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Archives of Applied Science Research, 2012, 4 (4):1857-1863
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Synthesis and characterization of chemically deposited $Cu_{2-x}Se$ thin films

A. S. Khomane *

Department of Chemistry, Government Rajaram College, S. U. Road, Vidyanagar, Kolhapur, Maharashtra 416 004, India

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ABSTRACT

Simple and economical chemical bath deposition (CBD) method has been used for the synthesis of copper selenide ($Cu_{2-x}Se$) thin film sample. Synthesized film samples of $Cu_{2-x}Se$ were subjected to XRD, SEM, UV-vis-NIR and electrical characterization techniques. XRD analysis showed cubic phase of annealed $Cu_{2-x}Se$ the film sample. The optical spectrum of as deposited film sample shows band energy 2.20 eV. The electrical resistivity of $Cu_{2-x}Se$ thin film was found to be of the order of 10^{-3}(Ωcm) with p-type of conduction mechanism.

Keywords: Semiconductors, Thin films, Chemical synthesis, X-ray diffraction.

INTRODUCTION

Copper selenide heterojunction solar cells are cost effective and high-efficiency devices in the solar energy conversions. CuSe is also used in the fabrication of photovoltaic devices such window material, super ionic conductor, electro-optical devices, optical filter, thermo electric converter and photo electrochemical cell [1-10].

CuSe thin films can be deposited by various methods such as spray pyrolysis, electro deposition, rf sputtering, pulse laser evaporation, physical vapour deposition, screen printing, metal organic vapour phase epitaxy (MOVPE)/metal organic chemical vapour deposition (MOCVD), successive ionic layer adsorption reaction (SILAR) and chemical bath deposition (CBD) [11-17].

We report the synthesis $Cu_{2-x}Se$ thin films by CBD technique. It is simple, inexpensive and does not require sophisticated instrument. The synthesized film samples were characterized by XRD, SEM and optical absorption/reflection spectroscopy and electrical techniques.

* Corresponding Author:

E-mail address: ashok_khomane@rediffmail.com

Tel: 91 231 2537840; **Fax**: 91 231 2531989

MATERIALS AND METHODS

2.1 Synthesis of CuSe thin films

Analytical grade chemicals such as copper sulphate dihydrate, maleic acid, selenium metal powder; sodium sulphite and ammonia were used for deposition of CuSe thin films. Sodium selenosulphate was obtained by refluxing 5 g Selenium powder and 12 g sodium sulphite in 200ml double distilled water for 9 hours at 90 ^{o}C, the concentration of the resulting solution was found to be 0.25 M. The non-conducting glass plates of dimensions 7.6 x 2.6 x 0.2 cm^3 were used for the deposition purpose.

In the synthesis of $Cu_{2-x}Se$ thin films, 10 ml (0.25 M) copper sulphate dihydrate was complexed with maleic acid. The complex was dissolved in excess of ammonia and whole solution was diluted up to 50 ml with distilled water. Then 10ml (0.25 M) sodium selenosulphate was added in the above reaction mixture. The pH was found to be 8.5 $\pm$ 0.05. The glass substrates were kept vertically in this reaction mixture for 24.0 hrs.The glass substrates were removed after 24.0 hrs. from the beaker, washed with distilled water and kept in a desiccator.

2.2 Sample analysis

The thickness of the $Cu_{2-x}Se$ films was determined by weight difference method. The film samples were characterized by using Philips PW-1710 X-ray diffractometer in 2θ range from 0° to 100° using Cu Kα_1, line (wavelength 1.54056 A$^{\circ}$). The surface morphology of the samples was observed using the JEOL-JSM 6360 scanning electron microscope (SEM). The optical absorption spectra were obtained in the wavelength range from 400 to 800 nm by using double beam spectrophotometer at room temperature. The analysis of spectrum was done by computing the values of absorption at every step of 2 nm. The electrical resistivities were measured in temperature range 300-550 K on Zintek - 502 BC Milliohm meter using two-probe method. Silver paste was used for better ohmic contact purpose. TEP measurements were carried by maintaining a temperature gradient along the length of the film and measuring, the potential difference across the terminals having a separation of 1 cm with the help of a digital micro voltmeter. A calibrated thermocouple probe (chrome-alumel) with a digital indicator was used to measure the working temperature.

RESULTS AND DISCUSSION

3.1 Reaction mechanism

The deposition of copper selenide film takes place when the ionic product of Cu^{2+} and Se^{2-} ions exceeds to solubility product of copper selenide. The reaction mechanism of $Cu_{2-x}Se$ thin films is given below [18-22].

$$Cu^{2+} + nMA \longrightarrow Cu(MA)_n \quad (1)$$

Where MA = Maleic acid

$$Na_2SeSO_3 + 2\,^{-}OH \longrightarrow Se^{2-} + Na_2SO_4 + H_2O \quad (2)$$

$$Cu(MA)_n + Se^{2-} \longrightarrow CuSe + nMA \quad (3)$$

$Cu_{2-x}Se$ films were found to be homogeneous, well adherent to the glass substrate and dark red in color.

3.2 X-ray diffraction analysis

X-ray diffraction technique was used for crystallographic analysis of film sample. XRD-spectrum of the annealed $Cu_{2-x}Se$ film at 150 ^{o}C is shown in Fig.1.

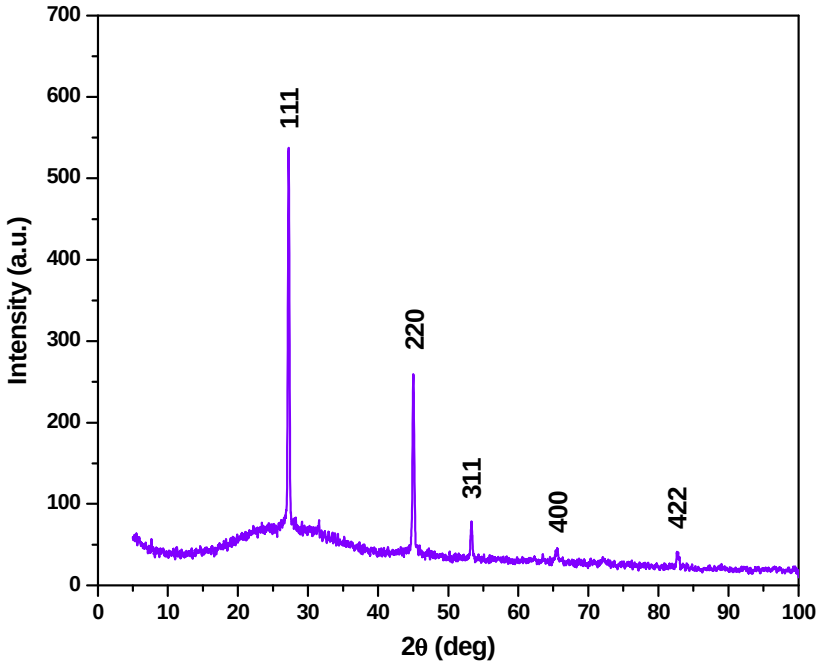

Fig.1 XRD - spectrum of annealed $Cu_{2-x}Se$ thin film at 150 °C.

The reflections are observed at 2θ angle 27.215°, 45.010°, 53.315°, 65.510° and 82.760° due to the 111, 220, 311, 400 and 422 hkl planes respectively .All the reflections are compared with JCPDS diffraction patterns from the PDF Card [23]. The observed d-values correspond to cubic phase of $Cu_{2-x}Se$ (Berzelianite) and therefore are indexed according to cubic crystal structure. The (hkl) indices are shown above the reflections in Fig.1. The lattice parameters of cubic $Cu_{2-x}Se$ films were determined by following relation.

$$a = d\,(h^2+l^2+k^2)^{1/2} \qquad (4)$$

The lattice parameter of film sample was found to be 5.6920 Å which is in good agreement with standard values. The grain size of film sample was calculated by using Scherrer formula.

$$D = K\lambda / \beta \cos\theta \qquad (5)$$

Where, D is crystallite size, K is constant (0.9), λ is the wavelength of the x-ray used, β is the broadening of diffraction line measured at half of its maximum intensity (in radians) and θ is Bragg's diffraction angle. The average crystallite size was calculated by resolving the highest intensity peak. The crystallite size of $Cu_{2-x}Se$ thin film was found to be 270 A° as listed in Table 1.

Film sample	d-values Å		hkl planes	Cell parameter (Å)	Grain size (Å)	Band gap (eV)
	JCPDS	Observed				
CuSe	3.33000	3.2740	111	5.6920	270	2.20
	2.03000	2.0124	220			
	1.72900	1.7169	311			
	1.43400	1.4237	400			
	1.17100	1.1652	422			

† Crystallographic parameters of $Cu_{2-x}Se$ thin films.

3.3 SEM Studies

Scanning electron microscopy (SEM) was used for the surface morphological characterization of the film sample. The SEM photograph of as deposited $Cu_{2-x}Se$ thin films at 10,000 X magnification is shown in Fig.2. CuSe photograph shows a compact structure composed of a single type of small, densely packed microcrystal's. Film sample shows a smooth grain background which is an indication of one step growth by multiple nucleations.

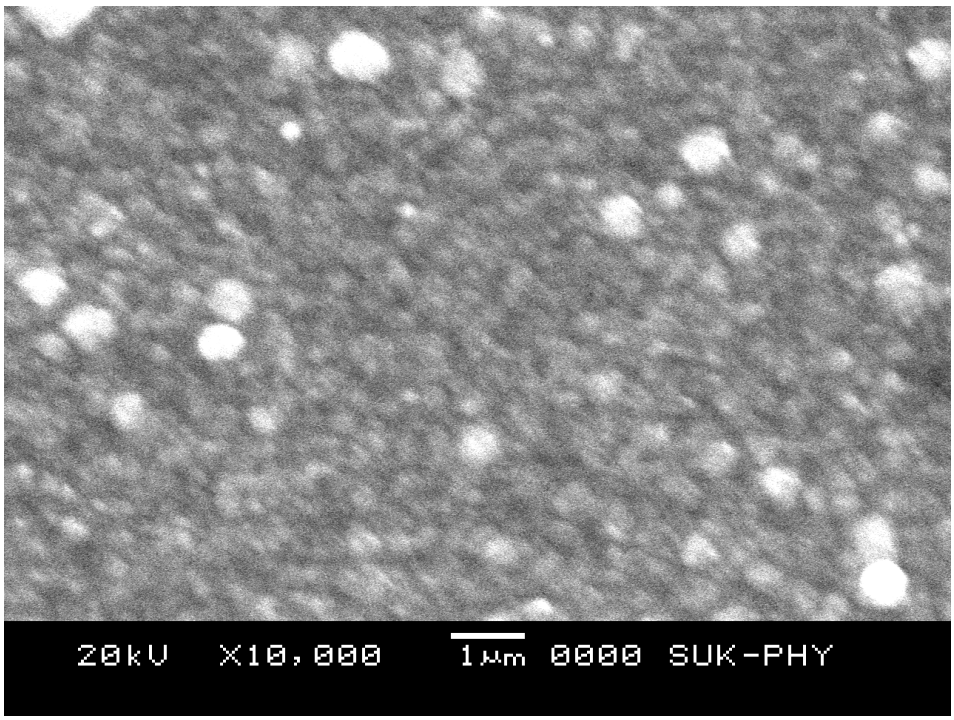

Fig.2 SEM photographs of as-deposited $Cu_{2-x}Se$ thin film.

3.4 Optoelectronic analysis

The optical absorptions/reflections were measured in the range of 400 to 800 nm at room temperature. A careful observation of the spectrum shows the presence of a broad absorption edge in the 500-650 nm range. The simplest form of equations obeyed near and above absorption edge is [24].

$$\propto h\nu = A\,(h\nu - Eg)^{n} \qquad (6)$$

Where α is absorption coefficient (cm^{-1}), $h\nu$ the photon energy (eV), A is complex parameter which depends on temperature, photon energy, photon energies etc. The n values are 0.5, 1.5, 2 and 3 for allowed direct, forbidden direct, allowed indirect forbidden indirect transitions respectively [25-26] and Eg. is the direct band gap energy. A plot of $(\propto h\nu)^{2}$ Vs $h\nu$ gives the optical band gap energy (Eg). 'Eg' was determined by extra plotting the straight line to the energy axis whose intercept to the x- axis gives the optical band gap shown in Fig.3. The band gap energy of $Cu_{2-x}Se$ films sample was found to be 2.20 eV [27-29].

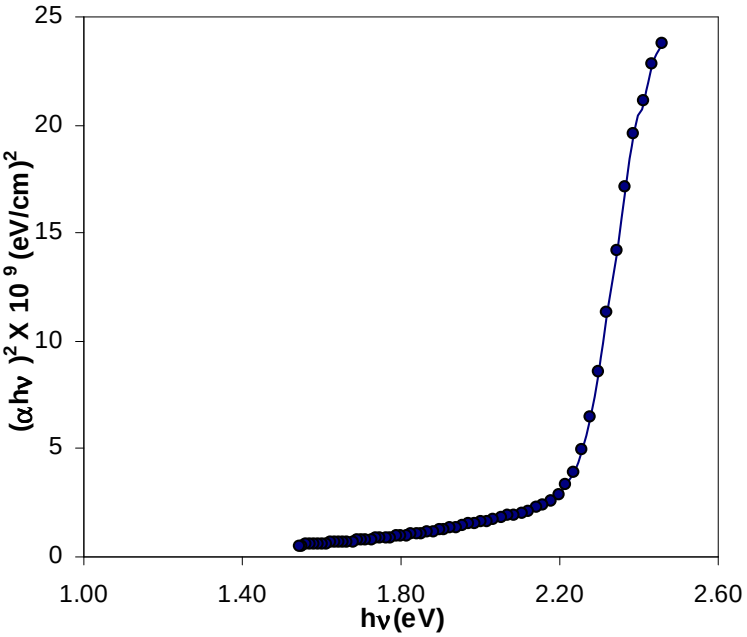

Fig.3 Plot of (α□h υ)^2 versus h υ of $Cu_{2-x}Se$ thin film.

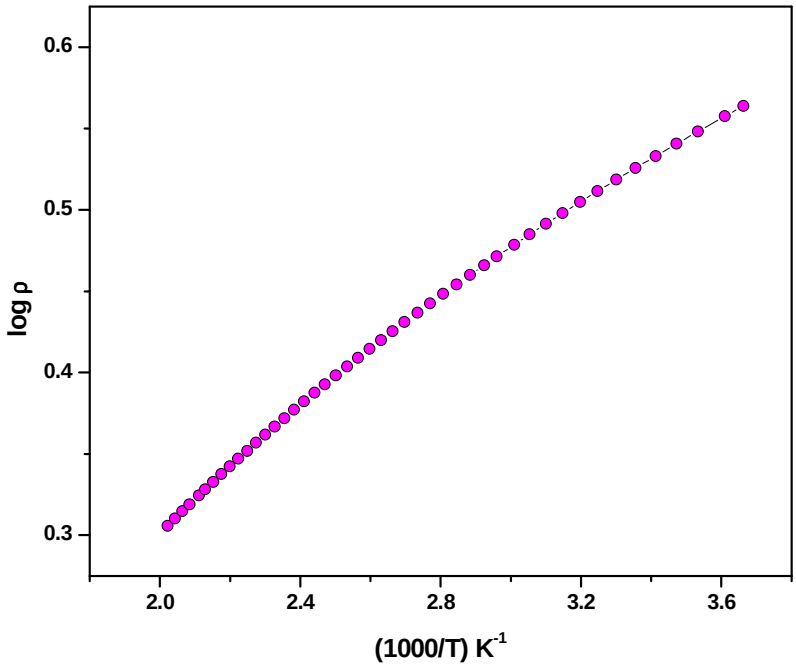

Fig.4 Plot of log (ρ) versus (1000/T) of $Cu_{2-x}Se$ thin film.

3.5 Electrical properties

The dark electrical resistivity of the sample was measured in temperature range of 300 to 500 K. The resistivity of the sample decreases with increase in temperature indicates the semi conducting nature of the sample. The plot of log ρ vs 1000/T of the film sample is shown in the Fig.4. The nature of the plot is linear type indicating the presence of one type of conduction mechanism. The electrical resistivity of $Cu_{2-x}Se$ films was found to be of the order of 10^{-3} (Ω cm) [27-28].The film sample showed high electrical conductivity can be used as radiation filters. The activation energy of film sample was determined by using the Arrhenius equation.

$\rho = \rho_o \exp(-Ea/kT)$ (7)

Where ρ is the resistivity, ρ_o is a constant, Ea, the thermal activation energy, k the Boltzmann constant and T the absolute temperature. The activation energy obtained from linear portion of the graph is found to be 0.650 eV. Which agree well with the reported value 0.650 eV [27-28] .Thermo-electric powers (TEP) of $Cu_{2-x}Se$ film sample increases with increase in temperature which indicates the degenerate nature of the film sample. In the measurement themoemf of film sample, the positive terminal was connected to the cold end from the sign of terminal connected to cold end of the sample, one can decide the sign of the predominant charge carrier; hence, the thermoelectric measurement confirms well-known p-type semi conducting behavior of $Cu_{2-x}Se$ thin films [27-28,30].

CONCLUSION

$Cu_{2-x}Se$ thin films can be deposited by using maleic acid as a complexing agent.XRD analysis revealed that $Cu_{2-x}Se$ exist in cubic crystal structure. The band gap energy of $Cu_{2-x}Se$ thin was found to be of in the order of 2.20 eV. Films samples shows p-type of conductivity can be useful in the fabrication of heterojunction solar cells.

Acknowledgement
The author Dr.A.S.Khomane gratefully acknowledges Dr.Smt.S.B. Maharaj (Patil), Principal of Rajaram College, Kolhapur, for co-operation in the research activity.

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