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XRD and UV-VIS-IR Studies of Chemically-Synthesized Copper Selenide Thin Films

Okereke N.A. [1] **and Ekpunobi A.J.** [2]
[1]Department of Industrial Physics, Anambra State University, Uli, NIGERIA
[2]Department of Physics and Industrial Physics, Nnamdi Azikiwe University, Awka, NIGERIA

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Abstract

Thin films of copper selenide have been prepared by chemical bath deposition method on a glass substrate at room temperature. The structural, optical and electrical properties of the films were investigated by X-ray diffraction, optical microscopeand spectrophotometer. The XRD pattern indicates that this film was crystallized in the structure. The band gap energy was found to be both direct and indirect. The results are analyzed and discussed.

Keywords: Semiconductor, copper selenide, thin film, chemical bath deposition, characterization.

Introduction

Copper selenide is an interesting metal chalcogenide semiconductor material. It exists in many phases and structural forms: stoichiometric compositions such as copper (I) selenide [Cu_2Se], copper (II) selenide [CuSe] and [$CuSe_2$] with various crystallographic forms as well as non-stoichiometric such as $Cu_{2-x}Se$. It has a number of applications in solar cells, super ionic conductors and photo-detectors[1]. Copper selenide is a semiconductor with p-type conductivity, a property useful in the solar cell production. It has both direct and indirect band gap. CuSe hasbeen reported to have a direct band gap of 2.2eV and indirect band gap of 1.4eV by[2]. Copper selenide has also reported to possess a direct band gap of 2.18eV by[3]. The use of these films to form ajunction with n-type semiconductors either as absorber in heterojunction with CdS or as window material in heterojunction with n-Si has been demonstrated and has shown conversion efficiencies of up to 8.8%[4]. Recently, the techniques of thin film growth of this compound has become of interest in fabricating low cost photocells. Thin films of copper selenide can be obtained by variety of techniques like vacuum evaporation[5], chemical bath deposition[6, 7].

Material and Methods

Thin films of copper selenide were depositedona glass substrate using chemical bath deposition technique. The reagents used for the deposition of CuSe were copper tetraoxosulphate (VI) [$CuSO_4$], selenium trioxosulphate (V) [$SeSO_3$], sodium thiosulphate [NaS_2O_3] as a complexing agent and ammonia (NH_3) for pH adjustment. The reaction bath was made up to 50ml and the deposition was allowed at room temperature. The cleaned glass substrate was vertically immersed in the reaction bath at room temperature. The growth parameters such as the deposition time and volume of ammonia were varied to optimize the growth. After the end of every deposition time, the substrate was taken out of the reaction bath, washed with distilled water and dried in air.

The equations governing the reaction and deposition of CuSe film are:

$$CuSO_4 + Na_2S_2O_3 \Leftrightarrow [Cu\,(Na_2S_2O_3)]^{2+} + SO_4^{2-}$$
$$[Cu\,(Na_2S_2O_3)]^{2+} \Leftrightarrow Cu^{2+} + Na_2S_2O_3$$
$$SeSO_3 + OH^- \Leftrightarrow HSe^- + SO_4^{2-}$$
$$Cu^{2+} + OH^- + HSe^- \Leftrightarrow CuSe + H_2O$$

The structural properties of the films were investigated by X-ray diffraction using CuK_α. (λ=1.5406A) radiation.Photomicrograph and optical absorption of the films were measured using an Olympus BH_2-UMA microscope and a Janway 6405 UV-VIS spectrophotometer at normal incident of light in the wavelength range of 200nm -1100nm respectively. The thicknesses of the films were estimated using optical methodby[8].

Results and Discussion

Figure-1 shows the micrograph obtained for the CuSe films. Isolated islands are found and some larger sports are also observed. However, they are actually the aggregate of the smaller island. The film is found to exhibit surface revealing grains well covering the substrate. The films had good adherence to the substrate. Figure-2 represents the x-ray diffraction pattern of CuSe films and it reveals the existence of (110), (200), (210), (012), (130), (310), (040), and (411) planes of reflections of a clinochalcomerite structure which is monoclinic with composition CuSe. The patterns show well defined peaks suggesting that the films are crystalline. The lattice parameters from the XRD results were found to be **a**=8.17Å, **b**=8. 61Å and **c** = 6.2Å. It was also shown from the XRD result that the percentage of copper is less than that of selenium. The crystallite size of the films was calculated using the Scherer formula. The calculations using the peaks at $2\theta=15.03^0$ (110), $2\theta=24.30^o$ (210) and $2\theta=30.53^0$ (012) in figure-2 indicate an average grain size of 3.78Å. The observed peaks are in a very close agreement with the reported values by[9]who reported the XRD pattern showing (102), (111) and (110) planes of mineral klockmannite

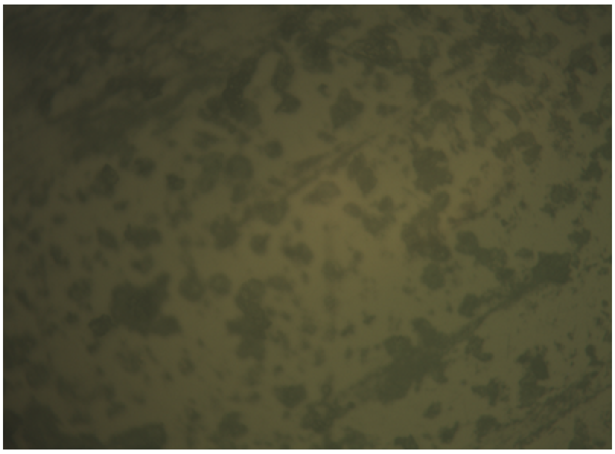

Figure-1
Photomicrograph of CuSe prepared at 300K

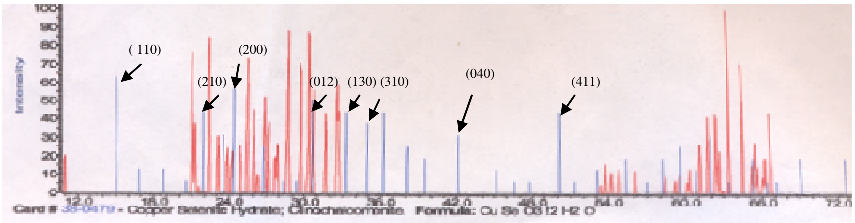

Figure-2
X-ray diffraction pattern of CuSe

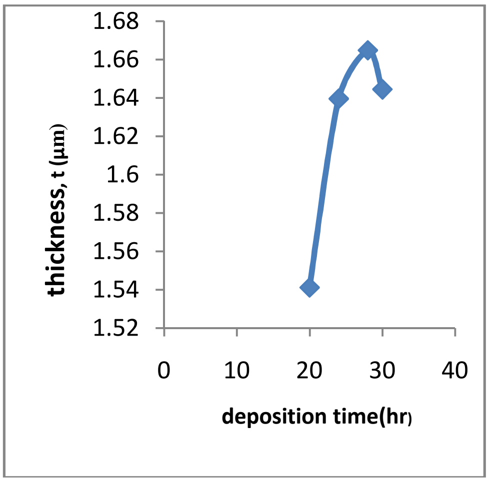

Figure- 3a
Variation of thickness versus time

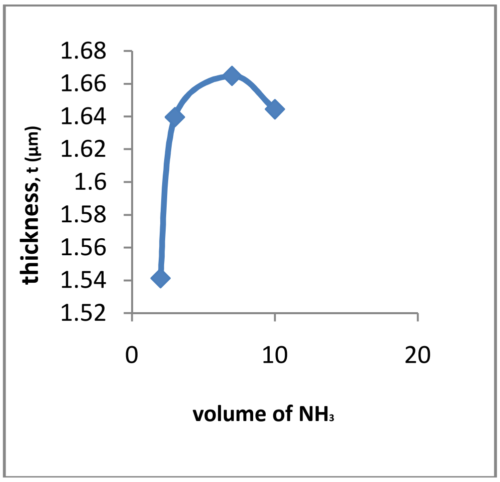

Figure-3b
Variation of thickness versus vol. of NH_3

Which is hexagonal with composition CuSe prepared using chemical bath deposition technique. The x-ray diffraction pattern of a single phase Cu_2Se with peaks corresponding to (111), (220), (311), (400) and (331) of cubic phase was reportedby[3]using brushelectroplating technique. Copper selenidefilm of orientation (111), (022), (113), and (004) which corresponds to the cubic phase of Cu_2Se using CBD method was obtained by[10]. The XRD pattern of copper selenide obtained through the chemical precipitation method with peaks at (101), (102), (006), (121), (108), (201), (202) and (116) planes of reflections with composition CuSe was reported by[11]. That showing only (102) and (006) reflection of CuSe was obtained by[12].

Figure-3a indicates the variation of film thickness with deposition time. It reveals that the thickness of the CuSe thin film increases as the time of the deposition increased. The maximum film thickness obtained at a deposition time of 28hrs is 1.66µm before decreasing to 1.64µm when the time of deposition further increased to 30hrs. The CuSe thin films deposited for up to 28hrs give maximum thickness (1.66µm) and decrease there after due to the formation of an outer porous layer of CuSe that peels off the outer portion of the film. Chemical bath deposition of semiconductor thin films involves a nucleation/incubation phase followed by a growth phase and a terminal phase [13]. Many chemically deposited thin films peel from the substrate at some stage of the growth phase before reaching the terminal thickness. In the present case, it was discovered that the thickness began to decrease on further increase of time, this is because of the increase in time after reaching the optimum thickness and the CuSe layer begins to peel off from the substrate. This is what led to the drop in the value of thickness from 1.66μm to 1.64μm on further increased of time of deposition from 28 hrs to 30 hrs. Similar behavior occurs in the variation of film thickness with volume of NH_3 of the reaction bath shown in figure-3b. The thickness of the film increases as the volume concentration of ammonia of the reaction bath increases. It reveals that at low concentration of ammonia, the terminal thicknesses of the films are less, which increases gradually with the increase of concentrations and then drop down at still higher concentrations. This behavior is in agreement with the results of [4,14]. CuSe films grown are non-absorbing for most part of the spectra except at the fundamental absorption edge occurring in ultraviolet region and this is shown in figure-4. Using the fundamental relations of photon transmission and absorbance,

$$T \approx \frac{I}{I_\circ} e^{(-\alpha t)} \quad \alpha \approx \ln \frac{(T-1)}{t}$$ where t is the thickness

The increase in the film thickness results in overall decrease in absorbance of the film as shown in figure-4. As earlier mentioned, having a very low absorption of energy makes CuSe useful for optical component in high laser window and multispectral applications providing good imaging characteristics. Transmittance is generally high in all the regions of the electromagnetic spectrum studied while reflectance is low. It was observed that the overall %T increases with the increase in film thickness. It varies from 85%-97%. The high transmittance of the film is brought about by the low absorbance of the film. This is revealed in figsure-4 and figure-5 respectively. The property of high transmittance in all regions makes the films suitable for solar energy collection because if coated on the surface of a solar collector, it will reduce reflection of solar radiation and transmit radiation to the collector fluid.

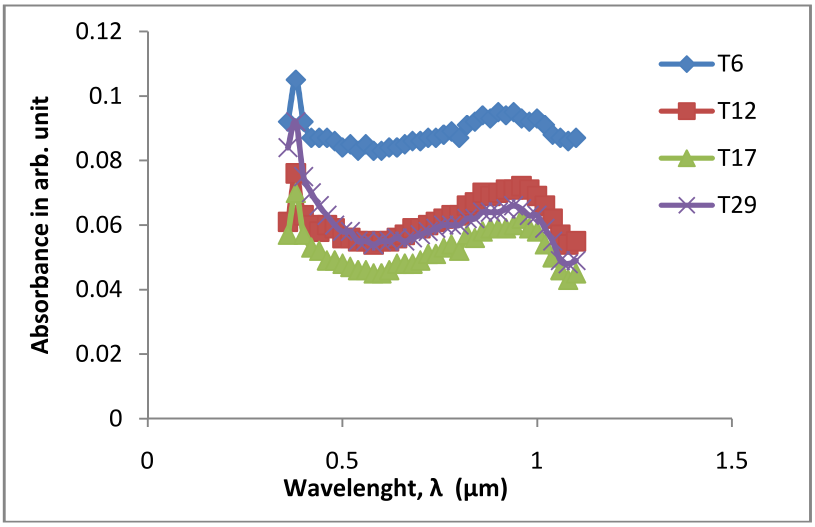

Figure-4
Spectral absorbance of CuSe films

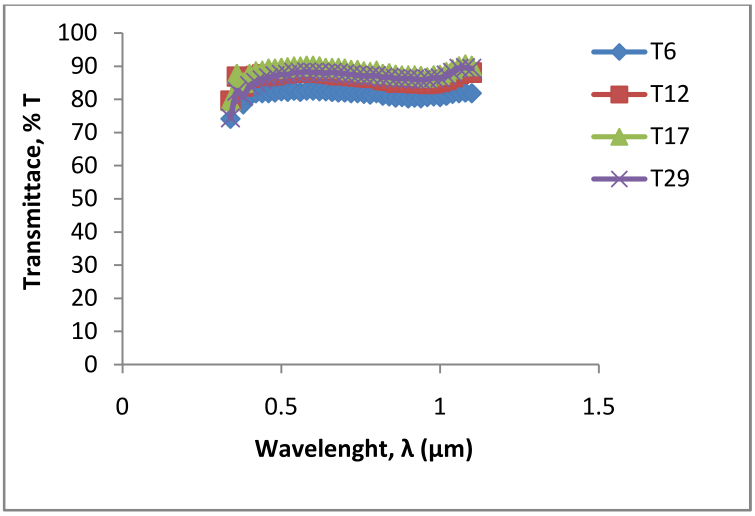

Figure-5
Spectral transmittance of CuSe films

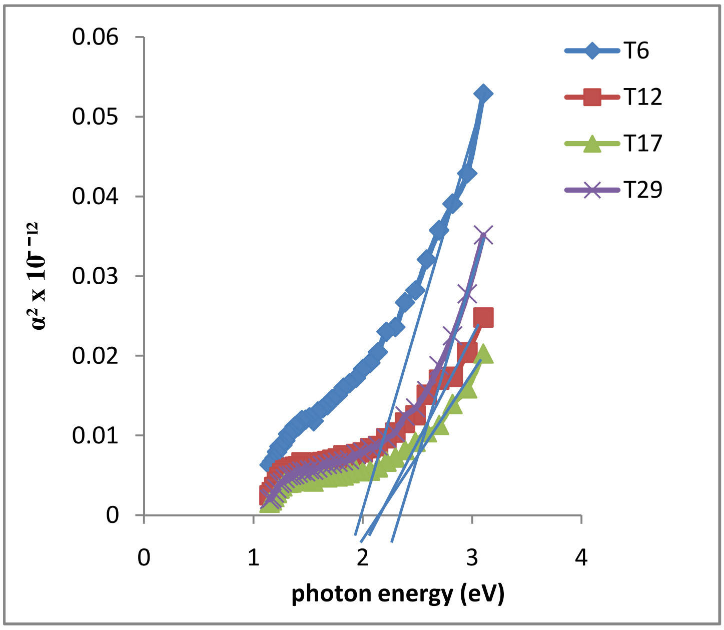

Figure-6a
Plot of α^2 versus photon energy

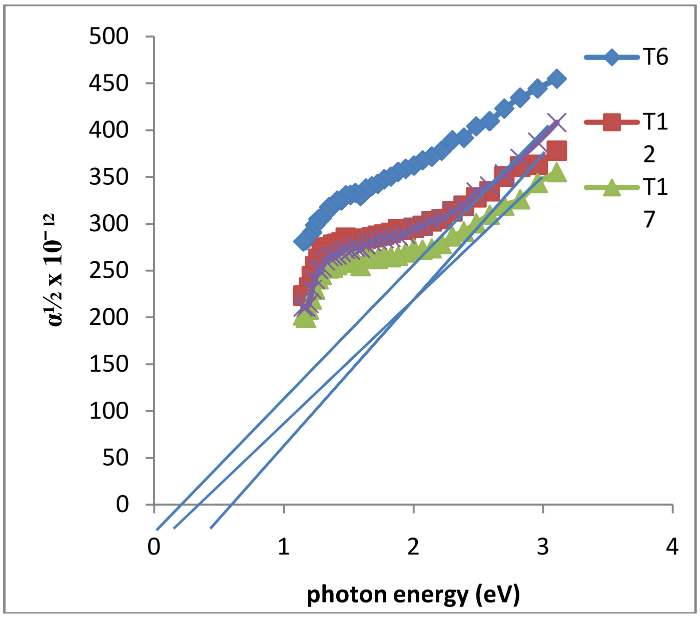

Figure-6b
Plot of $\alpha^{1/2}$ versus photon energy

Figure-6a and figure-6b show that CuSe film has both direct and indirect band gaps obtained from plots of α^2 and $\alpha^{1/2}$ respectively against the corresponding values of photon energy (hυ). Extrapolating the straight line part of the curves in figure-6a and figure-6b to the energy axis where $\alpha^2 = 0$ gives the values of band gap for direct transition and to where $\alpha^{1/2} = 0$ gives the values for indirect transitions. The direct band gap varies in the range of 2.0eV – 2.3eV as the thickness varies from 1.54µm – 1.67µm while the indirect band gap was found to vary from 0.4eV-0.8eV. The band gap values are close to those reported values for chemically deposited CuSe films by[9] whose direct band gap ranged from 2.35eV – 2.38eV and 1.20eV – 1.0eV for indirect band gap. Band gap energy of 2.33eV for chemical bath deposited copper selenide film was reported by[15]. The energy gap values of 2.33eV and 2.20eV respectively of chemically deposited CuSe films were obtained by[10, 16]. A direct band gap value of 2.18eV using brush electroplating and SILAR methods was reported by[3,17]. The optical band gap energy of 1.51eV prepared by electrophoretic deposition technique was determined by[11]. CuSe is one of the most interesting binary wide band gap semiconductors which have potential application in several optoelectronic devices. The wide band gap semiconductors are efficient emitters in the blue to ultraviolet spectra range and are likely candidates to replace materials like Gas, GaN in light emitting laser diode[18].

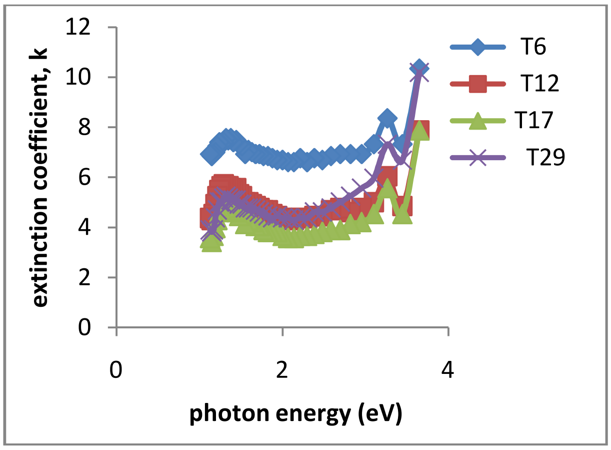

Figure-7
Plot of extinction coefficient versus photon energy

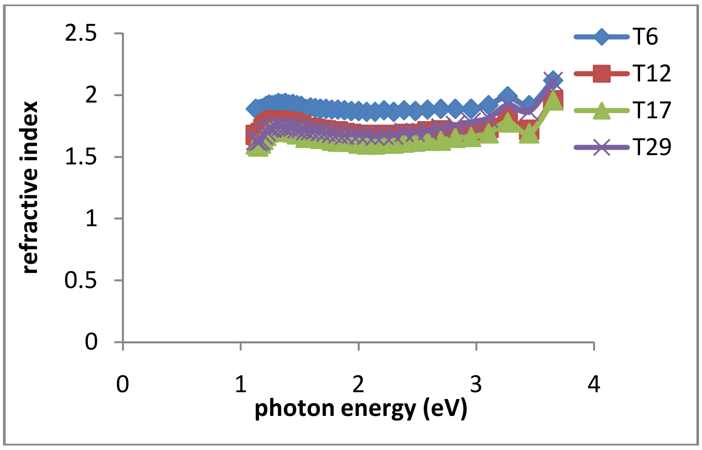

Figure-8
Plot of refractive index versus photon energy

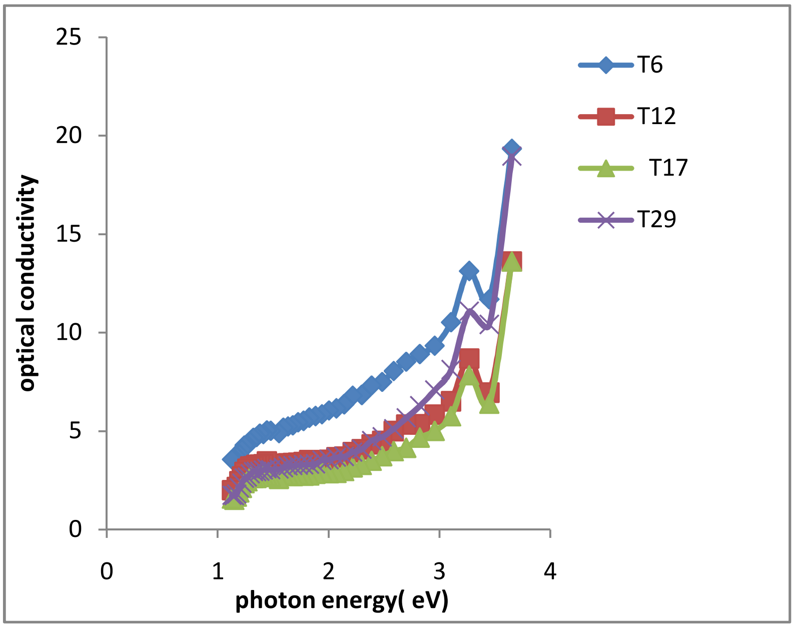

Figure-9
Plot of optical conductivity versus photon energy

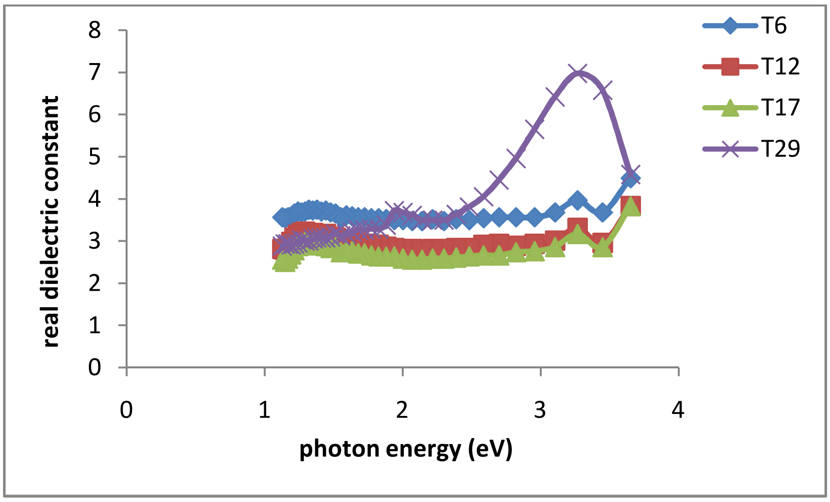

Figure-10
Plot of real dielectric constant versus photon energy

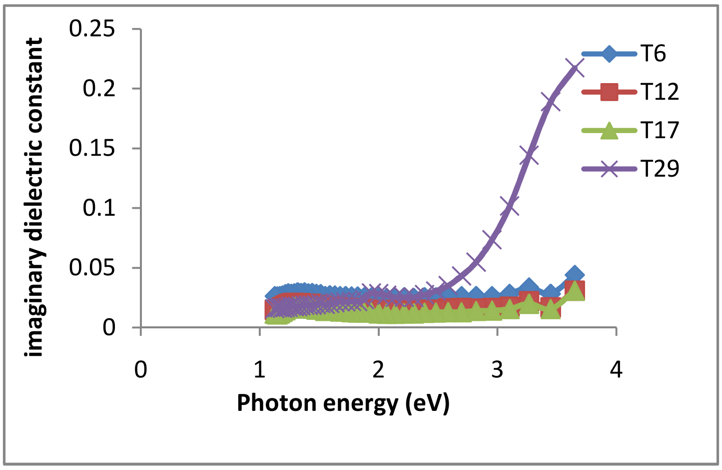

Figure -11
Plot of imaginary dielectric versus photon energy

Table-1
Optical properties and thicknesses of CuSe films grown under varying conditions

Reaction Bath	Dip time t (hr)	pH	Temp. ° C	Average α x10^5 (m^{-1})	Average K	Average n	Average σ_{op} x 10^{14}(S^{-1})	Thickness t (µm)	Direct E_g (eV)	Indirect E_g (eV)
T_6	20	8.0	26	3.42	0.039	1.120	-2.0	1.57	2.00	-
T_{12}	24	9.7	26	2.16	0.037	0.847	-2.1	1.64	2.20	0.80
T_{17}	28	10.5	26	2.01	0.036	0.790	-2.1	1.66	2.20	0.70
T_{29}	30	11.0	26	2.21	0.037	0.849	-2.1	1.64	2.30	0.40

CuSe film grown in this work has high refractive indices which lie between 2.1 and 2.3 and low extinction coefficient of 11 to 9 which is true for non-absorbing films. Theoptical conductivity in figure-9 varies from 55-14. The values of the refractive index, extinction coefficient and optical conductivity were found to decrease with increase in film thickness from 1.54µm to 1.64µm. The high refractive index makes CuSe film suitable for use in optoelectronic devices.

From the calculated refractive index and extinction coefficient of the copper selenide, its dielectric constants can be determined using the relation:

$$\varepsilon_r = n^2 - k^2; \qquad \varepsilon_i = 2nk$$

The real part of the dielectric constant varies from 3.9 to 7.0 and the imaginary part of the dielectric constant varies from 0.05 to 0.22. The thickness and deposition time have effect on both real and imaginary dielectric constants. They were found to decrease with the increase in thickness of the films. Different shapes of the curves for the real part of the dielectric constant were shown in figure-10. This is due to the different effective thickness of the insulator. Table-1 shows the average values of optical properties and thicknesses of CuSe films grown under varying conditions at room temperature.

Since thickness ranged from 1.54 – 1.67µm, it shows that the grown CuSe thin film has a high thickness of approximately 2µm which makes it suitable as a precursor material for forming copper indium selenide (CuInSe) thin films for thin film solar application.

Conclusions

The deposition of CuSe thin films have been successfully carried out in an alkaline medium using chemical bath deposition technique. The studies from XRD and spectrophotometer revealed a direct band gap ranging from 2.0eV - 2.3 eV and indirect band gap ranging from 0.4eV-0.8 eV and an average grain size of 3.78Å

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References

1. Pathan H.M., Lokhande C.D., Amalner D.P. and Seth T., Studies on the chemical bath deposition and physiochemical properties of CuIn chalcogenide thin films, *Appl. Surf. Sci.*, **21**, 48-55 **(2003)**

2. Herman A.M. and Fabick L., J. *Crystal Growth*, **61**, 658-666 **(1983)**

3. Murali R. and John X., *Chalcogenide Letters,* **6,** 683-687 **(2009)**

4. Chopra K.L., and Das S.R., Thin Film Solar Cells, Plenium Press, New York. Transparent conductors – a status review, *Thin Solid Films,* **102**, 1 -146 (**1983)**

5. Chen W.S., Stewart J.M. and Mickelson R.A., *Appl. Phys. Lett.,***46,** 1095-2000 **(1985)**

6. Padam G.K and Rao S.U.M., Preparation of and characterization of chemically deposited CuInS thin films, *Thin Solid Films,***150,** L89 **(1987)**

7. Okereke N .A., Ezenwa I.A. and Ekpunobi A.J., (2010). Effect of bath parameters on thicknesses of chemically deposited copper selenide thin films. *Natural and Appl. Sci. Journ., **11***, 170-173 **(2010)**

8. Theye M., Optical properties of thin films in Chopra K.L. and Malhotra L.K. (eds), Thin Films Technology and Applications, Tata McGraw Hill Pub. Co; New Delhi, 163-173 **(1985)**

9. Garcia V.M. Nair M.T.S., Nair P.K. and Zungaro R.A., Preparation ofhighly photosensitive CdSe thin films by a chemical bath deposition techniques, *Journ. of Semicond. Sci.Technol.,***11**, 427 – 432 **(1996)**

10. Bari R.H., Ganesan V., Potadar S. and Patil L.A., Structural, optical and electrically deposited copper selenide films,*Bull.Mater. Sci.,***32,** 37-42 (**2009)**

11. Fairul S., Abdul R. and Zulkarnain Z., Electrophoretic deposition and characterization of copper selenide thin films, *The Malaysian Journ. of Analytical Sci.,***II**, 324-330 **(2007)**

12. Ming-Zhe X., Yong-Ning Z., Bin Z., Le Y., Hua Z. and Zheng-Wen F., Fabricationand electrochemical characterization of copper selenide thin films by pulsed laser deposition, *Journ. of Electrochem.Soc.,* **153** (12), A2262-A2262 **(2006)**

13. Chopra K.L., Kainthla R.C., Pandya D.K., and Thakoor A.P., Physics of Thin Films **12** ed G Hass et al (New York: Academic) 201-210 **(1982)**

14. Vandeperre L. and Van der Biest O., Electrophoretic deposition of materials, *J. Ann. Rev. Mat. Sci.,* **29,** 327-352 (**1999)**

15. Grozdanov I.,*Semicon, Sci. Technol.* **9**, 6-9 **(1994)**

16. Lakshimi M., Bindu K., Bini S., Vijay Kumer K.P., Kartha C.S, Abe T. and Kashiuraba Y., *Thin Solid Films,***370**, 89 – 92 **(2000)**

17. Pathan H.M. and Lokhande C.D., Deposition of metal chalcogenide thin films by successive ionic layer absorption and reaction (SILAR) method, *Bull. Mater. Sci.,* **27,** 85-111 **(2004)**

18. Gutowski J., Michler P., Ruckman H., Brvnig H. Rowe M., Sebald K., and Voss T., Excitions in wide gap semiconductors coherence, dynamics, and lasing, *Phys. Stat. 501 B,* **234**, 70-82 **(2000)**