**OPTICAL PROPERTIES OF THE ZN1-XCUXSE THIN FILMS PREPARED BY CLOSE SPACE SUBLIMATION TECHNIQUE FOR SOLAR CELL APPLICATION.**

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***ABSTRACT:*** *For the estimation of optical properties of the Zn1-xCuxSe (0.00≤x≤0.15) thin films, the thin films of Zn1-xCuxSe (0.00≤x≤0.15) have been prepared on a glass substrate by the closed space sublimation technique (CSS). Through spectroscopic ellipsometery (SE) different optical properties such as refractive index (n), intrinsic coefficient (K), absorption coefficient (α), band gap energy (Eg), reflectance (R),electrical conductivity () and optical conductivity () have been investigated by varying the copper concentration. From the reflectance and absorption spectra observe that reflectance increases and as well as the absorption coefficient decreases with the increase of copper concentration. At various concentrations of copper the band gap energy (Eg) calculated from absorption spectra, shows that band gap energy (Eg) has direct relation with copper concentration.* Moreover *the deposited thin films have been annealed at different temperature 100, 200 300 400 and 500. The effect of heating treatment (annealing) on the optical properties of the Zn1-xCuxSe thin films has been investigated and observe that different optical parameters such as intrinsic coefficient (k), refractive index (n), reflectance (R), absorption coefficient (α), band gap energy (Eg), electrical conductivity () and optical conductivity ( have been significantly improved with annealing. Reflection and absorption spectra reveals that reflectance decreases while absorption increases with the increase of annealing treatment. At various annealing temperature, the band gap energy (Eg) of the deposited and annealed thin films have been calculated by k spectra through spectroscopic ellipsometery. It is observed that band gap energy of the thin films show inverse relation with annealing temperature while the dielectric constant show direct relation with annealing temperature.*

**Key Words:** Optical Properties, Refractive Index, Absorption Coefficient, Band Gap Energy, Dielectric Constant,

Reflection, Annealing.

**INTRODUCTION**

Thin films of semiconductor compounds of the group II-VI have got a lot of attraction for the past few decades due to their optical and electronic applications on a commercial scale. At the same time, played a vital role in the manufacturing of semiconductor devices. It was observed that ZnSe has wider band gap energy, i.e. (Eg=2.7eV) and an important member of II-VI group semiconductor compounds ZnSe have long been of interest for photoconductivity [1-4]. The thin films of ZnSe are widely used in the preparation of solid state devices such as Xerography, electroluminescent devices, photoconduction, laser material, pizo-electric transducer, optical detectors, photovoltaic solar energy conversion, ultrasonic transducer, optoelectronic devices and thin film transistor electronics [5, 6].

The thin films of ZnSe are used as window layer and buffer layer in the manufacturing of solar cell. ZnSe has a high absorption coefficient and yield high quantum efficiency when used in the visible region. Buffer layers of ZnSe transmit higher energy photons to the absorber layer with high optical transparency of the solar cell [7’8].

Various methods adopted for the deposition of thin films of ZnSe. Following deposition methods have been used for the synthesis of ZnSe thin films, these are molecular beam epitaxy (MBE) [9], spray pyrolysis, vacuum evaporation, and metal organic vapour phase epitaxy. The other important techniques are electrodeposition, the sol-gel, chemical solution reduction process, pulsed laser deposition, thermal evaporation, reactive magnetron sputtering, physical vapour deposition, laser ablation, electrophoresis, anodization and electro deposition. But in the recent work the simple convenient and inexpensive technique closed spaced sublimation is used for the thermal growth of ZnSe on the glass substrate. The closed spaced sublimation technique has already used for the growth of epitaxial layers of ZnTe, ZnxCd1-xTe and ZnSe at low pressure.

The deposited thin films of ZnSe show high resistivity and restrict their use in the photovoltaic applications However to improve the optoelectronic properties of these films different methods can be used i.e. doping, thermal treatment, preparation parameters etc.

Podestal *et. al* prepared the CdS thin films and doped by fluorine and observed the greater and better effect on the opto-electronic properties of the CdS thin films due to which efficiency of the CdS/ CdTe have been improved [10]. Hiie et al studied the effect of thermal treatment on the different properties such as its structure, and opto-electronic properties of the CdS:Cl. Significant improvement in the properties was observed when chemical bath deposition (CBD) and spray pyrolysis was used for the deposition of thin films [11]. Furthermore the effects of CdCl2 on the thin films of CdS and CdTe were investigated for solar cells [12, 13]. Amanullah observed that chlorine co-activation has great effect on the chemically deposited thin films of CdS [14]. In present work the effect of copper concentration on the optical properties of ZnSe thin films deposited by closed space sublimation on glass substrate were investigated. Moreover, different parameters such as refractive index and other properties of ZnSe thin films related to optics were investigated with greater concentration of copper.

**EXPERIMENTAL DETAIL**

Closed space sublimation method was used for the deposition of Zn1-xCuxSe thin films on a glass substrate .For preparation of thin films of Cu doped ZnSe, the substrate was made clean by using acetone before deposition. After that substrate was further cleaned by using distilled water and then the optical paper was used for drying. Cu and ZnSe with 99.99% purity mixed with different concentration of copper to form homogenous mixture. This homogenous mixture was kept in the molybdenum boat which is coated by a current source of two stainless steel electrodes and heated by quartz lamp. At higher temperature the vapour pressure of Cu and ZnSe are same over the same substrate. Molybdenum boat was filled with homogenous mixture of ZnSe and different concentration of copper (0%, 5 %, 10%, 15%) weight by composition formula

By microbalance the weight of each compound was taken. Pressure of the chamber was reduce to 5 × 10-6torr with the help of rotary pump and diffusion pump. Substrate to target distance was kept constant at 4mm. Temperature of the source and substrate was kept at room temperature, i.e. 300 K and 900 K respectively. Evaporation time was 10 min. Samples of all composition were deposited by keeping the ambient conditions same. For optical properties the transmission spectra was taken by the spectrophotometer. For the measurement of film’s thickness, dielectric constant and band gap energy, spectroscopic ellipsometer (Sentic 5500) was used. To analyze the sample with spectroscopic ellipsometer, the sample was firstly illuminated with polarized beam of light. Extent of Reflection of light show the measurement of change in polarization of sample. Ellipsometry is used for the characterization of change in extent of polarization. Delta and psi () was used as parameters. Following equation is used to express these parameters and as a function of wavelength

-------------- (1)

In the following equation is the ratio of p –polarized (rp) reflectivity to the s-polarized (rs) reflectivity. While is the phse and tan is reflectivity ratio magnitude.

At an incident angle 70, the experimental delta and psi () were measured. Above relation co related these parameters with the optical parameters of the thin films. Moreover the deposited thin films were annealed at 100 to 500 with rapid thermal processing for 1 min. in air to check the effect of thermal treatment on optical properties of Zn1-xCuxSethin films.

**OPTICAL PARAMETERS**

To estimate different optical parameters for example refractive index, band gap energy, extension coefficient, dielectric constant, reflection and absorption of deposited and thermally treated thin films of Zn1-xCuxSe spectroscopic ellipsometer is used. At an incident angle of 70 the delta and psi () was measured. To find optical parameters (n and K) a theoretical model, to fit experimental modal frohi Brumer was used.

The spectra of extrinsic coefficient and refractive index of the deposited and annealed thin films of Zn1-xCuxSe are shown in fig1 (a) and (b). The spectra show that the two properties as extension coefficient and refractive index show inverse behaviour with wavelength while direct relation with concentration of copper. The intrinsic ZnSe shows value of refractive index is 2.7 at wave length 450nm but as the copper concentration and wave length increases the refractive index value decreases low as 1.8 and 1.6. It is also clear that with increase of temperature these optical parameters increases and shows the value 2.6 at 450nm wave length when annealed at 300. Rusu et al also reported that there is a direct relationship between refractive index and annealing temperature, but in our results, the refractive index shows direct relation with heating treatment. This variation is observed due to betterment in grain size, improvement in the crystallinity of the thin films and reduction of dislocations. The change in the value of refractive index (n) and extension coefficient (K) with the increase of heating treatment confirms the formation of solid solution between ZnSe and Cu binary compounds .The mixing of high band gap semi-conductor with highly conductive metals results decrease in the optical constants. Till 10 %. Cu concentration samples the refractive index is directly related to the concentration of copper while sample suddenly shows a reverse trend at 15 % Cu sample. From 0 % Cu to 10% Cu sample the refractive index and intrinsic coefficient shows reverse trend with the increase of wavelength, but 15 % Cu show a direct relation between refractive index and wavelength. It may be due to increase in transmittance with increase of Cu concentration, the K value also shifted towards higher wavelength with annealing which may be increased in the transmittance of thin films with annealing. This is the fact that band gap energy increase with changes in the n and K with a variation of Cu concentration and annealing temperature shown in figure 1.

The absorption coefficient of thin films has been calculated using the following relation

------------------ (2)

Where the wavelength and K is intrinsic coefficient. The absorption coefficient depend on the value of intrinsic coefficient K. Absorption of thin films increase with the increase of k and decrease with the decrease of K. value of the intrinsic coefficient K increase as the copper concentration increase. It is may be due to larger absorption coefficient and decrease in transmittance of thin films with increase of copper. The absorption of the thin films decreases with increasing of copper concentration which may be due to shine surface of the films. The absorption of the thin films increases as the annealing effect increases because of improvement in the surface, decrease of dislocations shown in figure 2

ZnSe is a soft material than other semiconductor compounds of group II-VI and can be scratched easily. Due to high refractive index it requires anti-reflection coating to obtain low reflection and high transmission. From the transmission data reflection and refractive index was calculated.

Reflection of thin films can be calculated by the relation

----------- (3)

In the above relation absorption coefficient is denoted by A i.e. (A=t) while T represents transmittance across different wavelengths. The spectra of reflection at various concentration are shown in figure 3. Reflectance spectra show that reflectance and concentration of copper are directly proportional to each other, as well as with increase of wavelength, reflectance decreases which may be due to increase in transmittance with increase of wavelength [15]. Because of this property, ZnSe thin films are used in window layer in the solar cells. The spectra also shows that reflectance of thin films decreases up to 550nm wavelength and after that it was observed that linearity was shown at higher values of wavelength. With increase of copper concentration, the reflectance increases which is due to shiny surface. Moreover annealing temperature and reflectance show inverse trend with each other. The reflectance decreases with the increase of annealing effect. Figure 1 shows the result of refractive index as increase copper concentration and annealing effect. To calculate the electrical conductivity [16] and optical conductivity [17] following relation is used, shown in figure 4

(a)



(b)





(c)



(d)

**Figure 1 shows the refractive index (a & b), intrinsic coefficient (c & d), of deposited and annealed ZnSe thin films**

(a)



(b)

 **Figure 2 shows the absorption coefficient (a & b), of the deposited and annealed ZnSe thin films**

(a)



(b)



**Figure 3 shows the absorption coefficient (a & b), of the deposited and annealed ZnSe thin films**

------------------ (4)

------------------ (5)

Where velocity of light is c and n shows refractive index value of the deposited thin films. The behaviour of Opto- electronic conductivities of thin films with the increase of copper concentration as a wave function of energy of photon is shown in figure 4. The relation shows that optical conductivity strongly depends on refractive index (n) and absorption coefficient (while electrical conductivity depends on optical conductivity. Electrical and optical conductivity increases with the higher energy values because of higher absorption coefficient.

(a)



(b)



**Figure 4 shows the effect of concentration of copper on both optical and electrical conductivities of the thin films.**

To measure band gap energy and dielectric constant spectroscopic ellipsometer is used. Following relation is used for evaluation of the optical and electrical band gap energy of the coper doped ZnSe thin films

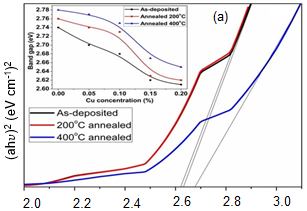
----------------- (6)

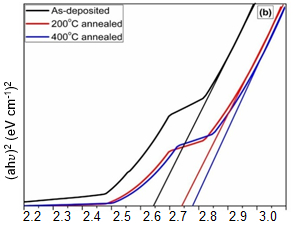
And

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Value of band gap energy varies from 2.78 to 2.62 for these films with variation in copper concentration 10% to 15 % shown in figure 5. Calculated value of band gap energy is very close to actual value of the material which is Eg =2.7ev for ZnSe [18] which shows the good quality of the films. Variation in the optical energy of thin films is linear, which indicates that the formation of the thin films Zn1-xCuxSe are homogenous Z.Ali et al reported that band gap energy also reverse trend with concentration of copper [19].

(a)





**Figure 5 shows the effect of heating treatment on the ZnSe thin film’s band gap energy.**

Dielectric constant of the deposited thin films was also calculated. The polarizability increases with the increase of dielectric constant of the material. Figure 6 shows the changes in dielectric constant with increase of copper concentration and increase of annealing treatment of Zn1-xCuxSe thin films.

The real part of the complex dielectric parameter is is shown here. All analysis reported in this paper wa done on both real and complex dielectric constants simultaneously.

Dielectric constant values increase with increase of copper concentration as well as wavelength. The average value of dielectric constant varies from 4.40 to 5.5 and 6.20 to 6.10 for x= 0 to x=15 respectively in the range 450 to 500. The value of the dielectric constant is 74% of the reported value of T.M Khan which is 7.8

Copper content perform an important role in the ZnSe films and produce variation in the dielectric properties of the deposited films. According to research or knowledge, there is no detailed work on dielectric properties of Zn1-xCuxSe thin films deposited by closed space sublimation. It was observed that there is a direct relationship between concentration of copper and dielectric constant which is due to high density of copper than purity of ZnSe in thin films. S.Venkatachalang et al also reported the same result of the ZnSe thin films, but using vacuuum technique for deposition.

(a)



(b)

 **Figure 6(a & b) shows the effect of concentration of copper dielectric constant of the thin films properties**

**CONCLUSION**

The thin films of Zn1-xCuxSe were synthesized successfully on a glass substrate by closed space sublimation technique. Investigated the different optical parameters such as band gap energy, dielectric constant, reflection, absorption, electrical and optical conductivities of the thin films with spectroscopic ellipsometery. From the spectra of absorption coefficient reveals that there is direct relationship between absorption coefficient and copper concentration while inverse relation with wavelength. Reflection shows direct relation with concentration of copper due to the shiny surface of the films. The results show that with copper concentration the band gap energy decreases, while dielectric constant increased with increase of band gap energy. Moreover the deposited films annealed at different temperature and observe the effect of thermal annealing on the optical properties of the thin films. The results shows that with annealing the optical properties of the thin films were significantly improved. The absorption coefficient has direct relation while reflection has inverse relation with heating treatment. The band gap energy of the thin films showed that band gap energy decreases with temperature of heating treatment (annealing).

**REFRENCES**

[1] S. Armstrong, P. Datta, and R. Miles, "Properties of zinc sulfur selenide deposited using a close-spaced sublimation method," *Thin Solid Films,* vol. 403, pp. 126-129, 2002.

[2] M. Arslan, A. Maqsood, A. Mahmood, and A. Iqbal, "Structural and optical properties of copper enriched ZnSe thin films prepared by closed space sublimation technique," *Materials Science in Semiconductor Processing,* vol. 16, pp. 1797-1803, 2013.

[3] P. K. Kalita, B. Sarma, and H. Das, "Structural characterization of vacuum evaporated ZnSe thin films," *Bulletin of Materials Science,* vol. 23, pp. 313-317, 2000.

[4] E. Khawaja, S. Durrani, A. Hallak, M. Salim, and M. S. Hussain, "Density of thin vapour-deposited films of zinc selenide," *Journal of Physics D: Applied Physics,* vol. 27, p. 1008, 1994.

[5] E. Krause, H. Hartmann, J. Menninger, A. Hoffmann, C. Fricke, R. Heitz*, et al.*, "Influence of growth non-stoichiometry on optical properties of doped and non-doped ZnSe grown by chemical vapour deposition," *Journal of crystal growth,* vol. 138, pp. 75-80, 1994.

[6] V. Kumar and T. Sharma, "Structural and optical properties of sintered ZnS x Se 1− x films," *Optical Materials,* vol. 10, pp. 253-256, 1998.

[7] S. Lakshmikumar and A. Rastogi, "Novel two-stage selenization process for the preparation of ZnSe films," *Thin Solid Films,* vol. 259, pp. 150-153, 1995.

[8] M. Matsuoka, "Nonohmic properties of zinc oxide ceramics," *Japanese Journal of Applied Physics,* vol. 10, p. 736, 1971.

[9] L. Yan, J. A. Woollam, and E. Franke, "Oxygen plasma effects on optical properties of ZnSe films," *Journal of Vacuum Science & Technology A,* vol. 20, pp. 693-701, 2002.

[10] E. Larramendi, O. De Melo, M. H. Vélez, and M. Tamargo, "Adsorption, desorption, and interdiffusion in atomic layer epitaxy of CdTe and CdZnTe," *Journal of applied physics,* vol. 96, pp. 7164-7167, 2004.

[11] R. Farrow, G. Jones, G. Williams, and I. Young, "Molecular beam epitaxial growth of high structural perfection, heteroepitaxial CdTe films on InSb (001)," *Applied Physics Letters,* vol. 39, pp. 954-956, 1981.

[12] S. Venkatachalam, S. Agilan, D. Mangalaraj, and S. K. Narayandass, "Optoelectronic properties of ZnSe thin films," *Materials Science in Semiconductor Processing,* vol. 10, pp. 128-132, 2007.

[13] P. D. File, "Joint committee on powder diffraction standards," *ASTM, Philadelphia, Pa,* pp. 9-185, 1967.

[14] W. Pies and A. Weiss, "1906-1930, References for Vol. III/7," in *References for III/7*, ed: Springer, 1974, pp. 1-14.

[15] T. Yeh and A. Blakeslee, "Junction delineation in gallium arsenide," *Journal of The Electrochemical Society,* vol. 110, pp. 1018-1019, 1963.

[16] J. I. Pankove and D. A. Kiewit, "Optical processes in semiconductors," *Journal of The Electrochemical Society,* vol. 119, pp. 156C-156C, 1972.

[17] A. Fatehmulla, A. Al-Shammari, A. Al-Dhafiri, W. Farooq, and F. Yakuphanoglu, "Structural, Electrical and Optical Properties of Chlorine Doped CdS Thin Films," *World Applied Sciences Journal,* vol. 31, pp. 2073-2078, 2014.

[18] M. Arslan, M. Zakria, N. A. Naz, R. Muhammad, *Journal of Electronic Materials,* vol. 44, pp. 4754-4759, 2015.

##### [19] M. Arslan, R. Muhammad, A. Mahmood, and R. Rasheed, *Acta Metallurgica Sinica (English Letters),* vol. 26, pp. 699-706, 2013.

[20] Venkatachalam, S., Soundararajan, and D, Peranantham, (2007c).Spectroscopic ellipsometry (SE) studies on vacuum-evaporated ZnSe thin films. *Materials characterization*, 2007.58(8): p. 715-720