can be modified to 2.8eV, 2.7eV and 2.65eV when increasing the annealing temperature to 200°C, 300°C but at 400°C respectively (Figure 4). The XRD patterns of deposited and annealed (at 200°C, 300°C, and 400°C) ZnSe thin films are shown in (Figure 4).

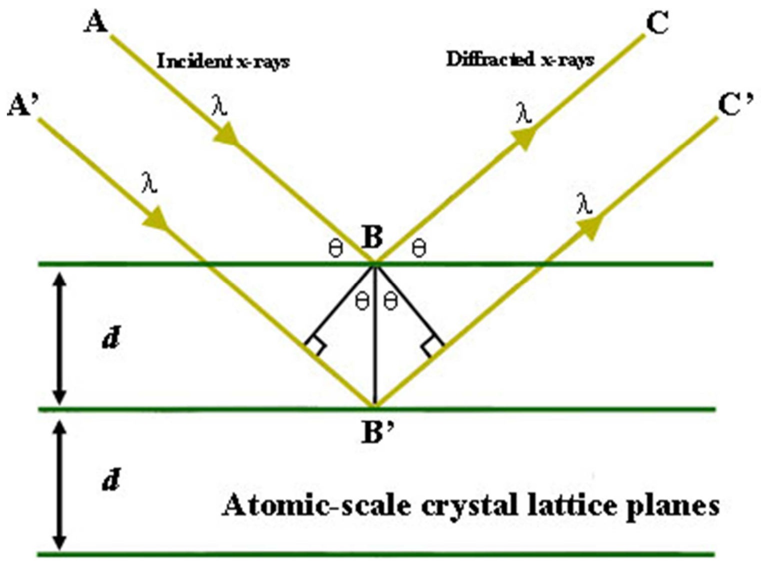


Figure 3. *Schematic of XRD detector and Bragg's geometry of X -rays reflection of the thin film sample [23].*

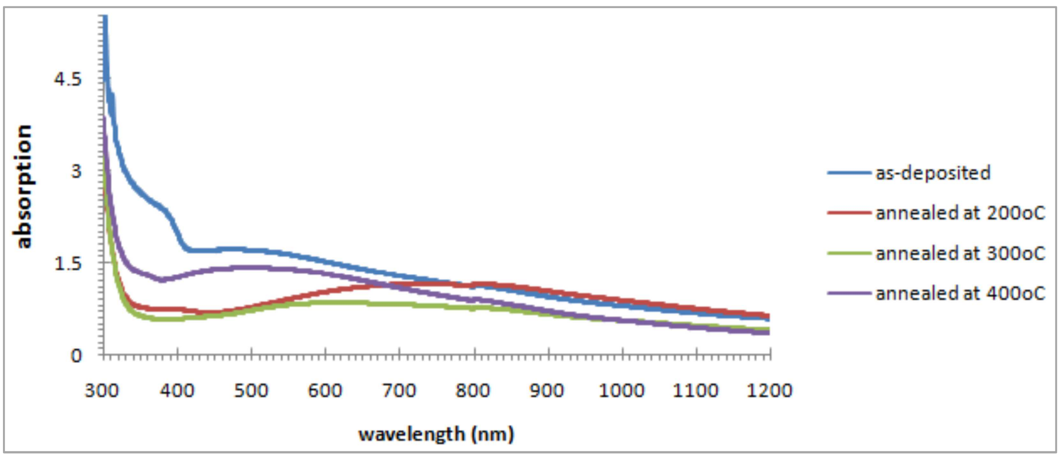


Figure 4. *Plot of as-deposited and annealed (at 200°C, 300°C and 400°C) absorption with respect to wavelength.*

4.4. Electrical Resistivity Studies

The effect of size on the electrical conductivity of nanostructures is increasing in the conductivity of ZnSe thin films may be due to the decrease in grain boundary scattering (Figure 5). As shown in (Figure 6) ZnSe annealed at 200°C, 300°C, and 400°C have a resistivity (-5x10^2MΩ, 5x10^2MΩ, and 2.5x10^2MΩ) respectively (Figure 6 a, b and c). However, the annealed films have not shown visible peaks (Figure 6 a, b and c). Thus the annealed films have amorphous nature (Figure 6).

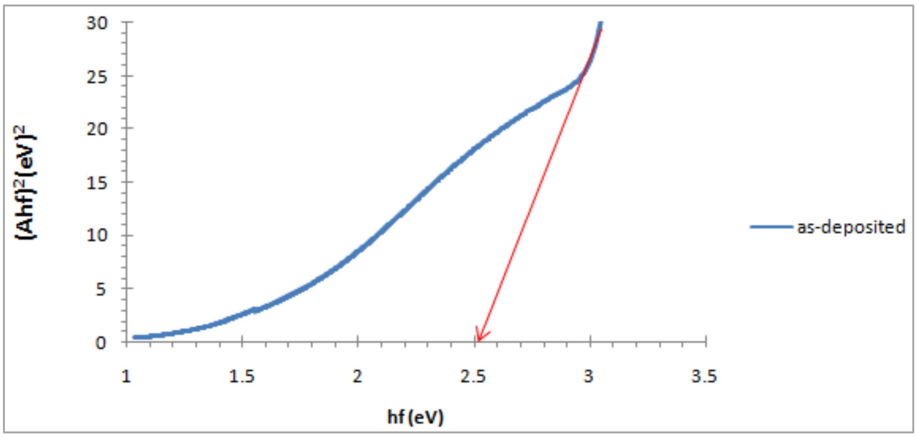
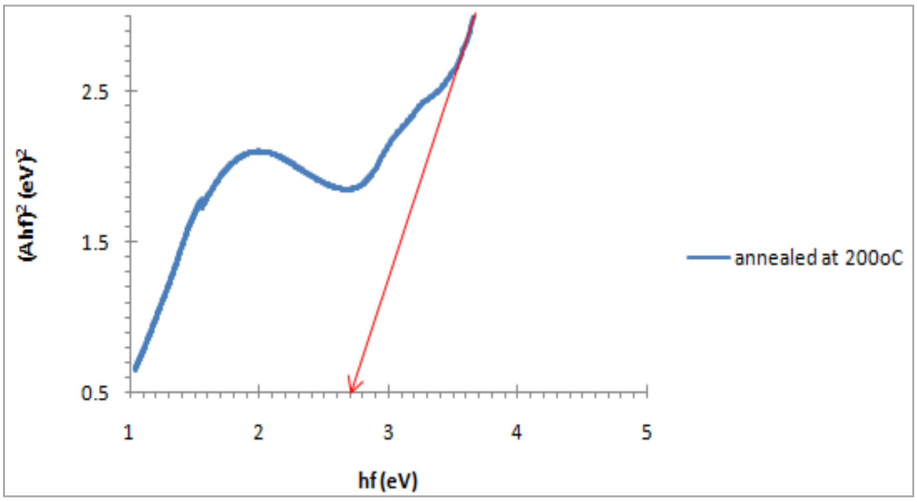
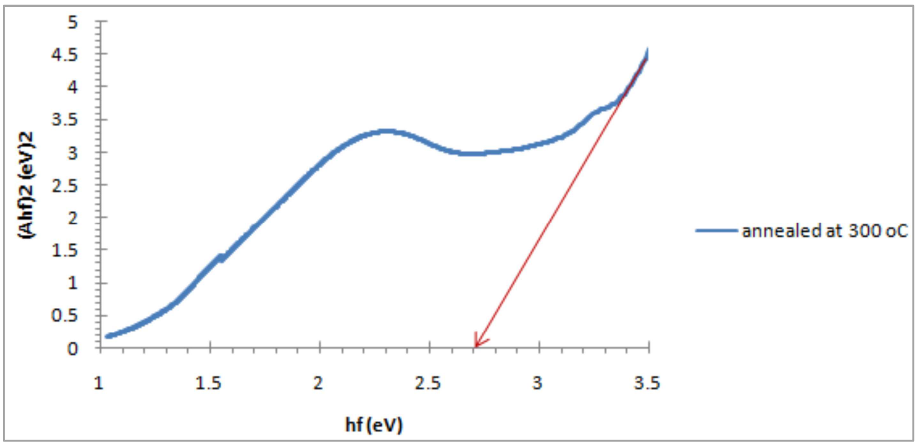


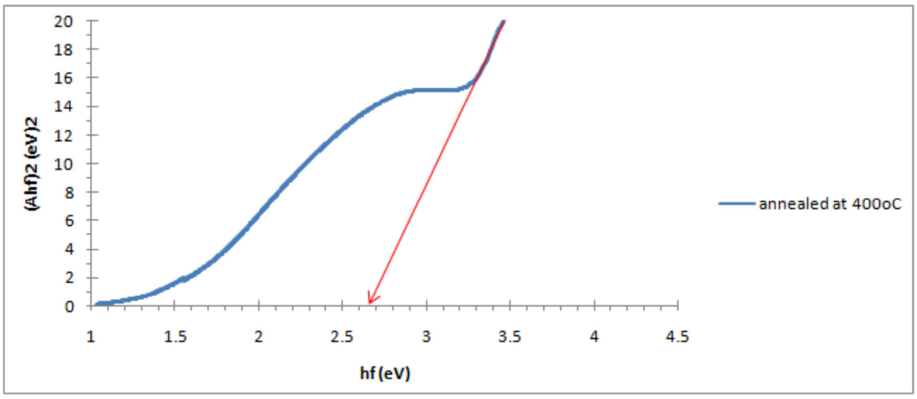
Figure 5. *The band gap for as-deposited thin film.*



a



b



c

Figure 6. *(a–c). The Band gap for as-deposited and annealed films.*

5. Conclusion

This research is of scientific and methodological importance as it explores the fundamental properties of ZnSe thin films and provides insights into the effectives of annealing on their physical properties. The study's findings could have practical implications for the development of novel optoelectronic devices. The authors employed XRD analysis, optical measurements, and electrical resistivity measurements to study the ZnSe thin films, respectively. The use of these complementary techniques allowed for a compressive understanding of the effect of annealing on the physical properties of the films such as solar cells, LEDs, and lasers. We conclude that the result of this study ZnSe is used for certain applications, it has been widely utilized in various optoelectronic devices such as thin film solar cells, green-blue light emitting diodes, lasers, photo-luminescent, and electro-luminescent devices.

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References

[1] Agawane Rowland, W. H., Hughes (2014). Complex decomposition ion-by-ion mechanism, and Complex decomposition cluster mechanism v17, (20).

[2] Aixiang Schetzina, J. F and Deshmukh, W., (2013). Zinc selenide thin films by using the reducing environment in the chemical growth V 14, pp2259.

[3] Boney, C., Yu, Z., Rowland, W. H., Hughes, W. C., Cook, J. W., Schetzina, J. F. (2006). II–VI Blue/Green laser diodes on ZnSe substrates. J. Vac. Sci. Technol. B, 14, 2259-2262.

[4] Callister, W. D., and Rethwisch, D. G. (2007). Materials science and engineering: an Introduction (Vol. 7): Wiley New York.

[5] Chopra, K. L., Kainthla, R. C, Pandya, D. K., and Thankoor, A. P., (2010)." Physics of thin films" volume 2, pg. 201.

[6] Chung, D. D. (2011). Applied materiasls science: applications of engineering materials.

[7] Neamen. D. A, and Pevzner, B. (2003). Semiconductor physics and devices: basic Principles, (Vol. 3): McGraw-Hill New York.

[8] Chen, D. Zhang, G. Zhai, Zhang J. Cardona Chem. Phys. (2010) Fundamentals of Semiconductors: fourth edition, 421.

[9] Chanrdamohan, A. Kathalingam, K. Kumar, D. Kalyanaraman, and T. Mahalingam, (2004), "Studies on Electro synthesized Semiconducting ZincSelenide Thin Films," Ionics, vol. 10, pp. 297. Electrodeposited Zinc Selenide Films and Their Characteristics," Chalcogenide Lett., vol. 6, pp-51, 2009.

[10] Chopra, K. and Kaur, I. Thin film Device Application, PlenumPress, (2003) Fundamentals of Semiconductors: fourth edition, 201.

[11] Cullity, D. "Elements of X-rays Diffraction", 3rd Edition, Prentice Hall, (2001).

[12] Dappadwad T, M. and Charita Mehta et al., (2013) the result revealed the presence of some small nanocrystalline particles in the reaction 17 (1): 140-219.

[13] Fisher, B. and Visoly, I. (2003) "Factors affecting the stability of ZnSe/ CdSe solar cell deduced from stress tests at elevated temperature" Advanced functional Materials 13 (4): 289-299.

[14] Ikhioya I. Lucky1, Okoli D. N and Ekpunobi A. (2017) "International Journal of ChemTech Research." Vol. 12 No. 05, pp 200-211.

[15] Lokhade Yamada, A (2008) Synthesized ZnSe thin films by CBD method and they revealed that the films are amorphous 167-173 (6).

[16] Liangyan Chen, Adachi, H (2009). Deposition of ZnSe and HgSe thin films by the chemical bath deposition technique 41 (9): 1-11.

[17] Mane, R and C. Lokhande (2000) "Chemical deposition method for metal chalgenide thin films" Materials chemistry and physics 65 (1): 1-31.

[18] Mahawela, G. Sivaraman, S. Jeedigunta, J. Gaduputi, M. Ramalingam, S. Subramanian (2012). "II–VI compounds as the top absorbers in tandem solar cell structures", Mater. pp. 283.

[19] Mondel, A., Chaudhuri, T. K., and Pramanik, P., (2013). Solar energy material vol. 7 page 431.

[20] Ohtake, Y., Kushiya, K., Ichikawa, M., Yamada, A., Konagai, M. (2005). Ploycrystalline Cu (InGa) Se2 Thin-film Solar Cells with ZnSe Buffer Layers. Jpn J. Appl. Phys., 34, 5949-5955.

[21] Thirumavalavan, et al. (2016). Synthesized the Zinc Selenide Deposition Technology Materials Chemistry and Physics, Vol. 82, No. 1, pp. 28-42.

[22] Swami, A., (2016), “Thin Film Fundamentals,” New Age International Pvt. Ltd., New Delhi.

[23] Soundeswaran, O. S. Kumar, R. Dhanasekaran, P. Ramasamy, R. Kumaresen and M. Ichimura, (2003), “Growth of ZnSe Thin Films by Electro crystallization Technique,” Materials Chemistry and Physics, Vol. 82, No. 2, pp. 268-272.

[24] Poortmans J. and V. Arkhipov (2009). “Thin film solar cell, fabrication, characterization and Applications.” Phys., 34, 5949-5955.

[25] Venkatachalam, D. Mangalaraj, Sa. K. Narayandass, K. Kim, J. Yi, (2001). "Composition, structural, dielectric and DC characterization.

[26] Witte, D. Hariskos; A. Eicke; R. Menner; O. Kiowsky, M. Powalla (2013). Thin Solid Films, 535, 180.

[27] Wasa, K., Kitabatake, M., and Adachi, H. (2004). Thin film materials technology: sputtering of Control Compound materials: Springer. Nano composites by Sealer method: Journal of Ovonic Research 267-273 (2016).