

Structural, optical and electrical properties of chemically deposited copper selenide films

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Abstract. Stoichiometric and nonstoichiometric thin films of copper selenide have been prepared by chemical bath deposition technique at temperature below 60°C on glass substrate. The effect of nonstoichiometry on the optical, electrical and structural properties of the film was studied. The bandgap energy was observed to increase with the increase in at % of copper in composition. The grain size was also observed to increase with the decrease of at % of copper in composition. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS), absorption spectroscopy, and AFM. The results are discussed and interpreted.

Keywords. Copper selenide; thin films; chemical bath deposition.

1. Introduction

Thin film heterojunctions solar cells play an important role as low cost, large area and high efficiency devices in solar energy conversion. Cuprous chalcogenides films such as Cu₂S, Cu₂Se and Cu₂Te are typically *p*-type and are used as *p*-type layers on *n*-type layer films to obtain various types of heterojunctions. Such heterojunctions have excellent photovoltaic properties. Copper selenide has recently caught much interest since it has been widely used as solar cell (Lakshmikummar 1994).

The attraction of this material also lies in the feasibility of producing the ternary material, CuInSe₂ (Chu *et al* 1984; O'Brien and Santhanam 1992) and as an important surface impurity in Cu-rich CuInSe₂ (Fons *et al* 1998). Copper selenide exists in the cubic, tetragonal or orthorhombic or monoclinic forms (Toneje and Toneje 1981; Kashida and Akai 1988; Haram *et al* 1992; Levy-Clement *et al* 1997). This material is stable over a wide range of departures from stoichiometry (Takahashi *et al* 1976; Okimura *et al* 1980; Vucic *et al* 1981; Haram and Santhanam 1994). A number of methods have been reported (Takahashi *et al* 1976; Toneje and Toneje 1981; Kashida and Akai 1988; Massaccesi *et al* 1993) for producing copper selenide. It is reported (Mondal and Pramanik 1983, 1984; Padam 1987; Sharma *et al* 1990; Levy-Clement *et al* 1997; Lakshmi *et al* 2000, 2001) that the copper selenide films were prepared by chemical bath deposition technique. The preparation and characterization of copper selenide thin films are reported in the present article.

2. Experimental

The chemical bath deposition technique was used to deposit the thin films of copper selenide on glass substrate. The starting materials used were cupric chloride, elemental selenium, and sodium sulphite. Sodium hydroxide and ammonia solution were used to adjust pH of the reaction mixture. The stoichiometric and non-stoichiometric copper selenide films have been prepared on glass substrate. Initially the volume of the copper and selenium precursors was taken in the ratio of 2.25 : 1. By changing the volume of copper and selenium precursors films were obtained. The optimum time, temperature and pH were kept constant throughout the experiment i.e. 2 h, 60°C and 10, respectively.

The process involves the reaction of Cu⁺ ions with Se²⁻ ions in deionized water solution. Elemental selenium (99.95%) was dissolved in aqueous solution of sodium sulphite (pH > 9) at 90°C to form a partial unstable Na₂SeSO₃ solution. Tetraamine copper was mixed with Na₂SeSO₃. In the solution partially unstable Na₂SeSO₃ yields Se²⁻ and SO₃²⁻ ions. Sulphite ions reduce tetraamine copper and generate Cu⁺ ions.

The structural properties of thin films were investigated by X-ray diffraction (XRD) using CuKα (λ = 1.5418 Å) radiation. The optical absorption of the films was measured using Hitachi U-2000 spectrophotometer. The scanning electron microscopic studies were carried out using JEOL model, JSM-6360A SEM. Elemental analysis was carried out with an EDAX using energy dispersive X-ray spectrophotometer (EDS). An AFM Nanoscope digital instrument with a silicon nitride cantilever was used to

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probe different portions of the films surface in 'contact mode AFM'.

3. Results and discussion

3.1 Structural analysis

Figure 1 represents the X-ray diffractograms of Cu_2Se . It is a XRD of sample 3 (an approximately stoichiometric sample). The (111), (022), (113) and (004) peaks match well with the standard data (JCPDS card 6-680). All the peaks correspond to the cubic phase of Cu_2Se .

3.2 Elemental analysis by EDS

The quantitative elemental analyses of copper selenide films were determined using energy dispersive analysis (EDAX) technique at room temperature. Table 1 shows the elemental composition of the Cu_2Se films from EDAX. Theoretically expected stoichiometric composition of Cu_2Se (in terms of at %) is Cu = 66.7% and Se = 33.3%. Among the four samples the elemental composition of sample 3 is nearer to stoichiometry.

3.3 Microstructural studies

The surface morphology of the as synthesized copper selenide films were studied by using scanning electron microscopy (SEM). Figures 2(a), (b), (c) and (d) show SEM images of sample 1, sample 2, sample 3 and sample 4, respectively. The particles associated with all films are nearly spherical or elliptical in nature. The average grain sizes calculated from the SEM images are presented in table 2. The average grain size goes on decreasing with

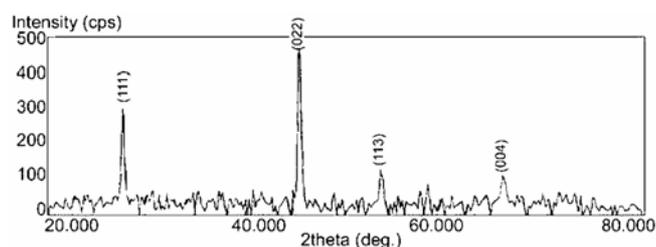


Figure 1. XRD of the sample.

Table 1. Elemental compositions of the samples.

Sample no.	Cu (at%)	Se (at%)	Cu/Se (at%)
1	77.57	22.43	3.46
2	68.63	31.37	2.19
3	65.63	34.37	1.91
4	58.97	41.03	1.41

the increase in at % of copper in the film composition. Larger the concentrations of copper smaller the grains. For films with higher concentration of copper ions, the growth occurs with multiple nucleation centres resulting in a lower grain size, while for lower concentration of Cu ions, comparatively lower nucleation centres give higher grain size. The amount of feed material available in the reaction vessel is constant for a particular reaction. If the same material would be divided on the larger number of nucleation centres, the grain would not grow larger but remain smaller (Sinnott 1958; Patil et al 1998; Patil and Wani 2001). The grains are submicrocrystalline.

3.4 Surface morphology

A copper diselenide film was morphologically characterized using atomic force microscopy (AFM). Figure 3 represents the AFM pictures of sample 3 (Cu/Se = 1.91). AFM pictures reveal the granular nature of the particles. There would have been agglomeration of particles in most of the cases as evident from the 2D (figure 3b) micrographs. The root mean square value indicating the surface roughness of the film (Rg_{AFM}) is calculated from different areas of the film. It was observed that the surface roughness of the film was 34.84 nm/ $1 \mu\text{m} \times 1 \mu\text{m}$. This observation infers that the film surface is somewhat rough.

3.5 Optical studies

Figure 4 shows the optical absorbance of the samples. It is clear from table 3 that the bandgap energy values go on decreasing while film thicknesses go on increasing with the decrease in at % of copper in the film composition. The bandgap energies of the samples were calculated from the absorption edges of the spectra. The decrease in bandgap energy with decreased Cu (or increased Se) content in the film can be attributed to the increase in the grain size of the film. A similar behaviour of materials was reported by several workers (Oztas et al 2005; Sonawane and Patil 2007). Reported bandgap energy of Cu_2Se is 2.33 eV (Grozdanov Ivan 1994). Bandgap energy of sample 3 is approximately same as the reported one.

3.6 Electrical studies

3.6a Electrical conductivity and activation energy: Electrical conductivity of the copper selenide thin films

Table 2. Effect of Cu/Se on grain size.

Sample no.	Cu/Se (at%)	Grain size (nm)
1	3.46	110
2	2.19	186
3	1.91	198
4	1.44	230

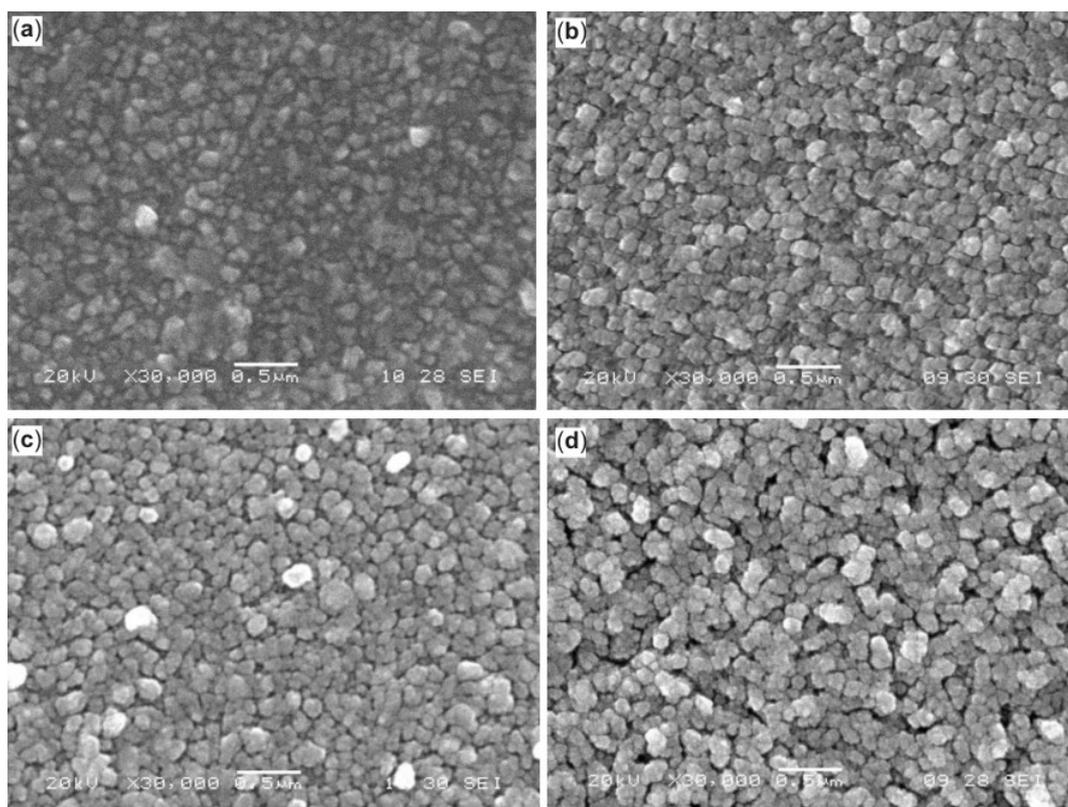


Figure 2. (a)–(d). SEM images of the samples 1, 2, 3, 4, respectively.

Table 3. Bandgap energies calculated from the absorption edges.

Sample no.	Cu/Se (at%)	Thickness (nm)	Bandgap energy (eV)	Grain size (nm)
1	3.46	150	2.51	110
2	2.19	196	2.40	186
3	1.91	207	2.29	198
4	1.44	250	2.11	230

Table 4. Dependence of conductivity and activation energies on Cu/Se.

Sample no.	Cu/Se (at%)	Conductivity (σ) (Ωcm) ⁻¹ (at 448K)	Activation energy (eV)
1	3.46	2.50E-06	0.034
2	2.19	7.50E-07	0.037
3	1.91	3.73E-08	0.046
4	1.44	1.02E-08	0.049

was measured by using d.c. two-probe method in the temperature range 313–448 K. Figure 5 shows variation in the logarithm of conductivity with an inverse of temperature for various compositions of copper selenide.

It is clear from figure 5 that the conductivity increases with the increase in temperature indicating the semiconducting nature of copper selenide thin films. Moreover, conductivity increases with increase in Cu/Se ratio in the film.

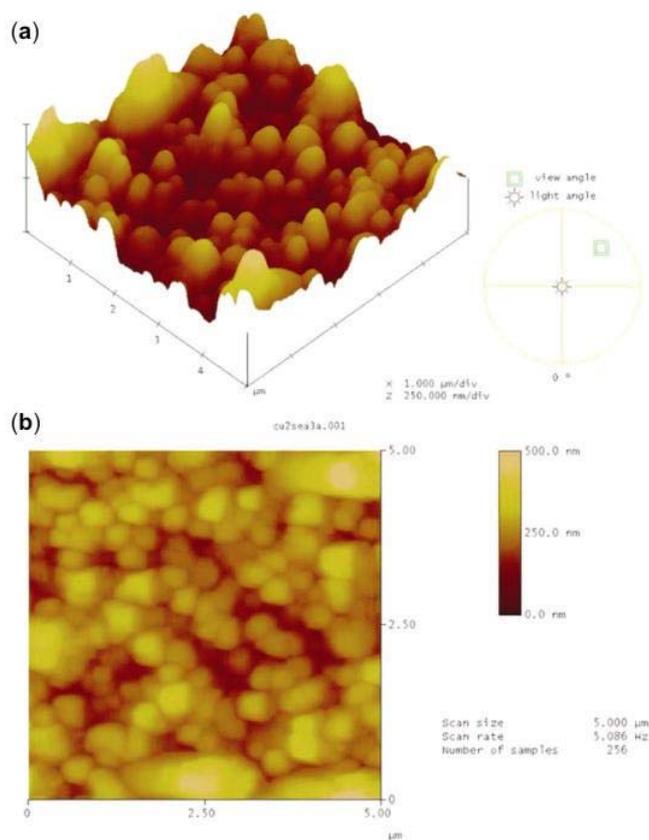


Figure 3. (a)–(b). AFM pictures of the sample.

Figure 6 shows variation of electrical conductivity with Cu/Se ratio at a temperature, 448 K.

The activation energies were calculated from the slopes of the graphs of logarithm of conductivity plotted against inverse of temperature and is presented in table 4. It is clear that the activation energy goes on decreasing with the increase of Cu/Se ratio as shown in figure 7. Lower activation energy in case of the sample having higher atomic percent of copper, could be attributed to high reactivity of copper ions with available anions. Due to high reactivity, larger at % of copper ions would be incorpo-

rated in the composition, which lead to higher conductivity, and in turn, lower activation energy (Bari and Patil 2006).

3.6b *Thermoelectrical power*: Figure 8 shows the curves of TEP vs temperature for different samples of copper selenide in the range 280–390 K, which are almost straight lines indicating that TEP increases with increasing temperature. The positive sign of the TEP indicates that conduction should occur predominantly due to holes and the material is *p* type.

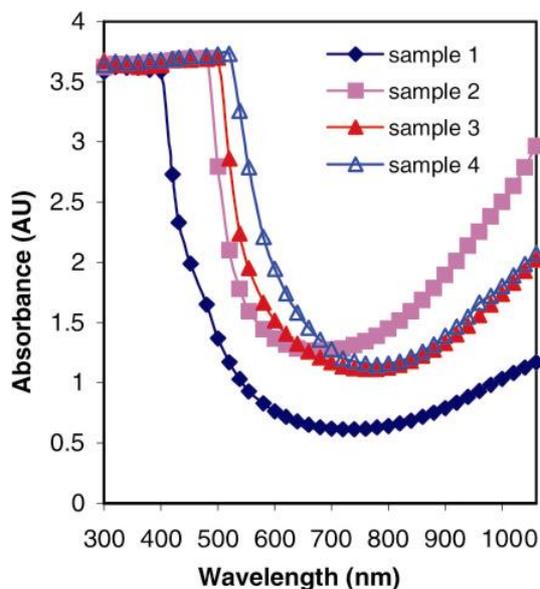


Figure 4. Plot of optical absorbance vs wavelength (λ).

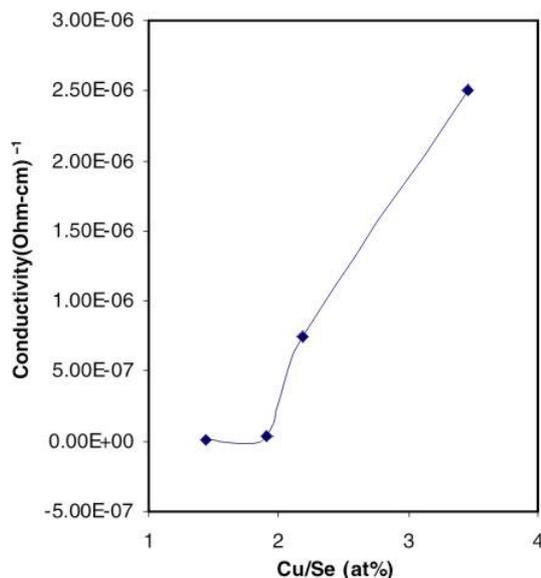


Figure 6. Variation of electrical conductivity with Cu/Se ratio at 448 K.

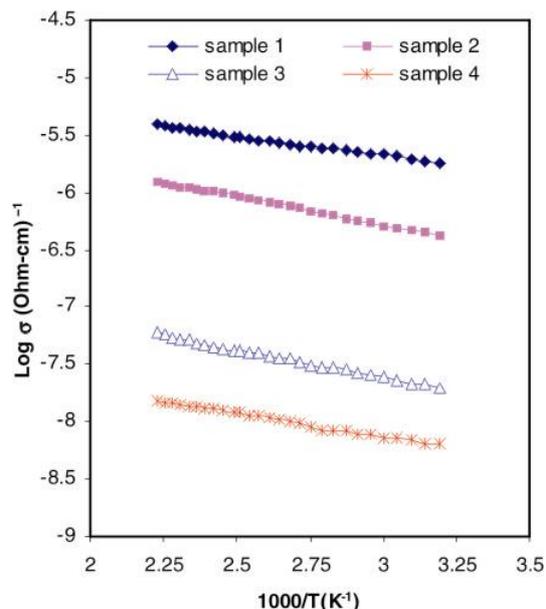


Figure 5. Variation of electrical conductivity with Cu/Se ratio.

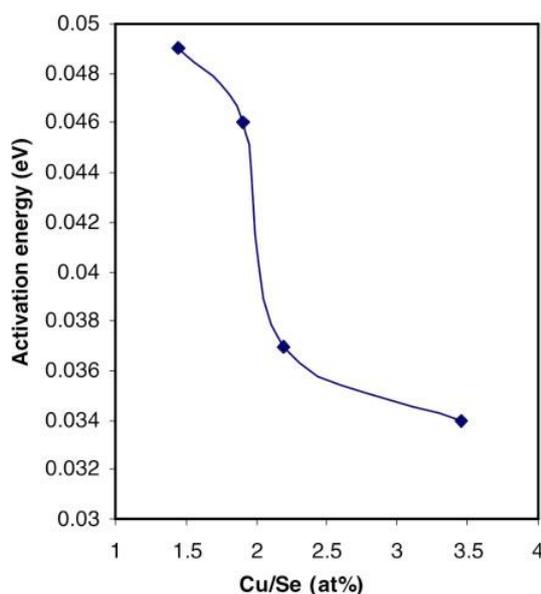


Figure 7. Variation of activation energy with Cu/Se ratio.

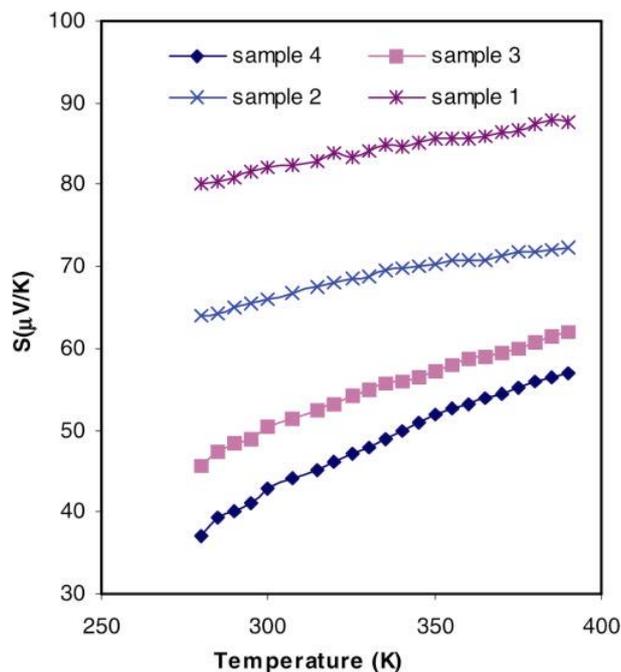
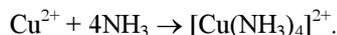


Figure 8. Plots of TEP (S) versus temperature.

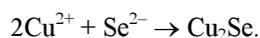
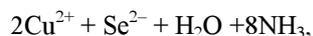
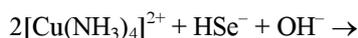
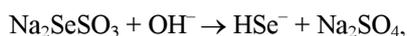
3.7 Discussion

3.7a Growth mechanism of the copper selenide films:

The uniform, transparent copper selenide thin films were possible due to the reaction given below:



Sodium selenosulfate hydrolyzes in alkaline solutions, producing selenide ions and reducing the Cu^{2+} into Cu^+ . The latter then combines with the selenide ions to give insoluble Cu_2Se precipitate as represented below:



The bandgap energies of the samples go on decreasing with the decrease of at % of copper in the composition. Smaller the number of copper atoms, smaller would be the nucleation centres and larger would be the grain size.

4. Conclusions

Following statements can be made to summarize the results:

(I) Copper selenide thin films were successfully deposited onto glass substrate by simple chemical bath deposition technique.

(II) The films were uniform and had good adherence to the substrate.

(III) The XRD of copper selenide film confirmed the formation of Cu_2Se .

(IV) It is clear from SEM images of copper selenide that average grain size was decreasing with the increase in at % of copper in the film composition.

(V) It was observed that the surface roughness of the copper selenide film is somewhat rough.

(VI) The bandgap energies of the copper selenide samples were decreasing with the decrease of at % of copper in the composition of the film.

(VII) The average grain size of copper selenide was observed to decrease with the increase of at % of copper in composition.

(VIII) Increase in the conductivity with the increase in temperature indicated the semiconducting nature of copper selenide thin films. Moreover, conductivity was observed to increase with increase in Cu/Se ratio in the film.

(IX) The activation energy was decreasing with the increase of Cu/Se ratio in copper selenide.

(X) TEP increases with increase in temperature in copper selenide. The positive sign of the TEP indicated that conduction would predominantly be due to holes and Cu_2Se would be *p*-type in nature.

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