

Growth and Characterization of Electroplated Copper Selenide Thin Films

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Abstract: Copper Selenide thin films have been prepared on indium doped tin oxide coated conducting glass substrates from an aqueous electrolytic bath consists of CuSO_4 and SeO_2 using potentiostatic electrodeposition technique. Deposition mechanism has been analyzed using cyclic voltammetry. X-ray diffraction pattern showed that the prepared films possess polycrystalline nature with hexagonal structure. Film composition and surface morphology showed that films with smooth surface and better stoichiometry are obtained under optimized condition. Band gap value of the deposited films is determined using optical absorption measurements. Variation of film thickness with time and its dependency on structural, morphological, compositional and optical properties are investigated.

Keywords: metal chalcogenides; electrodeposition; strain; dislocation density

1. INTRODUCTION

Metal chalcogenides have received much attention due to its wide variety of applications in electronics, electro-optical devices, photovoltaic devices, cathode material in Li rechargeable batteries, photoelectrochemical solar cells, superionic conductors, photodetectors, electroconductive electrodes etc., [1-5]. Moreover, copper selenide (CuSe) has been extensively studied for the fabrication of window material in photovoltaic devices, optical filters, solar cells, Li ion cells, thermoelectric converters, photo-thermal conversion and microwave shield coatings [4,6,7]. CuSe is a direct band gap p-type semiconductor with an energy gap value in the range between 2.3 and 2.7 eV mainly focussed this material for the fabrication of solid liquid junction solar cells [4,8]. Thin films of CuSe are normally crystallized in hexagonal structure (JCPDS-ICDD 2003, PDF 20-1020) structure with lattice constants ($a = 3.94 \text{ \AA}$; $c = 17.23 \text{ \AA}$) and in cubic structure (JCPDS-ICDD, PDF 88-2045) with lattice constant ($a = 5.564 \text{ \AA}$). So many researchers have attempted to prepare CuSe thin films through thermal evaporation [1], vacuum evaporation [2], solution growth [6], chemical bath deposition [9] techniques etc., Chemical bath deposition and

electrodeposition are the alternative methods that are particularly adapted for the preparation of chalcogenide materials in the form of thin films. Thin and continuous films with desired electrical and optical properties is required for the preparation of photoelectrochemical solar cells. It is easier said than done to obtain continuous and single phase CuSe film with the above mentioned properties. Electrodeposition is one of the suitable methods to prepare thin and continuous semiconducting films. This technique provides numerous advantages such as low temperature processing, low cost of synthesise, no need of vacuum facility, no contamination to the surrounding, it is simply possible to control film thickness and morphology by readily adjusting the electrical parameters as well as composition of the electrolytic solution [3,10-12]. Yakuphanoglu and Viswanathan [1] have obtained CuSe thin films by thermal evaporation and investigated their structural, electrical and optical properties. Preparation of CuSe thin films by vacuum evaporation technique and its annealing effect on structural, morphological, compositional and optical properties have been investigated by Peranatham et al [2]. Growth of CuSe thin films using thermal evaporation method and their properties are investigated using structural, optical absorption and Raman spectroscopic techniques by Sakr et al [4]. Hankare et al [8] have obtained solution

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grown CuSe thin films and investigated their properties using X-ray diffraction, Scanning Electron Microscopy and Optical absorption techniques. To the best of our knowledge, there is no such detailed investigation is available for studying the properties of CuSe thin films which have been obtained using electrodeposition technique.

In the present investigation, we have described the growth of CuSe thin films on indium doped tin oxide coated conducting glass (ITO) substrates using potentiostatic electrodeposition technique. Deposition mechanism has been analyzed using cyclic voltammetry. Film thickness has been measured for films obtained at various deposition time. Prepared films have been subjected to X-ray diffraction, Scanning electron microscopy, Energy dispersive analysis by X-rays and Optical absorption techniques, respectively. Effect of film thickness on structural, morphological, compositional and optical properties of the deposited films is studied. The observed results are discussed in detail.

2. EXPERIMENTAL

The chemicals used in the present work were of Analar Grade Reagents (99.5 Purity, SD Fine Chemicals, Mumbai, India). Thin films of CuSe were coated on ITO substrates from an aqueous acidic bath containing CuSO_4 and SeO_2 . The first working solution was obtained by liquifying 15.6062 g of CuSO_4 in 250 cc distilled water and the second working solution was obtained by liquefying 0.06935 g of SeO_2 in 250 cc distilled water. Each 20 cc of the two solutions forms the reaction mixture and this mixture was used as an electrolytic bath for all depositions. At lower pH value such as below 2.0 ± 0.1 , adherence of the deposited film to the substrate was very poor. At higher pH value such as above 5.0 ± 0.1 the solution became cloudy due to precipitation of electrolytic bath which in turn yields films with poor quality. Hence, an optimum solution pH value of 3.5 ± 0.1 must be fixed to get films with better quality. All the electrochemical experiments were carried out using a scanning potentiostat/galvanostat unit (Biologic SP 50 Potentiostat/Galvanostat Unit, France) employing three electrode cell configuration with ITO substrate as working electrode, platinum electrode as counter electrode and saturated calomel electrode as reference electrode, respectively. The deposition potential, bath temperature and solution pH were fixed as -750 mV versus SCE, 70°C , 3.5 ± 0.1 , respectively.

Thickness of the deposited films was measured using Stylus Profilometer (Mitutoyo SJ 301, Japan) and Weight difference techniques. X-ray diffractometer with CuK_α radiation with wavelength ($\lambda=0.15418$ nm) was used to determine the structural properties of the deposited films (XPRT PRO ANALYTICAL, Netherland). Surface morphology of the deposited films was analyzed using Scanning Electron Microscope (JEOL JSM 840). Film composition was measured using Energy Dispersive Analysis by X-rays set up attached with scanning electron microscope. Optical properties of the prepared films was recorded using an UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics).

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Cyclic voltammetry is a powerful analytical tool which has been utilized for studying electrochemical reaction in an electrolytic bath

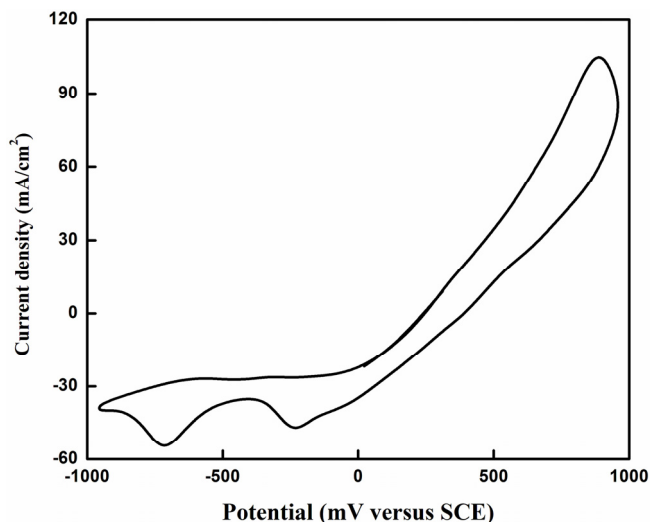
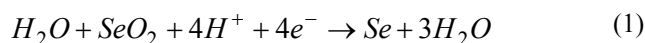


Figure 1. Cyclic voltammogram recorded for ITO glass electrode in an aqueous acidic bath containing CuSO_4 and SeO_2

consists of CuSO_4 and SeO_2 . Voltammetric analysis has been carried out using a standard three compartment cell containing ITO substrate as working electrode, platinum electrode as counter electrode and saturated calomel electrode as reference electrode in the scanned potential range between -1000 to $+1000$ mV versus SCE. Cyclic voltammogram recorded for ITO glass electrode in an aqueous electrolytic bath containing CuSO_4 and SeO_2 is shown in Figure 1. Reduction peak 1 observed at -230 mV versus SCE may be due to the reduction of H_2SeO_3 to Se according to Eq.(1). It is noted that the reduction potential around -750 mV versus SCE which may be due to growth of CuSe start at this potential. A hysteresis is obtained in the potential range between -750 mV versus SCE and -710 mV versus SCE represents that the deposition of CuSe occurs more easily on CuSe electrode than those on the surface of ITO, since the working electrode is covered initially with CuSe instead of ITO. The reduction of H_2SeO_3 to Se is rate controlling step in the deposition process, the first is reduction of Cu^{2+} to Cu on ITO surface which is followed by electrochemical reduction of H_2SeO_3 with element Cu according to the following Eqs.



3.2. Film thickness

Electrochemical deposition of CuSe thin films has been controlled by two individual variables such as (i) film thickness and its uniformity (ii) surface morphology [13-14]. By controlling the deposition time, potential thickness of the deposited films could be controlled. At lower temperature (such as below 40°C) films with lower thickness and at higher bath temperatures (such as 70°C) films with higher thickness value is obtained. If the bath temperature is increased above certain value such as above 70°C , thickness of the deposited films could be hindered due to the process of hy-

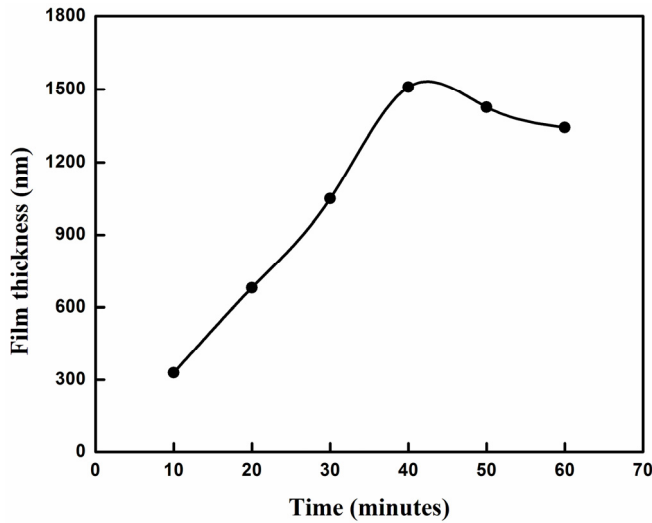


Figure 2. Variation of film thickness with deposition time for CuSe thin films prepared at bath temperature 70°C

drogen evolution reaction [15]. Variation of film thickness with deposition time for films obtained at bath temperature around 70°C is shown in Figure 2. It is noted that the film thickness is found to increase while increasing the deposition time upto 40 minutes, thereafter there is slight decrement is observed which is shown in Figure 2. Films with higher thickness value is obtained at a deposition time of 40 minutes.

3.3. X-ray diffraction

X-ray diffraction analysis has been carried out to identify the crystalline nature and phases of the deposited films. The interplanar spacing d_{hkl} is calculated using the following Eq.(3) [14,16].

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \left[\frac{l^2}{c^2} \right] \quad (3)$$

Where ' λ ' is the wavelength of X-ray used, 'd' the interplanar spacing, and ' θ ' is Bragg's diffraction angle. The crystallite size of the deposited films has been calculated using FWHM data and Debye-Scherrer formula [10-14,16].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4)$$

Strain is defined as the restoring force acts on the surface of the film to restrict the formation of crystallites on its surface [11]. The value of strain is calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$ plot using the following Eq.(5) by Williamson-Hall method. Dislocation density is defined as the number of dislocation lines per unit volume of the crystal and it can be calculated using Eq.(6) [10-14,16].

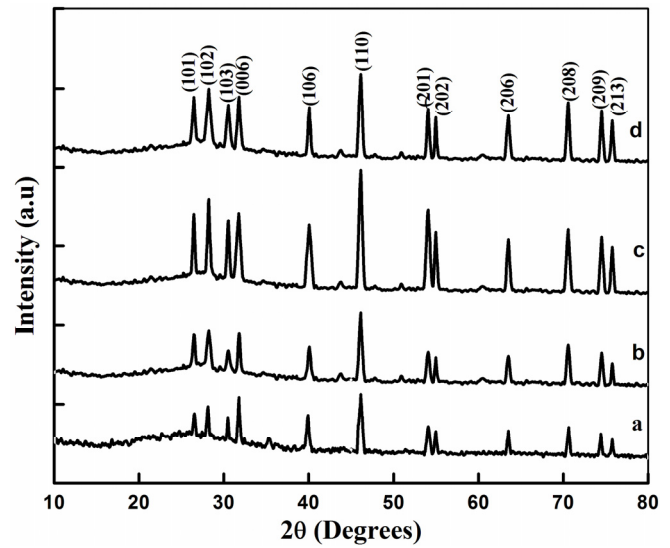


Figure 3. X-ray diffraction pattern of CuSe thin films prepared on ITO substrates at different deposition time: (a) 10 (b) 20 (c) 30 (d) 40 minutes

$$\beta \cos \theta = \left(\frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta \right) \quad (5)$$

$$\delta = \frac{1}{D^2} \quad (6)$$

X-ray diffraction pattern recorded for CuSe thin films prepared at different deposition time with various film thickness value is shown in Figure 3. XRD patterns showed that the prepared films are found to be polycrystalline in nature with hexagonal structure with lattice constants ($a = 3.92 \text{ \AA}$; $c = 17.21 \text{ \AA}$). Diffraction peaks of CuSe are found at 2θ values of angles 26.46, 28.11, 30.53, 31.96, 40.10, 46.14, 54.05, 54.88, 63.62, 70.71, 74.45, 75.70 corresponding to the lattice planes (101), (102), (103), (006), (110), (201), (202), (206), (208), (209) and (213), respectively. Different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing ' d_{hkl} ' is calculated and compared with standard JCPDS-ICDD file for hexagonal CuSe [17]. It is observed that all the observed lines are from CuSe and hence no additional line corresponding to Cu and Se are present. The intensity of (110) plane is found to be higher than all other peak intensities in the diffractogram which indicates that the crystallites are preferentially oriented along (110) plane. Crystallite size of the deposited films are estimated using FWHM data and Debye-Scherrer formula and its value is found to be in the range between 37 and 63 nm.

3.4. Microstructural analysis

Figure 4a shows the variation of crystallite size and strain with film thickness value for CuSe thin films obtained at different deposition time. It is noted that the value of crystallite size is observed to increase while increasing the film thickness value upto 1550 nm, thereafter its value decreases slightly which is shown in Figure 4a.

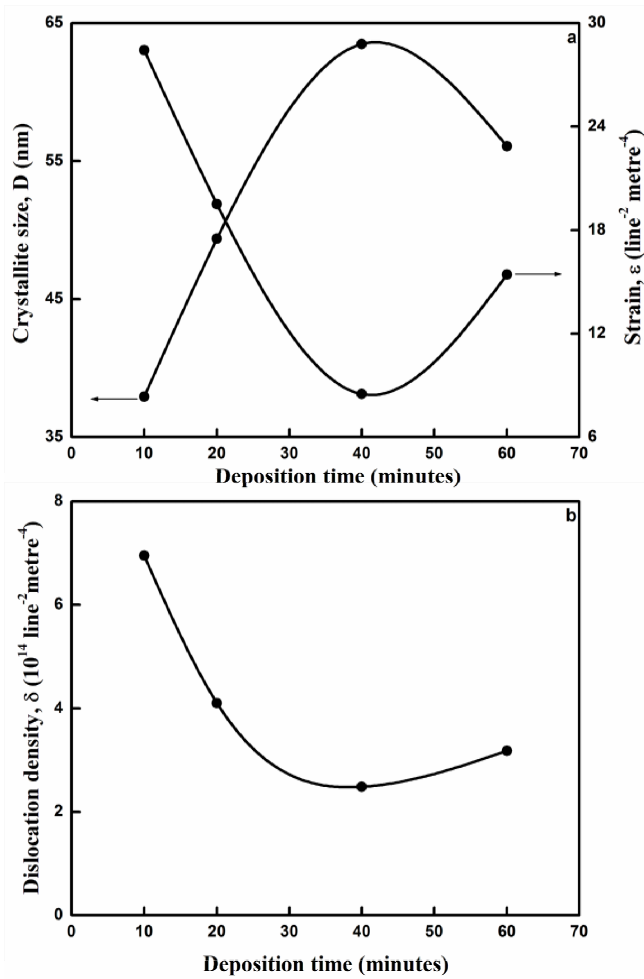


Figure 4. a. Variation of Crystallite size and Strain with deposition time for CuSe thin films b. Variation of Dislocation density with deposition time for CuSe thin films.

Due to the removal of strain with film thickness value, strain in the deposited films gets released and reaches its minimum value at film thickness value around 1550 nm. Further increasing of film thickness value above 1550 nm the value of strain increases which is indicated in Figure 4a. Variation of dislocation density with film thickness value for CuSe thin films obtained at various deposition time is shown in 4b. It is noted that the value of dislocation density is found to decrease while increasing the film thickness value upto 1550 nm, thereafter it increases slightly which is indicated in Figure 4b. A sharp increase in crystallite size and decrease in value of strain with film thickness value is shown in Figure 4a. Such a release in strain reduced the variation of interplanar spacing thus leads decrease in value of dislocation density of CuSe films. CuSe films with lower strain and dislocation density improves the stoichiometry of the films which in turn causes volumetric expansion of the films. Crystallinity improvement with film thickness value enhances the concentration and mobility of Cu ion vacancies within the lattice and hence reduces the resistivity of the deposited films. Studies on functional dependency of crystallite size, strain

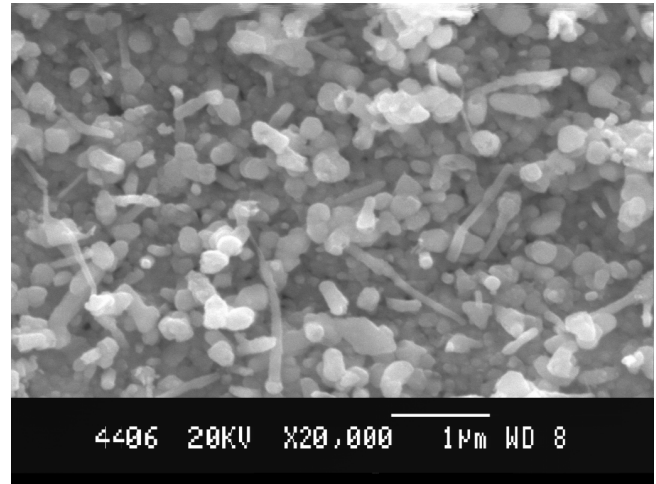


Figure 5. SEM image of CuSe thin films prepared at bath temperature 70°C

and dislocation density with film thickness value showed that the value of strain and dislocation density decreases with film thickness value whereas the crystallite size increases. Similar functional dependency of microstructural parameters with film thickness value for FeSe₂ and CdSe thin films has been reported earlier [18,19]. Surface morphology of the deposited films has been analyzed using scanning electron microscope. SEM picture of CuSe thin films prepared at a deposition time of 40 minutes is shown in Figure 5. It is found that the film surface is observed to be smooth for films and covered with tiny spherical shaped grains. The sizes of the grains are found to be in the range between 0.30 and 0.65 μm and its average size is found to be 0.39 μm .

3.5. Compositional and optical absorption analyses

Film composition has been analyzed using an Energy dispersive analysis by X-rays set up attached with scanning electron microscopy. A typical EDX spectrum of CuSe thin films electrodeposited at bath temperature around 70°C is shown in Figure 6a. It is observed that the presence of emission lines Cu, Se are present in the investigated energy range indicates the formation of CuSe thin films. Compositional analysis has been carried out with an aim to determine the relationship between film composition (Cu, Se content) with film thickness values. Variation of film thickness with Cu and Se content for CuSe thin films prepared at bath temperature around 70°C under various deposition time is shown in Figure 6b. It is found that the content of Cu decreases and the content of Se increases, thickness value of the film increases from 330 to 1550 nm. The atomic molar ratio (Cu:Se) of CuSe thin films prepared at bath temperature around 70°C is found to be indicating stoichiometric nature of the deposited films. This result is consistent with X-ray diffraction analysis of the sample with phase corresponds to CuSe. Similar behavior is exhibited for CuSe thin films reported earlier [9].

Optical absorption and transmittance measurements have been taken out using an UV-Vis-NIR spectrophotometer to determine the band gap value of the material. The absorption coefficient of

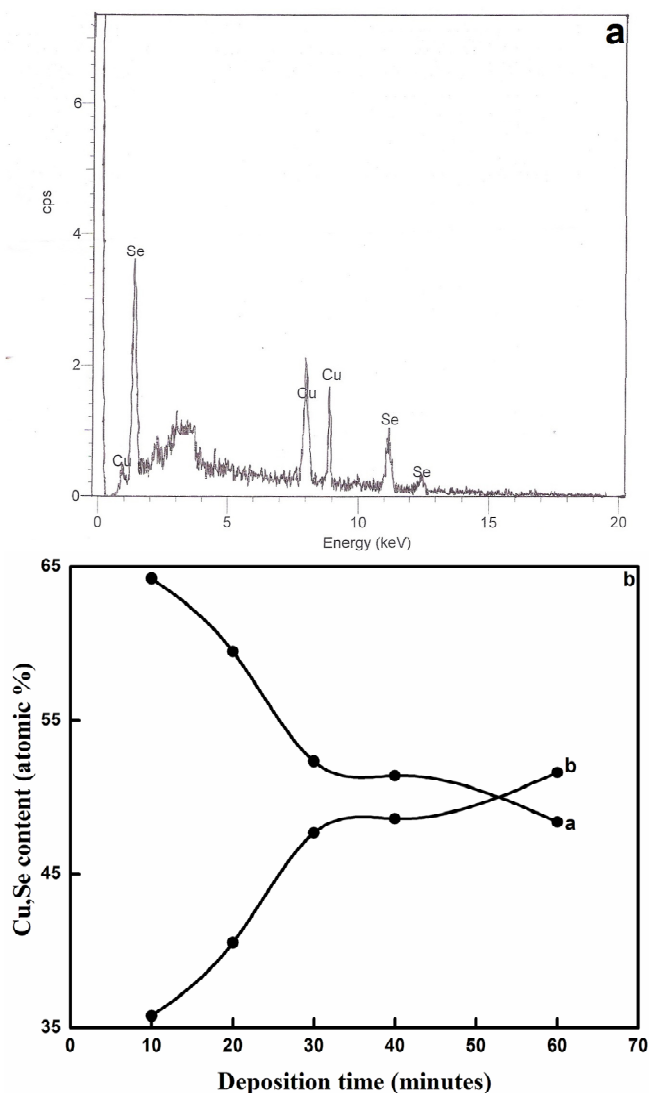


Figure 6. a. Typical EDX spectrum of CuSe thin film prepared at bath temperature 70°C b. Variation of Cu and Se content with film thickness value for CuSe thin films

the deposited films is calculated from the observed absorbance and transmittance values using the following Eq. (7) [10,20].

$$\alpha = \frac{1}{t} \ln \left(\frac{A}{T} \right) \quad (7)$$

where 'α' is absorption coefficient in cm⁻¹, 't' is the film thickness in nm, 'A' is absorbance and 'T' is transmittance. The nature of transition is determined using the following Eq.(8) [10,13].

$$\alpha h\nu = K(h\nu - E_g)^n \quad (8)$$

where K is an energy dependent constant, E_g is band gap energy of the material, 'hν' is photon energy. Optical absorption and transmission spectra of CuSe thin films have been recorded as a func-

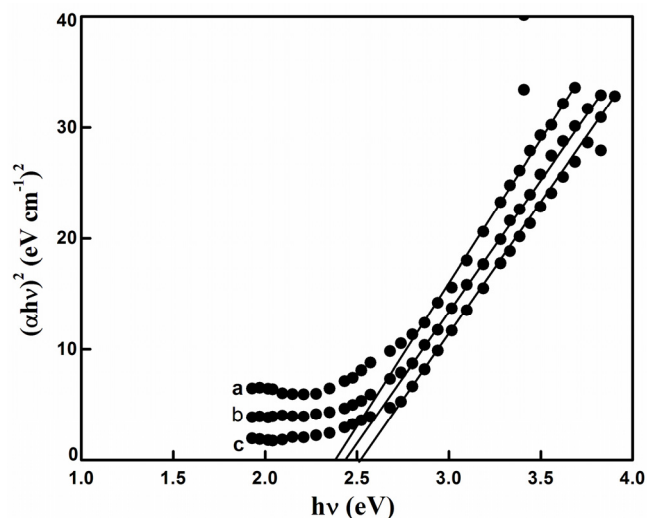


Figure 7. Plot of (hν) versus (αhν)² for CuSe thin films prepared at 70°C under different deposition time: (a) 10 (b) 20 (c) 40 minutes

tion of wavelength in the range between 300 and 1200 nm. Substrate absorption if any is corrected by introducing an uncoated ITO substrate in the reference beam. The value of absorption coefficient rises sharply owing to band-to-band transition and levels off latter. An analysis of absorption spectrum in the energy range between 1 and 3 eV indicates that α follows the relation. A plot of (hν) versus (αhν)² is plotted for films with various film thickness value is shown in Figure 7. The linear portion of the plot is extrapolated to the energy axis gives the band gap energy of the material. The band gap value of the material obtained in the present work is found to be in the range between 2.49 and 2.53 eV. The band gap value of the material obtained in the present work is found to be in close agreement with the value reported earlier [8].

4. CONCLUSIONS

CuSe thin films have been successfully prepared on ITO substrates using potentiostatic electrodeposition technique. X-ray diffraction analysis revealed that the prepared films possess polycrystalline in nature with hexagonal structure with most prominent reflection along (110) plane. Films with better crystallinity and well defined stoichiometry have been obtained at bath temperature 70°C. Microstructural parameters have been determined using Williamson Hall plot analysis and its dependency shows that the parameters exhibit monotonic variation with film thickness. Morphological analysis showed that films exhibit smooth surface with well defined stoichiometry is obtained at optimized condition. Optical absorption analysis showed that the films possess direct band gap value in the range between 2.49 and 2.53 eV.

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