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STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF COPPER SELENIDE THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Abstract

A low cost chemical bath deposition (CBD) technique has been used for the preparation of $Cu_{2-x}Se$ thin films on glass substrates. Structural, electrical and optical properties of these films were investigated. X-ray diffraction (XRD) study of the $Cu_{2-x}Se$ films annealed at 523K suggests a cubic structure with a lattice constant of 5.697Å. Chemical composition was investigated by X-ray photoelectron spectroscopy (XPS). It reveals that absorbed oxygen in the film decreases remarkably on annealing above 423K. The Cu/Se ratio was observed to be the same in as-deposited and annealed films. Both as-deposited and annealed films show very low resistivity in the range of $(0.04–0.15) \times 10^{-5}$ Ω-m. Transmittance and Reflectance were found in the range of 5–50% and 2–20% respectively. Optical absorption of the films results from free carrier absorption in the near infrared region with absorption coefficient of $\sim 10^{8}$ m^{-1}. The band gap for direct transition, Eg.dir varies in the range of 2.0–2.3 eV and that for indirect transition Eg.indir is in the range of 1.25–1.5 eV.**1.**

1. Introduction

Copper selenide is a semiconducting material, which has electrical and optical properties suitable for photovoltaic application. The techniques adopted for deposition of this metal chalcogenide vary from reaction of metallic copper with selenium dissolved in a benzene medium [1] or an aqueous medium [2], flash evaporation [3], vacuum evaporation [4-7], melting of Cu and Se [8,9], and electrodeposition [10], to the simplest method of chemical bath deposition (CBD) [11-22]. Copper selenide exists in widely differing crystallographic structures depending on the method of preparation even at room temperature. Okimura and Matsumae deposited $Cu_{2-x}Se$ thin films on to glass substrates by vacuum evaporation method and reported the dc electrical properties. They found p-type conduction with low resistivity. They fabricated $Cu_{2-x}Se$ thin film solar cells, which showed conversion efficiency of about 8.8% and good stability [5]. Chen *et al.* used copper selenide as an absorbing layer and reported a $Cu_{2-x}Se/CdS$ heterojunction solar cell with an efficiency of 5.38% [7]. Lakshmi *et al.* reported the depth profiling of as-deposited Cu_3Se_2 film [21, 22].

During the last two decades, less expensive methods, like chemical and electrochemical conversion, precipitation, ion displacement, electrodeposition and low temperature dip type for the preparation of copper selenide and their characterization have been reported by several authors [1, 2, 8-23]. CBD is a method of growing thin film of certain materials on a substrate immersed in an aqueous bath containing appropriate reagents at temperatures ranging from room temperature to 373K. It has been identified as one of the techniques for growing $Cu_{2-x}Se$ films at low cost.

The optical properties of interest for solar cell application of a material are reflectance, transmittance, absorptions, emittance and index of refraction [24]. An ideal absorber is one that completely absorbs the incident solar energy and does not emit any radiation. In this experiment copper selenide thin films with various ratios of copper and selenium were deposited onto a glass substrate using low cost CBD method. In general, the growth of good quality semiconductor thin films by CBD technique proceeds at a slow pace. This technique is ideally suited for producing uniform films with thicknesses of 0.05-0.3 μm in most cases. Recently, we have reported the brief result on the characterization of copper selenide thin films deposited by CBD technique [25]. This paper describes the detail results observed by XPS, X-ray diffraction (XRD), electrical, and optical investigations on the $Cu_{2-x}Se$ film prepared by CBD. An attempt is made here to correlate the observed results.

2. Experimental details

The chemicals used for the preparation of thin films were LR grade (Merck) cupric chloride di-hydrate ($CuCl_2$, $2H_2O$), selenium powder of 99.99% purity, sodium sulfite (Na_2SO_3), tri-ethanol amine (TEA) and ammonium hydroxide (NH_4OH). First, sodium selenosulfate was made by refluxing fine selenium powder with sodium sulfite solutions for about 30 minutes at 393K by stirring in a beaker. A constant stirring machine with a constant temperature bath was used during the reaction. Secondly, $CuCl_2$ $2H_2O$ solution was mixed with $NaSeSO_3$ at constant stirring. 10 ml TEA (0.1 M) was added to this solution. NH_4OH was used to adjust the pH of the reaction bath. Microscope glass slides of $76 \times 26 \times 1$ mm^3 were used as substrates. The substrates were cleaned with detergent and distilled water, and were kept in H_2SO_4 for about 1h. Then the substrates were rinsed with distilled water and were dried in air prior to film deposition. The substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. The deposition was allowed to proceed at room temperature for different time durations from 15 to 180 minutes. After deposition, the glass slides were taken out from the bath, washed with distilled water and were dried in blowing air. All the samples were annealed in air at higher temperatures up to 523K to observe annealing effects.

Identification of the deposited film material was carried out by a Philips X'Pert X-ray diffractometer where the powder diffraction technique was used with a primary beam power of 40 kV and 30 mA for Cu Kα radiation. The XPS technique was employed for the analysis of the chemical composition of the films. XPS experiments were performed in a VG ESCALAB MkII photoelectron spectrometer, at Surface Science Laboratory, TU Darmstadt, Germany, the ultra-high vacuum (UHV) chamber is directly connected to a home-made deposition chamber by a sample transfer system (base pressure $\sim 10^{-9}$ mbar). Electrons were excited with an X-ray source (Mg Kα: hν=1253.6 eV). The samples for XPS measurements were annealed in UHV at 473 and 523K for 30 min.

A laboratory dc power supply (GPR-3020, GW, Taiwan), an electrometer Keithley 614 (Keithley Instrument Inc. USA) and a digital multimeter (GDM-354A, GW, Taiwan) were used for electrical measurements. Two points (1.5mm width and 13.6 mm length) on the surface of the film 45 mm apart were made with silver paste for electrical contact.

The optical measurements were performed using a UV-121V spectrophotometer (Shimadzu Corp., Japan). The thickness of the films was determined by using data pack in spectrophotometer. Using data pack for the determination of the thickness of the sample is a completely automatic process.

3. Results and discussion

3.1. Growth of the films

The temperature dependence of film formation has been shown in Fig.1. In all cases, the film growth sets in after an initial nucleation period of about 5–10 minutes. With the increase of bath temperature up to 363K, the rate of deposition of films decreases due to an increase in the kinetic energy of the reacting ions, i.e., an increase in the frequency of collisions among the ions. Powdery deposits and lack of specular reflection usually accompany higher deposition rate and higher film thickness. The films start peeling off from the substrates at higher bath temperatures (above 373K). Moreover, at higher bath temperatures, the deposition is not uniform. Hence, deposition at room temperature is always preferred. In this study, good samples of $Cu_{2-x}Se$ thin film deposited for 1 hour at room temperature of thickness between 0.12 and 0.18 μm were characterized, and these parameters are the same for all the samples used in the present measurements.
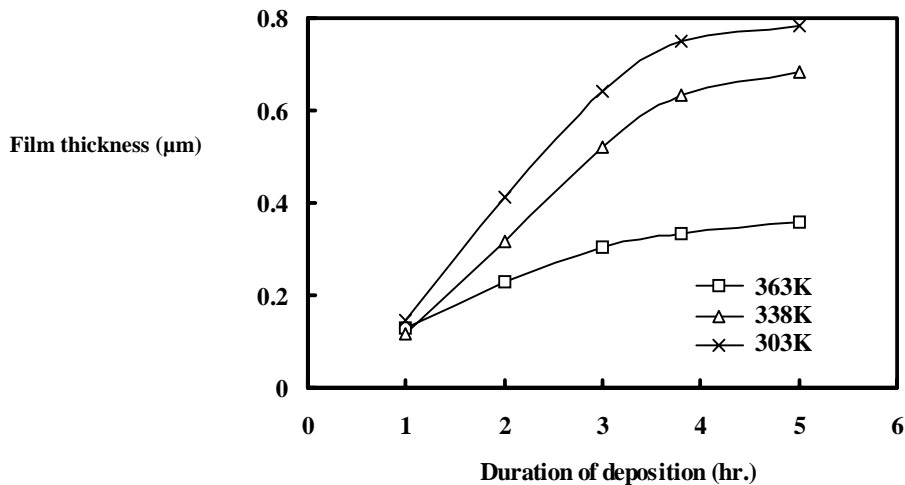

Figure 1. Film thickness versus deposition time.

3.2. Structural characterization

Figure 2 shows the XRD pattern of $Cu_{2-x}Se$ thin film. In the figure, (a) is for the as-deposited $Cu_{2-x}Se$ thin film and (b) for the $Cu_{2-x}Se$ thin film followed by annealing at 523K in air. Lots of noise is observed in the XRD pattern may be due to the growth of disordered film. From this pattern it shows that no well-defined peak was found and no well-defined plane was obtained in the case of as-deposited films, which suggests that the as-deposited films were

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disordered. A slight tendency of increasing peaks is found with annealing at an angle $2\theta =$ 27.30, 45.35 and 52.78°. The intensity of the observed peaks is very low, but becomes stronger after annealing at 523K.
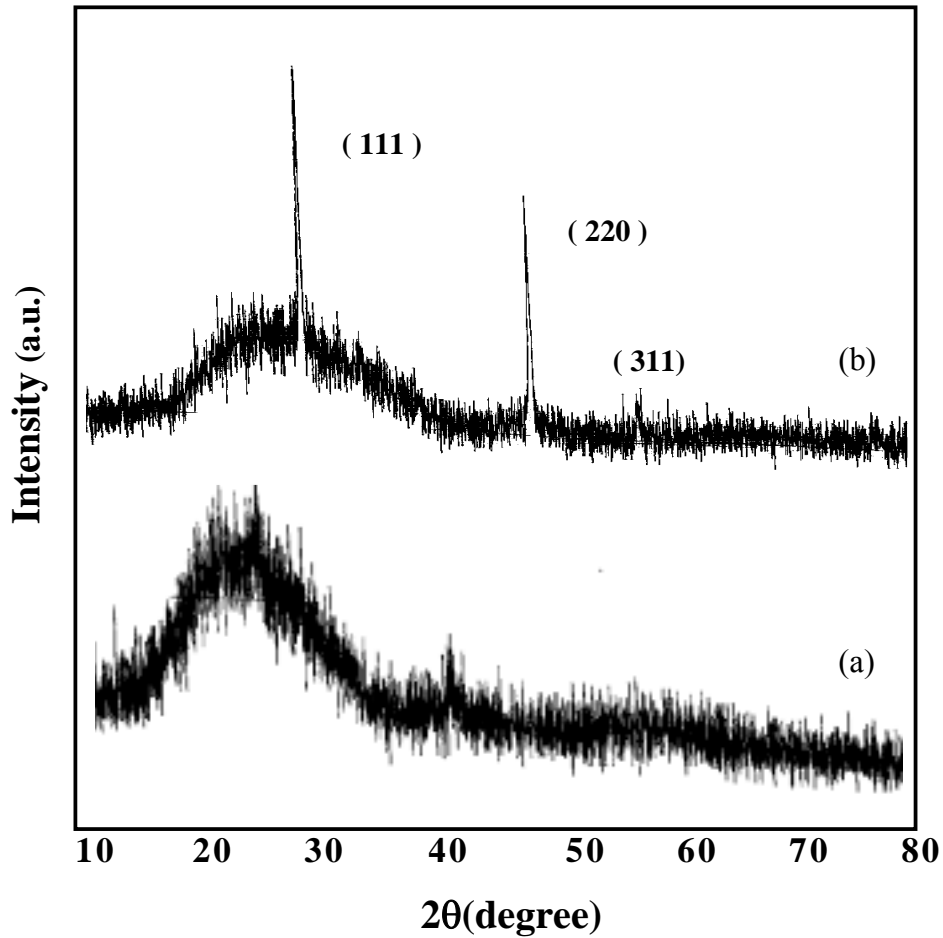

Figure 2. X-ray diffraction pattern of (a) as-deposited $Cu_{2-x}Se$ thin film and (b) $Cu_{2-x}Se$ thin film followed by annealing at 523K in air for 1 hr.

Figure 2b shows well-defined peaks suggesting the formation of crystalline film due to annealing at higher temperatures. A comparison of the observed pattern with the standard JCPDS cards shows that the annealed samples with above condition possess a structure matching the mineral spherulites (JCPDS 26-512), $Cu_{2-x}Se$ with x=0.2 which belongs to the cubic system with a=5.697Å. The observed peak positions of the annealed sample are in agreement with those due to reflection from (111), (220) and (311) planes of the reported structure of $Cu_{2-x}Se$ thin film. The same reflection plane and crystal structure were observed for as-deposited $Cu_{2-x}Se$ thin films prepared by CBD method using $CuSO_4$ and tri-sodium citrate solution [19, 21, 22].
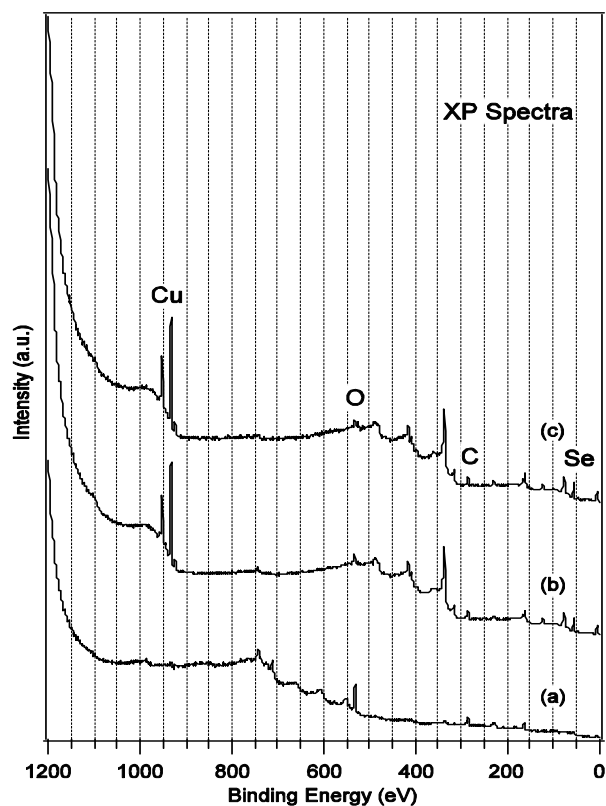
Figure 3. XPS spectra of $Cu_{2-x}Se$ thin film: (a) as-deposited, (b) after annealing at 473K for 30 min, (c) after annealing at 523K for 30 min. The annealing is performed in UHV chamber.

3.3. XPS measurement

The XP spectra of different copper selenide thin films are presented in Fig. 3. In the figure, spectrum *a* represents the as-deposited sample, spectrum *b* represents the sample annealed at 473K and spectrum *c* represents the sample annealed at 523K. It is observed that the as-deposited film is mostly covered with oxygen and carbon (spectrum *a*), whereas the peak intensities of Cu and Se are very weak. It is common for the chemically-deposited sample to be contaminated with oxygen (at 531eV) and carbon (at 285eV) from the environment as the sample was exposed to the environment during preparation. The peaks corresponding to Cu and Se became prominent in the sample annealed at 473K (spectrum *b*) and after annealing at 523K, the intensity of Cu and Se peaks (spectrum *c*) increased further, thereby indicating further lowering of oxygen contamination. Upon annealing above 573K, Se starts to desorb from the surface (data are not shown), which means that the copper selenide film remains stable up to the temperature of about 573K. It was also observed that colour of the film was changed from greenish to orange due to annealing. This means that the as-deposited film is

contaminated by oxygen, and oxygen contamination is removed during annealing process. The amount of oxygen decreases significantly but Se also starts to decrease due to annealing above 573K. With a 473K anneal, the colour becomes greenish orange and at 523K, the colour changes to fully orange, which does not change on annealing above 573K.
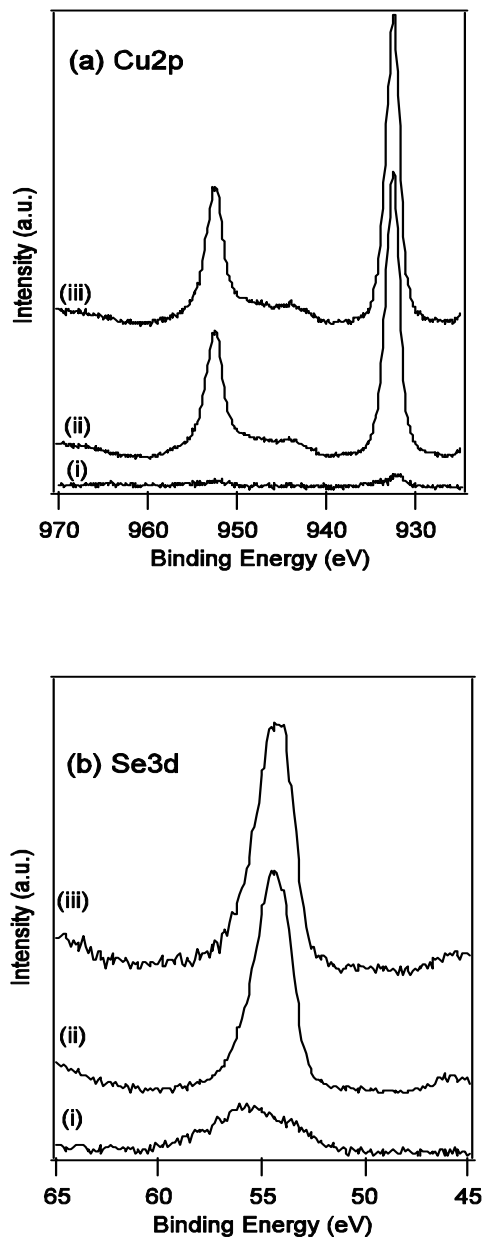

Figure 4. Core-level XPS spectra of $Cu_{2-x}Se$ thin film: (a) Cu $2p^{1/2}$ level (i) as-deposited, (ii) after annealed at 473K for 30 min, (iii) after annealed at 523K for 30 min and (b) Se $3d$ level (i) as-deposited, (ii) after annealed at 473K for 30 min, (iii) after annealed at 523K for 30 min. The annealing is performed in UHV chamber.

The core level spectra of Cu *2p* and Se *3d* are shown in Fig. 4. In figure 4, the Cu *2p* core level spectra and the Se *3d* core level spectra are shown for the as-deposited sample, and for the samples annealed at 473 and 523K. The Cu *2p* and Se *3d* peaks of the as-deposited sample are very weak due to the O and C contamination. Both the Cu *2p* and Se *3d* peaks become prominent after annealing, thereby indicating reduction of contamination by annealing. The binding energies of Cu *2p$^{1/2}$* and Se *3d* peaks of as-deposited sample are observed to be at 932.0 and 55.4 eV respectively. The binding energy of both the Cu *2p$^{1/2}$* and Se *3d* peaks are changed to 932.4 and 54.4 eV respectively, due to annealing at 473K. The binding energy of Cu *2p$^{3/2}$* peak of as-deposited and annealed sample is observed to be at 952.0 and 952.4 eV respectively. It is also observed that the peak positions of Cu *2p$^{1/2}$* and Se *3d* are not changed any more by annealing at 523K. The peak area of Cu *2p* and Se *3d* has been calculated and the Cu/Se ratio is estimated to be about 1.8 for all the samples.

3.4. DC Electrical properties

Figure 5 shows the I-V characteristic curves for the film deposited at room temperature and that followed by annealing at 523 K for one hour. The calculated resistivity is found in the range from 0.05×10^{-5} to 0.15×10^{-5} Ω-m. The I–V characteristic has been studied over the range from 5 mV to 14 V. An ohmic contact is observed in as-deposited and annealed samples.
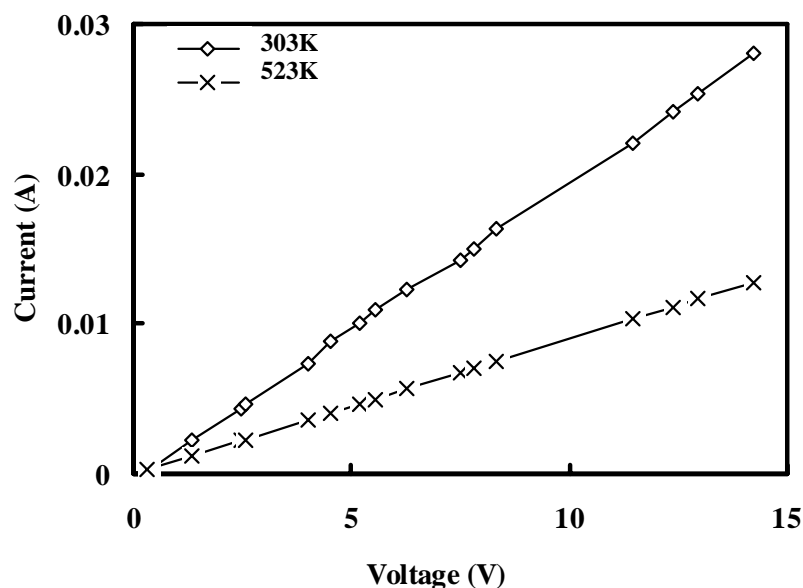

Figure 5. Current-voltage curve for Cu$_{2-x}$Se thin film: (a) as-deposited, (b) annealed at 523K for 1 hr.

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Figure 6 represents the change of room temperature resistivity with the increase of annealing temperature. Initially the resistivity decreases slowly with the increase of annealing temperature up to 473K and then increases rapidly. As observed in XPS, the surface of the as-deposited $Cu_{2-x}Se$ is mostly covered with oxygen. In as-deposited and samples annealed at lower temperatures ionization take place on the surface owing to the presence of oxygen resulting in lower resistivity because of the interaction of the ionic current with the electronic current. However, for the sample annealed above 473K, the ionic contribution becomes less due to desorption of oxygen from the surface. As a result, the resistivity increases rapidly.
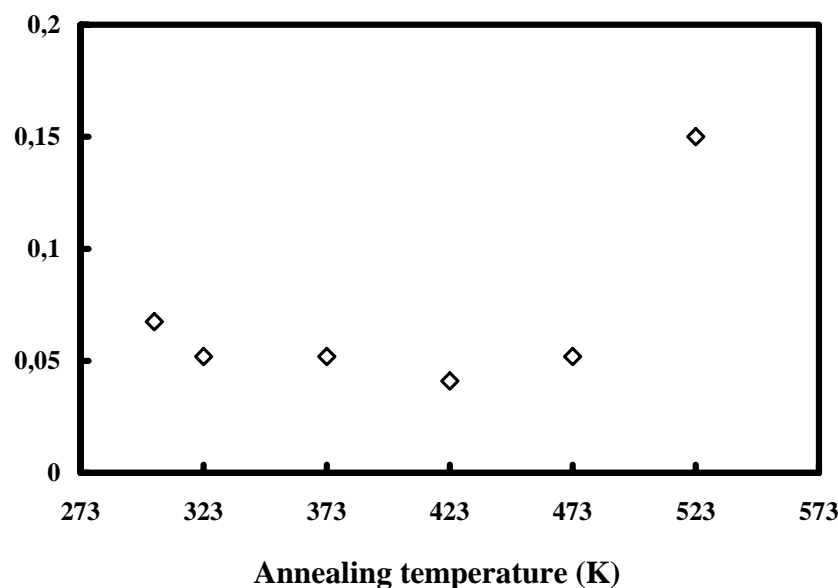

Figure 6. Variation of resistivity with annealing temperature for $Cu_{2-x}Se$ thin films of thickness 0.16 μm.

3.5. Optical absorption spectra

The variation of transmittance (T %) of $Cu_{2-x}Se$ thin films with wavelength λ at different annealing temperatures is shown in Fig. 7. Transmittance is obtained to be about 3-50% in the wavelength range 400–1100nm. A gradual decrease in transmittance upon annealing is observed in the lower wavelength region, which may be due to absorption by free carriers in the degenerate films. The peak values of transmission spectra are seen at around 820-880 nm. The absorption starts around this wavelength and the transmittance becomes very low at λ < 500 nm. In the near infrared, the transmittance decreases with the increase of wavelength for samples annealed up to 473 K. For the sample annealed at 523K, the

transmittance is observed to be less dependent on λ above 900nm. The decrease of transmittance in the lower wavelength region is due to free carrier absorption.
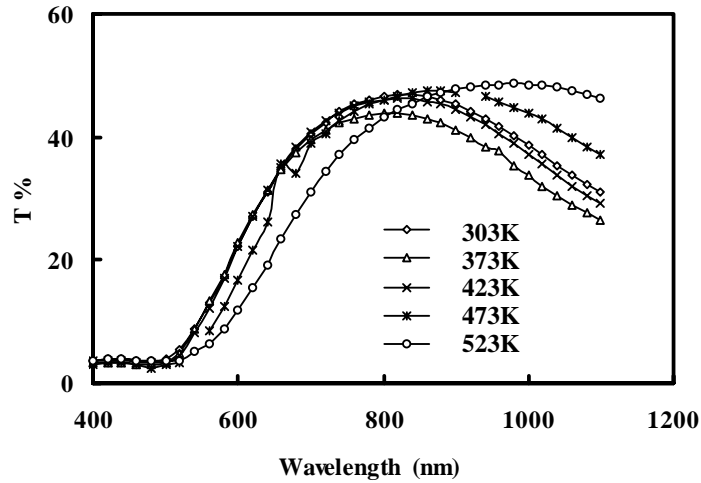

Figure 7. The optical transmittance spectra of $Cu_{2-x}Se$ thin film: as-deposited films were annealed at different temperature in the range 303-523K.
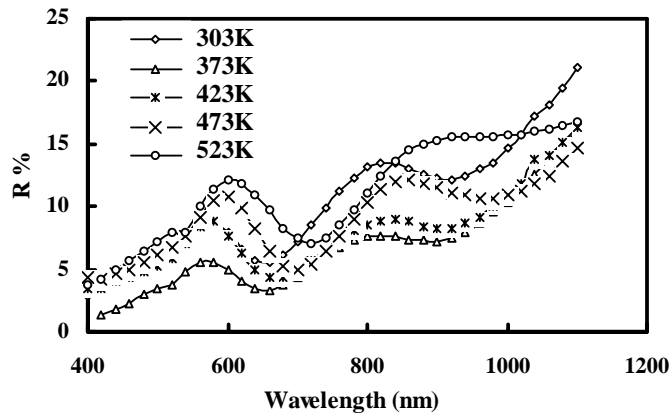

Figure 8. The optical reflectance spectra of $Cu_{2-x}Se$ thin film: as-deposited films were annealed at different temperature in the range 303-523K.

Figure 8 represents the variation of reflectance (R %) of $Cu_{2-x}Se$ thin films with λ for samples annealed at different temperatures. Reflectance is found to be about 4–20% in the wavelength region 400–1100nm. Reflectance becomes very small at around 400nm. It is observed in the R (%) vs λ curves that there are two peaks around 575–600nm and 800nm. Both the peaks shift to higher wavelength with annealing temperature. The second R (%) peak

appears at the same wavelength region where the transmittance peak appears in Fig. 7. Similar behavior was reported for $Cu_{2-x}Se$ thin films prepared by CBD technique with $CuSO_4$, $5H_2O$ at 298K for 8 hours [20]. The behaviour of high transmittance and low reflectance obtained in this experiment may make the materials suitable as an electro-conductive window coating. Peak wavelength values of transmittance and reflectance are listed in Table 1.

Temperature (K)	Direct band gap (eV)	Indirect band gap (eV)	Peak value for T%		Peak value for R%			
					1st peak		2nd peak	
			λ (nm)	T%	λ (nm)	R%	λ (nm)	R%
303	2.3	1.3	820	46.9	580	8.6	820	13.5
373	2.3	1.4	820	43.8	560	5.6	820	7.7
423	2.3	1.5	840	46.2	580	8.8	840	9.0
473	2.1	1.4	880	47.5	600	10.8	860	12.1
523	2.0	1.25	980	48.6	600	12.1	940	15.6

Table 1. Direct and indirect band gap values, peak wavelength values of T% and R% and their corresponding maximum T% and R% values for different annealing temperatures.

The absorption coefficient (α) at different wavelengths was calculated using the corrected transmittance values from $\alpha = (1/t)\ln(100/T_{corr.})$, where corrected transmittance, $T_{corr.}$, can be obtained using the relation $T_{corr.} = \{T(\%)/(100 - R(\%))\} \times 100$ [19, 26]. The α vs $h\nu$ curve is presented in Fig. 9. It is seen that α is non-linear with $h\nu$. A maximum of 10^8 m^{-1} absorption coefficient is observed around 2.5 eV. Using the optical spectra, the band gap values for the films were estimated. The direct and indirect band gap values are obtained from the plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ respectively, against photon energy $h\nu$ (eV). Such plots for the films (as-deposited and annealed) are shown in Figs. 10 and 11 for the determination of direct and indirect band gaps. Extrapolating the straight-line part of the curves in these figures to the energy axis, where $(\alpha h\nu)^2=0$, gives the values of band gap for direct transitions (Eg.dir) and to where $(\alpha h\nu)^{1/2}=0$ gives the values of band gap for indirect transitions (Eg.indir). The Eg.dir varies in the range of 2.0–2.3 eV and the Eg.indir is in the range of 1.25-1.5 eV for all samples from as-deposited to all annealed samples up to 523K. These kinds of values of band gap are reported for $Cu_{2-x}Se$ thin film deposited by CBD technique using $CuSO_4$ and N, N-dimethylselenourea [19, 21, 22]. It is observed that both direct and indirect band gap values of

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as-deposited samples are less compared with those of the annealed samples. The increase of band gap due to annealing may be understood by the improvement of crystallinity of the as-deposited film on annealing as observed in XRD.
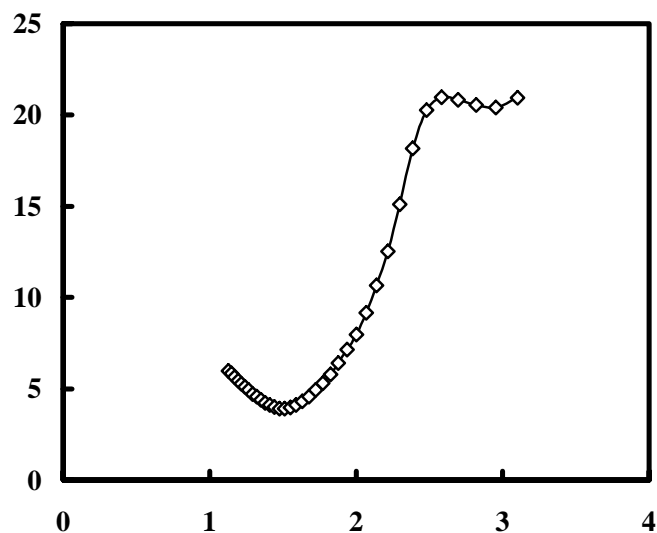

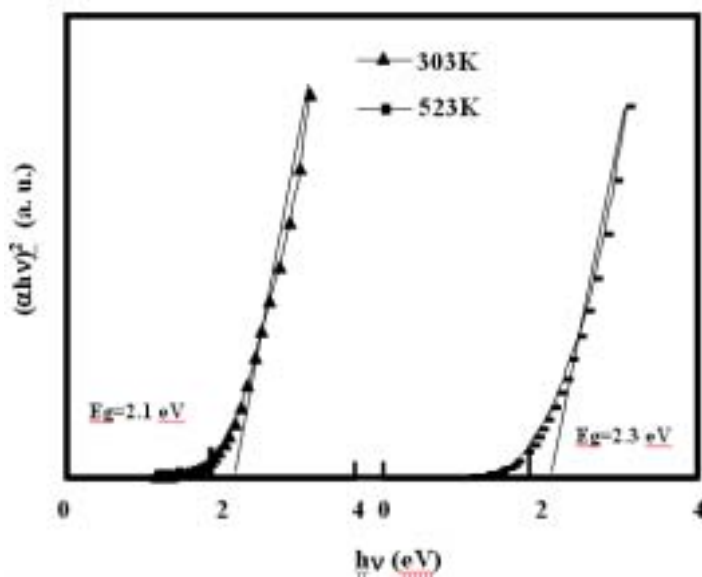**Figure 9.** α versus hν curve for as-deposited $Cu_{2-x}Se$ thin film.

Figure 10. $(\alpha h\nu)^2$ vs hν plots of $Cu_{2-x}Se$ thin film: (a) as-deposited, (b) annealed at 523K for 1 hr.
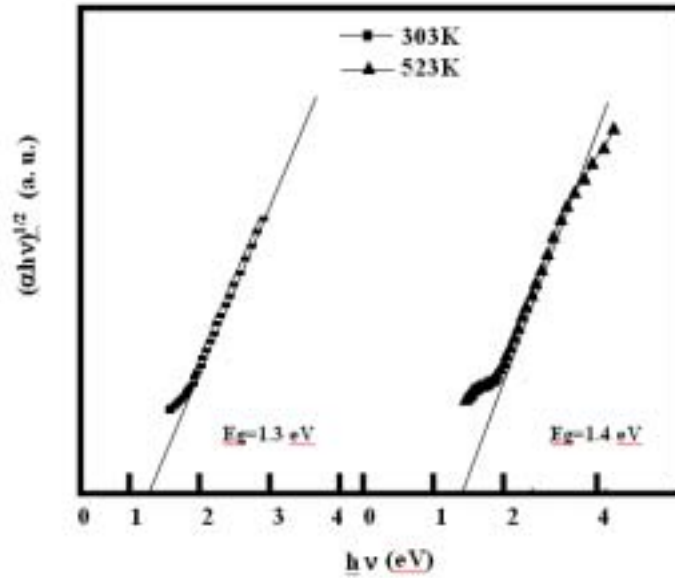
Figure 11. $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of $Cu_{2-x}Se$ thin film:
(a) as-deposited, (b) annealed at 523K for 1 hr.

4. Conclusions

A thin film of copper selenide of composition $Cu_{1.8}Se$ of cubic structure with a lattice constant of 5.697Å was deposited from chemical baths using sodium selenosulfate. It is found that as-deposited samples and films annealed up to 523K have low resistivity between 0.04×10^{-5} and 0.15×10^{-5} Ω-m. Optical absorption in the films are found from free carrier absorption in the near infrared region with a maximum absorption coefficient of $\sim 10^8$ m^{-1}. The band gap for direct transitions, Eg.dir, varies in the range 2.0–2.3 eV and that for indirect transition, Eg.indir, is in the range 1.25–1.5 eV.

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