



## Structural, Optical and Photoconductive Properties of Brush Plated Copper Gallium Selenide films

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Received : 28.01.1013 Revised : 13.02.2013 Accepted : 18.03.2013

### Abstract

Copper Gallium selenide films were deposited for the first time by the brush electrodeposition technique. The films were deposited at different bath temperatures in the range of 30 - 80°C at a constant current density of 3.0 mA cm<sup>-2</sup>. The films exhibited single phase Copper Gallium selenide. Optical band gap of the film deposited at 80°C was 1.68 eV. Room temperature resistivity of the films were in the range of 0.1 - 14.0 ohm cm. Photoconductivity measurements were made at room temperature. Photocurrent Capacitance voltage measurements indicated the films to exhibit p-type behaviour. The flat band potential ( $V_{fb}$ ) was 0.60V (SCE) and a carrier density in the range of  $2.5 \times 10^{17}$  cm<sup>-3</sup> was obtained. A single Photoluminescence peak was observed at 1.64 eV.

**Keywords:** Chalcopyrite; I-III-VI<sub>2</sub>; Ssemiconductors; Thin films.

### 1. INTRODUCTION

Thin-film copper chalcopyrites have recently received attention as candidate materials for photoelectrochemical water splitting (Fernandez et al. 2005; Leisch et al. 2006). They exhibit properties that render them particularly attractive for solar energy conversion applications, including: (1) a direct bandgap with steep absorption edge; (2) good carrier transport properties; and (3) band edges that are tunable by composition. Although the photovoltaic properties of p-CuGaSe<sub>2</sub> (CGSe) films have been studied previously by electrochemical means using organic electrolyte (Scherrer et al. 1918) or V<sup>2+</sup>/V<sup>3+</sup> electrolyte (Kessler et al.1990), little work to date has characterized the photoelectro chemical interface of CGSe in aqueous media for possible application in hydrogen evolution devices. CG Se films have been deposited by different techniques like vacuum evaporation (Bjorn Marsen et al.2008), Chemical vapour deposition (CVD) (Fischer et al.2001), MOCVD (Grossberg et al.2009) etc.

work, CGSe films were deposited for the first time by the brush electrodeposition technique.

### 2. EXPERIMENTAL METHODS

CGSe films were deposited at different bath temperatures in the range of 30 - 80°C at a constant current density of 3 mA cm<sup>-2</sup>. The deposition current density was maintained as - 0.9V (SCE). The precursors used were 10 mM GaCl<sub>3</sub>, 5 mM CuCl<sub>2</sub> and 100 mM SeO<sub>2</sub>. The pH of the bath was adjusted to 1.5 by HCl. Tin oxide coated glass substrates (5 ohms / sq) were used. A microprocessor controlled pulse plating unit was used. Thickness of the films measured by Mitutoyo surface profilometer was in the range of 1.2 - 1.5 micrometers. The films were characterized by Xpert analytical x-ray diffraction unit with Cu ka radiation. Optical measurements were recorded using an Hitachi UV-VIS-IR spectrophotometer. Composition of the films was estimated by EDAX attachment to JOEL SEM. Surface morphology of the films was studied by molecular imaging atomic force microscope. Electrical measurements were made by Hall Van der Pauw method. The dark and photo conductivity

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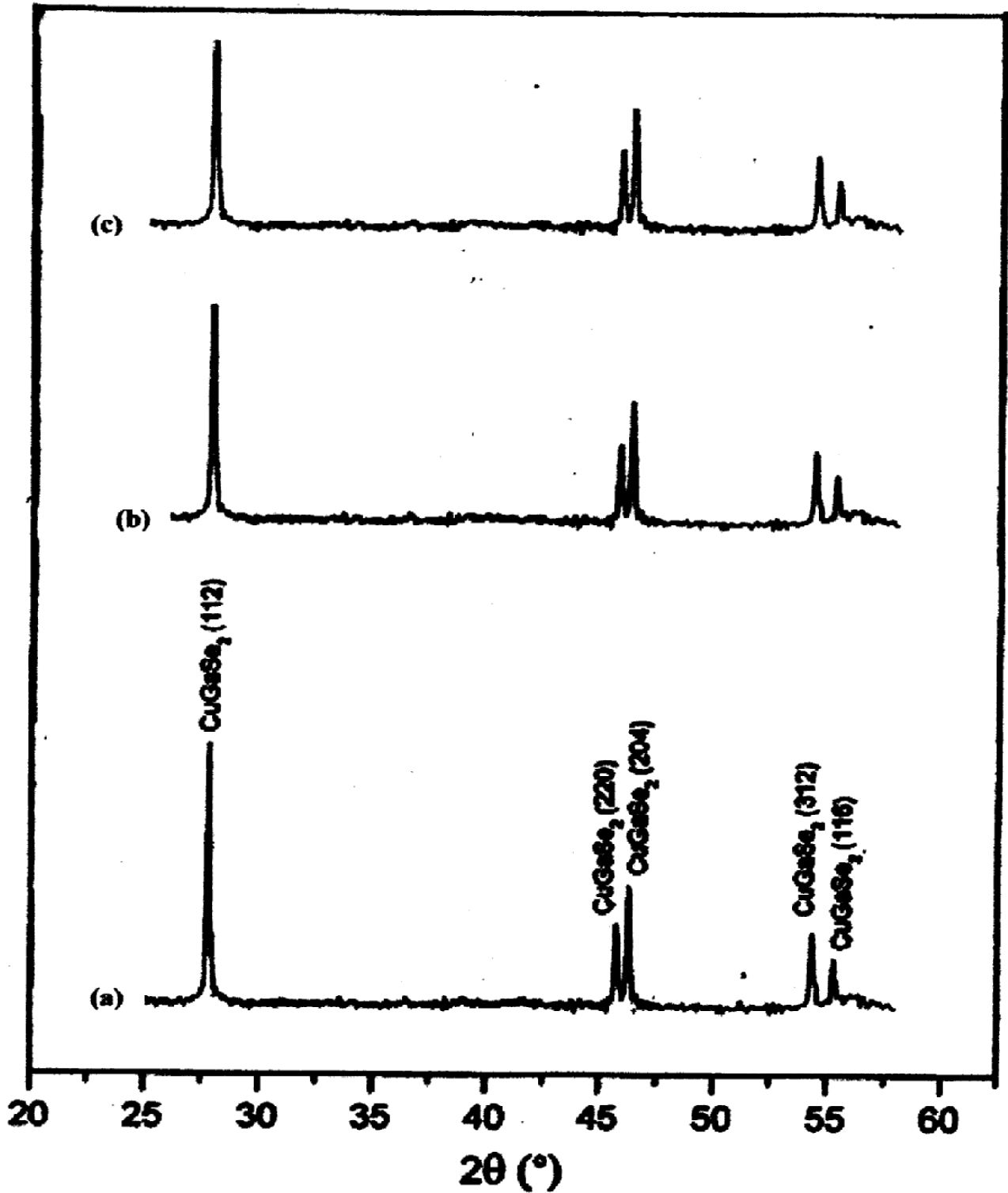


Fig. 1 : X-ray diffraction pattern of CuGaSe<sub>2</sub> films deposited at different substrate temperature (a) 30°C (b) 50°C (c) 60°C

measurements were carried out at room temperature. The measuring system consists of a regulated dc power supply (Aplab) in series with the sample and Keithley electrometer (model 610 C). A tungsten lamp of 200W was used for illumination. The intensity of the light source was measured with the help of a power meter. The spectral distribution of photocurrent was measured with Photophysics monochromator.

The plating tool, typically graphite (anode), was wrapped with an absorbent material that both held and distributed the solutions uniformly over the work area. Solution was supplied to the work area by either dipping the tool into a container, or by pumping it through the tool and recirculating. The plating tool was then moved over the work area. In the brush plating process, the movement between the plating tool and the part (move the tool over the part) was a must. A portable power pack (rectifier) provided a source of direct current for all the processes. The power pack had at least two leads. One lead was connected to the anode and the other is connected to the part being finished (cathode). Direct current supplied by the power pack was used in a circuit that was completed when the tool is touching the work surface. The tool was always kept in motion whenever it was in contact with the work surface. Movement was required to ensure a quality finish.

### 3. RESULTS AND DISCUSSION

The films were polycrystalline with a strong (112) preferred orientation as revealed by XRD. The lattice parameters calculated from XRD are  $a = 5.635 \text{ \AA}$ ,  $c = 11.035 \text{ \AA}$  and  $c/a = 1.96$ . These values are in good agreement with the reported values on single-crystals (Romeo et al. 1977). The X-ray diffractograms of the films formed at different substrate temperatures are shown in Fig. 1. The films exhibit chalcopyrite structure with single phase of  $\text{CuGaSe}_2$ , indicating that the films were near stoichiometric. The peaks are found to increase in intensity and decrease in width with increase of the substrate temperature. The grain size of the films have been calculated using Scherrer's formula (Scherrer et al. 1918),

$$D = 0.94 \lambda / \beta \cos \theta \quad (1)$$

where  $\lambda$  is the wavelength of X-ray used,  $\beta$  the full-width half-maximum (FWHM) and  $\theta$  the Bragg angle.

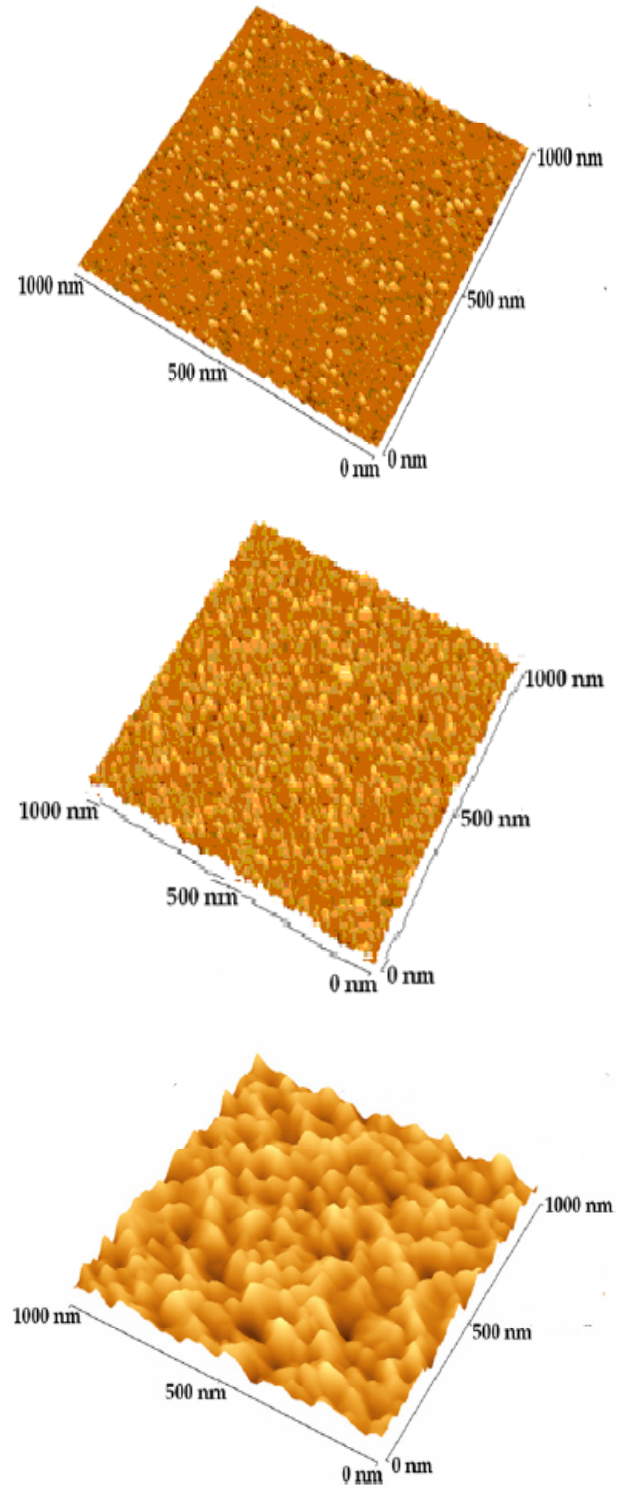


Fig. 2 : Atomic force micrographs of  $\text{CuGaSe}_2$  films deposited at different substrate temperature (a)  $30^\circ\text{C}$  (b)  $60^\circ\text{C}$  (c)  $80^\circ\text{C}$  (Z - 1 div - 50 nm)

The grain size varied from 30 nm to 70 nm as the substrate temperature increased. The dislocation density  $\delta$ , defined as the length of dislocation lines per unit volume of the crystal has been evaluated using the formula (Williamson et al.1956).

$$\delta=1/D^2 \quad (2)$$

The dislocation density, grain size and strain are presented in Table-1. From the table it is observed that the dislocation density decreases with increase of grain size. Information on the strain for the CuGaSe<sub>2</sub> films was obtained from the full-width at half-maximum of the diffraction peaks. The full-width at half-maximum  $\beta$  can be expressed as a linear combination of the contributions from the particle size, D and strain,  $\epsilon$  through the relation (Sherrif et al.1996).

$$\beta \cos\theta/\lambda = 1/D + \epsilon \sin\theta/\lambda \quad (3)$$

The plot of  $\beta \cos\theta/\lambda$  vs  $\sin\theta/\lambda$  allows us to determine strain from slope of the graph. The estimated values for films deposited at different substrate temperatures are listed in Table.1.

The deviation in the lattice parameter values from the bulk value observed in the present case clearly suggests that the grains in the films are under stress. Such a behaviour can be attributed to the change of nature, deposition conditions and the concentration of the native imperfections developed in thin films. This results in either elongation or compression of the lattice and the

structural parameters. The density of the film is therefore found to change considerably in accordance with the variations observed with the lattice constant values [11]. The stress developed at higher substrate temperatures is likely to be due to the formation of native defects developed from the lattice misfit or dislocations. The defects have a probability to migrate parallel to the substrate surface with the surface mobility greatly influenced by the substrate temperature, so that the films will have a tendency to expand and develop an internal tensile stress. This type of change in internal stress is always predominant by the observed recrystallization process in polycrystalline films. The stress relaxation is mainly considered as due to dislocation glides formed in the films. The decrease of internal stress may be attributed to a decrease in dislocation density. The reduction in the strain and dislocation density with increase of substrate temperature may be due to the reduction in concentration of lattice imperfections due to the improved crystallinity at higher substrate temperature.

Composition of the films were determined from EDAX measurement. As the substrate temperature increased the films became more stoichiometric. Table-2 shows the composition of the films with substrate temperature. At lower temperatures, slight excess of copper is deposited, since, in the electrochemical series, copper is more positive compared to gallium and a lower concentration of gallium ions are available for deposition. At higher temperatures, the concentration of the gallium ion increases and the amount of gallium deposited increases, compared to that

**Table 1. Microstructural parameters of CuGaSe<sub>2</sub> films deposited at different substrate temperatures**

Subs Temp (°C)	Thickness (µm)	Lattice parameter (Å)		Grain size (nm)	Strain (x10 <sup>-4</sup> )	Dislocation density (x10 <sup>14</sup> cm <sup>-3</sup> )
		"a"	"c"			
30	1.20	5.59	10.96	30	2.71	11.1
50	1.30	5.57	10.96	45	2.45	4.98
60	1.40	5.58	10.97	56	2.14	3.18
80	1.50	5.60	10.99	70	1.41	2.04

at lower duty cycles. Due to the increase of gallium concentration, the Cu/Ga ratio approaches unity at a substrate temperature of 80°C.

Surface morphology of the films was studied by Atomic force microscope. The grain size increases with increase of substrate temperature. Lower substrate temperature results in smooth surfaces (Fig 2). As the substrate temperature increases, the surface becomes slightly rough. The surface roughness increases from 0.15 nm – 1.05 nm.

The optical absorption coefficient was calculated from the transmittance versus wavelength spectrum. Near the absorption edge the absorption coefficient is given by (Annappurna et al. 1986).

$$A = A (h\nu - E_g)^n / h\nu$$

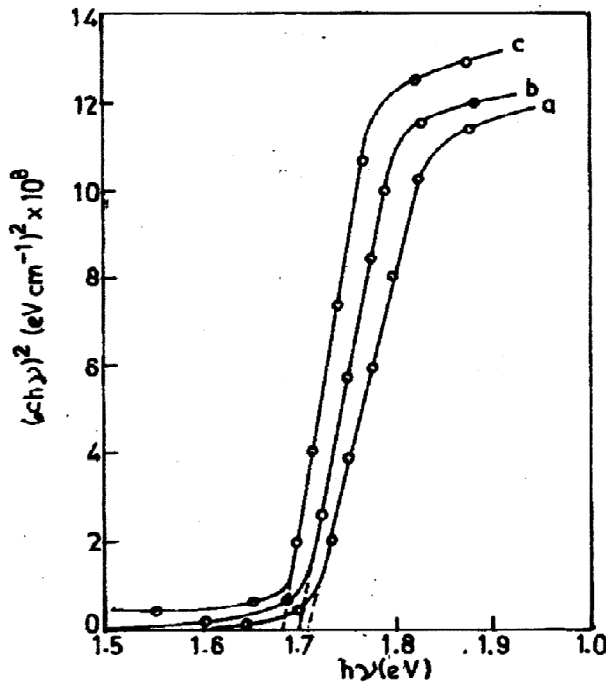


Fig. 3 : Tauc's plot of CuGaSe<sub>2</sub> films deposited at different substrate temperature (a) 30°C (b) 60°C (c) 80°C

$h\nu$  is the photon energy. For direct allowed transitions  $n=1$  and a plot of  $(\alpha h\nu)^2$  versus  $h\nu$  will have an intercept with the  $h\nu$  axis which gives the band gap,  $E_g$ . Fig.3 shows the variation of  $(\alpha h\nu)^2$  versus  $h\nu$  for the films formed at three different duty cycles. It is seen from the figure that as the duty cycle increases, the band gap decreases due

Table-2. Composition of CuGaSe<sub>2</sub> films deposited at different substrate Temperatures

Subs Temp (°C)	Cu (at.%)	Ga (at.%)	Se (at.%)	Cu/Ga
30	24.95	23.99	51.06	1.04
50	24.73	23.89	51.38	1.035
60	24.51	23.79	51.70	1.03
80	24.05	24.05	51.90	1.00

to the increase in grain size with duty cycle. The films deposited at 50 % duty cycle showed an optical band gap of 1.68 eV, which is in good agreement with the reported value(Rusu et al.2001). Various crystalline imperfections in the film, such as vacancies, dislocations and grain boundaries act as trapping or recombination centers of the carriers and play an important role in photoconduction. These traps act as localized positive potential centers for electrons and negative potential centers for holes. Therefore some localized discrete energy levels are formed in the band gap, in the vicinity of the conduction and valence bands respectively.

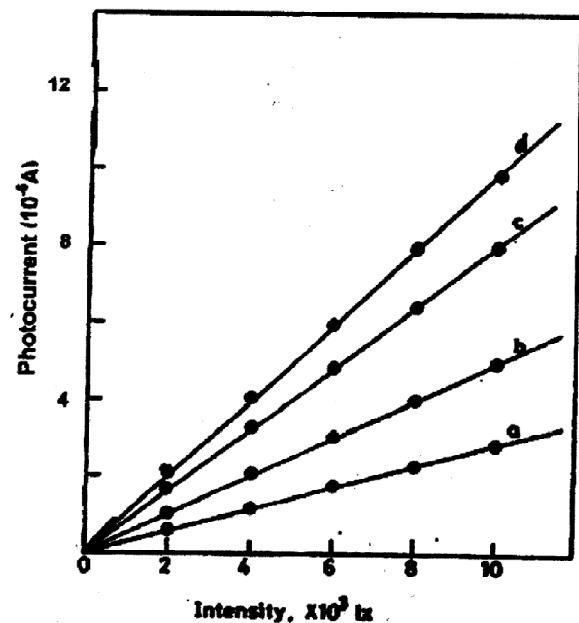


Fig. 4 : Photocurrent vs intensity of CuGaSe<sub>2</sub> films deposited at different Substrate temperature (a) 30°C (b) 50°C (c) 60°C (d) 80°C

Fig. 4 shows the variation of photocurrent with light intensity of CuGaSe<sub>2</sub> films deposited at different substrate temperatures. The photocurrent is found to increase with an increase of substrate temperature, due to increase in film thickness and light intensity. As the thickness of the film increases the crystalline nature increases (Table 1) and this helps in the improvement of photocurrent. The increase in photocurrent is attributed to an increase in the majority carrier concentration and/or an increase in impurity centers acting as traps for minority carriers. The variation of photocurrent with applied voltage in CuGaSe<sub>2</sub> films is shown in Fig. 5. The photocurrent increases with an increase in voltage. Similar behaviour of the photocurrent has been reported by (Shahidi et al.1985).

Photocurrent spectra of CuGaSe<sub>2</sub> films deposited at different substrate temperatures are shown in Fig. 6. The photocurrent spectra show a peak near the absorption edge which was also observed by (Rose et al. 1955). The band gap of CuGaSe<sub>2</sub> films determined from the spectral response is 1.68 eV. This is in good agreement with the bandgap value obtained from optical absorption measurements. The low photocurrent in the

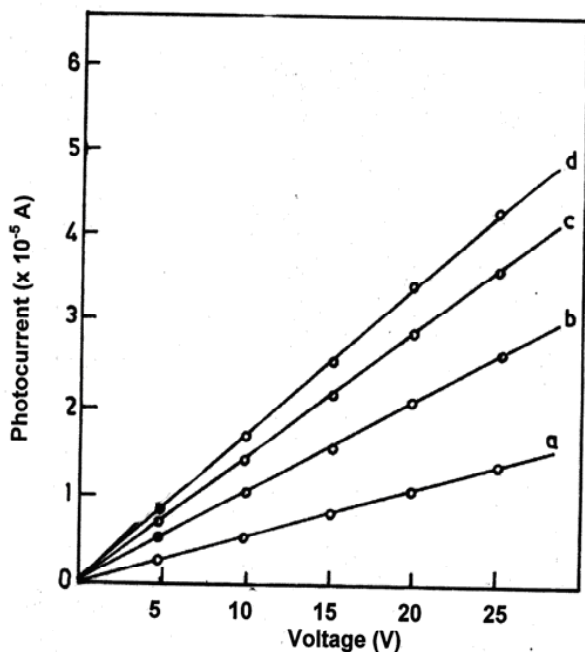


Fig. 5 : Photocurrent vs voltage of CuGaSe<sub>2</sub> films deposited at different substrate temperature (a) 30°C (b) 50°C (c) 60°C (d) 80°C

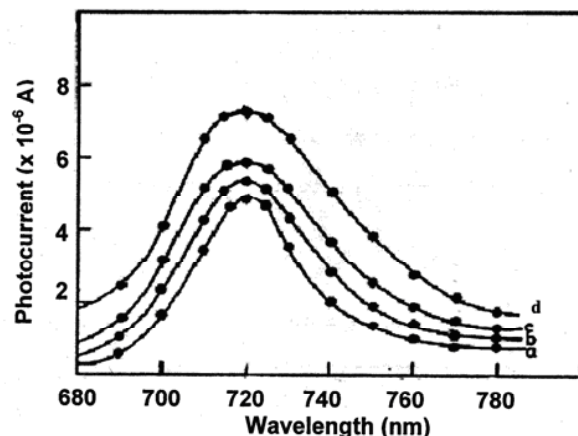


Fig. 6 : Photocurrent spectra of CuGaSe<sub>2</sub> films deposited at different substrate temperature (a) 30°C (b) 50°C (c) 60°C (d) 80°C

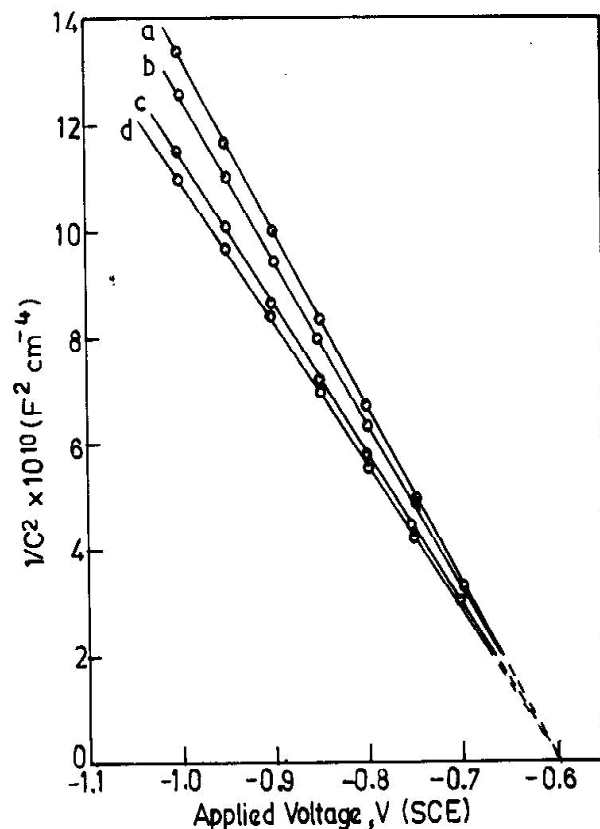
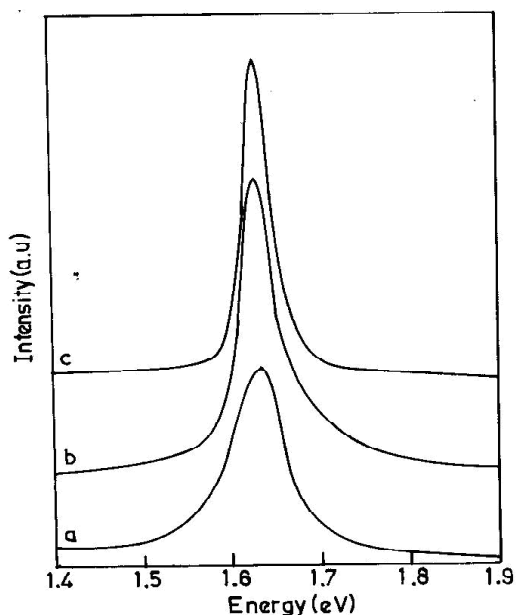


Fig. 7 : - Photocurrent - capacitance characteristics of CuGaSe<sub>2</sub> films deposited at different substrate temperature (a) 30°C (b) 50°C (c) 60°C (d) 80°C



**Fig. 8 :** Photoluminescence spectra measured at 77°K for CuGaSe<sub>2</sub> films deposited at different substrate temperature (a) 30°C (b) 50°C (c) 80°C

short wavelength range may be due to the high absorption coefficient and only surface region, where defect states give a shorter life time, is excited. In the high wavelength region the radiation is only partially absorbed giving rise to less photocurrent than the peak value. Tails of the spectra extending to 1200 nm are attributed to direct excitation of the carriers from the defect levels. Similar results have been reported by several workers for CuInSe<sub>2</sub> films (Pal et al. 1994; Kazmerski et al. 1983).

The charge distribution at the semiconductor and electrolyte interface is often determined by measuring the capacitance of the space-charge layer  $C_{sc}$  as a function of the electrode potential  $V$ . The Mott-Schottky relationship expresses the potential dependence of  $C_{sc}$  of a semiconductor electrode under depletion conditions (Cheng et al. 1999; Vijayakumar et al. 2005)

$$1/C_{sc}^2 = [2/eN_D\epsilon\epsilon_0][(V - V_{fb}) - kT/e]$$

where,  $C_{sc}$  is the space charge capacitance;  $V$  represents the applied potential;  $V_{fb}$  is the flat-band voltage;  $N_D$  is the concentration of donors,  $N_D$  can be determined from the slope of the experimental  $1/C_{sc}^2$  versus  $V$  plots, while  $V_{fb}$  comes from the extrapolation for  $1/C_{sc}^2 = 0$ . The validity of the Mott-Schottky analysis is based on the

assumption that the capacitance of the space charge layer is much less than that of the Helmholtz layer. When the measured frequency is high enough ( $>1$  kHz), the contribution of Helmholtz capacitance to the measured electrode capacitance is negligible. Thus the capacitance of the semiconductor/ electrolyte interface mainly expresses the capacitance of the space charge layer of the semiconductor. Fig.7 shows the Mott-Schottky plot of the CuGaSe<sub>2</sub> films deposited at different substrate temperatures. 1M Na<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> blocking electrolyte was used, the AC frequency was 10 kHz. Linear plots were obtained. The nature of the plot with positive slope indicates p-type behaviour.  $V_{fb}$  of -0.60V (SCE) and a carrier density in the range of  $2.5 \times 10^{17} \text{ cm}^{-3}$  were obtained.

Typical luminescence at 77 K of CuGaSe<sub>2</sub> films deposited at different substrate temperature is shown in Fig.8. The PL emission is generally attributed to native defects. Taking into account the composition of the films, the dominant defects could be Cu, Se and Ga vacancies, Cu interstitial and Cu or Ga in antisite. Among them,  $V_{Cu}$ ,  $V_{Ga}$  and  $Cu_{Ga}$  act as acceptors, while  $Cu_i$  and  $V_{Se}$  introduce donors levels (Lai et al. 1997). The films show only a large and intense peak at 1.64 eV, that could notably be related to donor-acceptor transitions. The intensity of the peak increases with increase of substrate temperature.

#### 4. CONCLUSIONS

The results of this work, clearly indicate that nano crystalline CuGaSe<sub>2</sub> films can be deposited by the pulse electro deposition technique. Films with band gap of 1.68 eV can be prepared. P-type films exhibiting photoconductivity can be deposited. Films exhibiting photo luminescence at 1.64 eV can be prepared.

#### ACKNOWLEDGEMENT

The authors thank the Institute for Environmental Nanotechnology for their joint support of this study.

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