CHARACTERISTICS OF BRUSH ELECTROPLATED COPPER SELENIDE THIN FILMS

K.R.MURALI*, R. JOHN XAVIER[a]
Electrochemical Materials Science Division
Central Electrochemical Research Institute, Karaikudi – 630 006, India
[a]Dept of Physics, H.H. The Rajah's College, Pudukottai – 622 001, India

Cu_2Se thin films were prepared for the first time by the brush electrodeposition technique on conducting tin oxide substrates. The deposition temperature was varied in the range of 30 - 80°C from the precursors copper chloride and selenium di oxide. Film thickness varied in the range of 2.0 – 2.5μm. The films were polycrystalline and exhibited cubic structure. Optical measurements indicated a direct band gap value of 2.18 eV. The value of the resistivity decreased with deposition temperature. Mobility and carrier concentration of the films increased with deposition temperature. The films exhibited reasonable photo activity from photoelectrochemical studies.

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1.Introduction

Cu_2Se thin films have attracted the attention of many researchers owing to the interesting optical and electrical properties [1,2]. Cu_2Se thin films are also considered as promising materials for heterojunction solar cells[3,4]. Cu_2Se thin have been prepared earlier by vacuum evaporation[5 – 10], mechanical alloying [11], electrodeposition [12 – 14], sol gel method [15], chemical bath deposition(CBD)[13,16,17], combination of chemical precipitation and dip coating methods[18]. In this work, Cu_2Se thin films were deposited for the first time by brush electrodeposition technique, and the films were characterized for their structural, optical, electrical and photoelectrochemical properties.

2. Experimental

Cu_2Se thin films were deposited by brush plating technque at different tenperatures in the range of 30 – 80°C. The deposition current density was 80 mA cm^{-2}. Conducting tin oxide substrates(5 ohms/sq cm) were used for the deposition. The precursors for deposition were Analytical grade copper chloride(0.1M) and selenium di oxide(0.05 M)The details of brush plating technique is given elsewhere[19]. Structural properties were studied using Panalytical XRD unit and with CuK_α radiation. Optical absorption was measured using Hitachi U3400 UV-VIS-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) model ESCA 3-MK II at radiation wavelength of MgKa=1253.6 eV.Photoelectrochemical measurements were taken using 250W Tungsten Halogen lamp and 1M polysulphide redox electrolyte(1M each, NaOH, Na_2S and S). Thickness of the films estimated by Mitutoyo surface profilometer was in the range 2.0 – 2.5 μm with increase of deposition temperature.

*Corresponding author: muraliramkrish@gmail.com

3. Results and discussion

X-ray diffraction studies indicated the formation of single phase Cu_2Se (JCPDS 06-680). The peaks corresponding to (111), (220),(311),(400) and (331) of the cubic phase was observed. Whereas, the height of the peaks increased, the width decreased with increase of deposition temperature indicating the improvement in crystallinity (Fig.1). The grain size estimated using Scherrer's equation increased from 10 nm – 15 nm as the depsoition temperature increased. The value of dislocation density and strain were calculated using the following relations:

$$\text{Strain}(\varepsilon) = \beta\cos\theta/4$$

where θ is the Bragg angle, β is the full width at half maximum of the XRD peak.

$$\text{Dislocation density}(\delta) = 15\ \varepsilon / aD$$

where ε is the strain, a is the lattice parameter and D is the grain size. The value of strain decreases from 3.5×10^{-2} – 1.6×10^{-2} as the deposition temperature increases. The dislocation density was observed to $9.5 \times 10^{14}\ m^{-2}$ – $1.5 \times 10^{14}\ m^{-2}$.

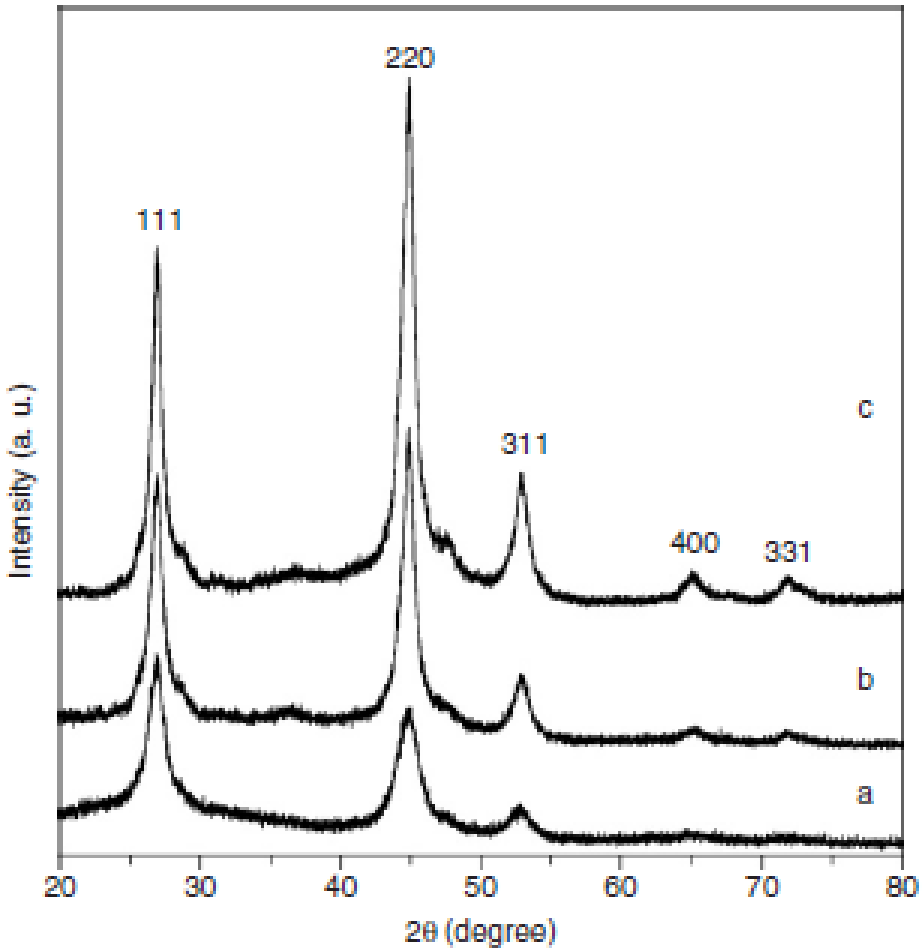

Fig.1. X-ray diffraction patterns of Cu_2Se films deposited at different temperatures (a)30˚C (b) 50˚C (c) 80˚C.

EDAX studies indicated Cu–67.0 atomic % and Se – 33.0 atomic % (fig.2).

The optical properties were studied by recording the variation of absorbance with wavelength. The absorption coefficient was estimated from the relation

$$\alpha = A/h\nu(h\nu - E_g)^{1/2}$$

A plot of $(\alpha h\nu)^2$ vs $h\nu$ is shown in Fig.3. By extrapolating the straight line portion of the plot on the energy axis, a direct band gap of 2.18 eV is observed. This is in good agreement with the value 0f 2.20 eV obtained with chemically deposited films[20].

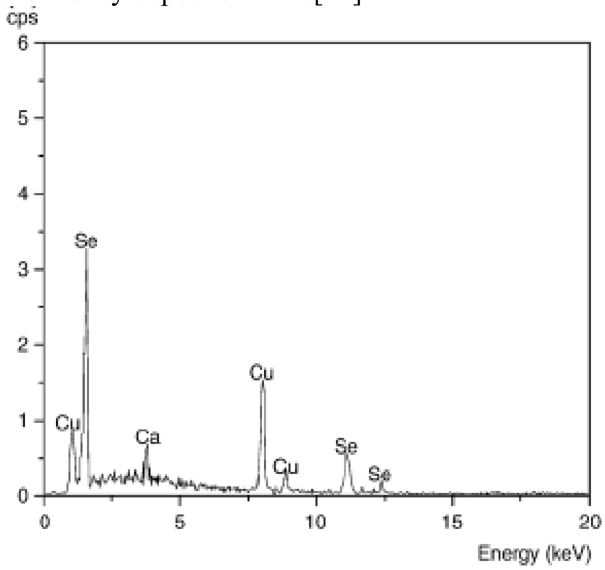

Fig.2 - EDAX spectrum of Cu_2Se films deposited at 80˚C.

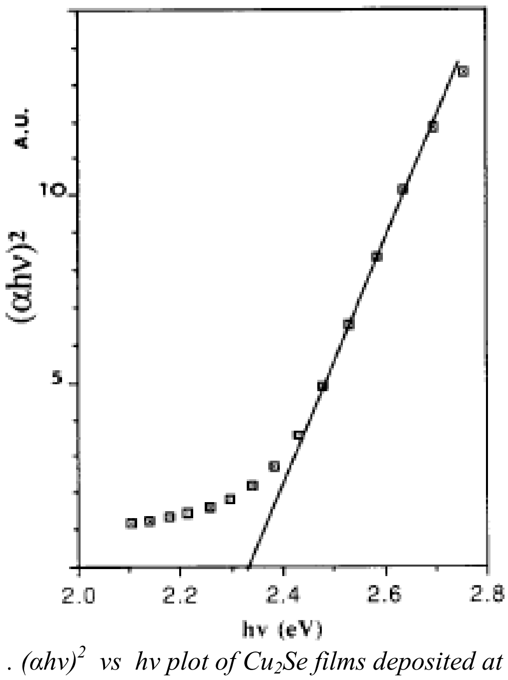

Fig. 3 . $(\alpha h\nu)^2$ vs $h\nu$ plot of Cu_2Se films deposited at 80˚C.

Electrical properties of the films were studied by mechanically transferring the Cu_2Se film from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [21]. The electrical properties of the CdSe layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. The values of resistivity, carrier concentration and mobility for the films deposited at different temperatures are shown in Table-1. It is observed from the table, that, the mobility and carrier concentration increase with deposition temperature, the resisitivity is found to decrease with deposition temperature by two orders. The films exhibited p-type behaviour. The value of resistivity is comparable with that of chemically deposited films[22].

Table-1 Variation of Transport Parameters with Deposition Temperature

Deposition Temp(˚C)	Resistivity (ohm cm)	Mobility ($cm^2V^{-1}s^{-1}$)	Carrier concentration (cm^{-3})
30	10	5.0	1.2×10^{17}
50	1	12.5	5.0×10^{17}
70	0.3	22.0	9.2×10^{17}
80	0.09	57.8	1.2×10^{18}

Photoelectrochemical cell studies in 1M polysulphide indicated weak photoactivity. After post heat treatment in argon atmosphere in the range of 350 - 450˚C, the films exhibited reasonable photo output. Films deposited at 80˚C exhibited maximum photo output, hence further studies were made on this sample. Fig.4 shows the load characteristics of Copper selenide films deposited at 80˚C and post heat treated at different temperatures. It is observed that the photo output is highest for the films post heat treated at 425˚C, beyond which, it decreases due to the partial evaporation of Cu_2Se.

4. Conclusions

The results of this investigation clearly shows that Cu_2Se films with low resistivity and high mobility as well as carrier concentration can easily be deposited by the brush plating technique. These layers could be used in the deposition of $CuInSe_2$ films by introducing Indium in the deposition mixture.

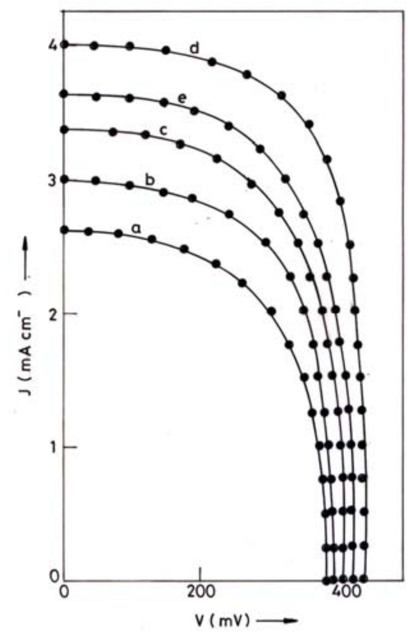

Fig. 4. Load characteristics of Cu_2Se films deposited at 80˚C and post heat treated at different temperatures (a) 350˚C (b) 375˚C (c) 400˚C (d) 425˚C (e) 450˚C.

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