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Effect of annealing on the opto-electronic properties of $Cu_{0\cdot9}In_{1\cdot0}Se_{2\cdot0}$ films

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Abstract. The influence of annealing on the structure and opto-electronic properties of $Cu_{0\cdot9}In_{1\cdot0}Se_{2\cdot0}$ films prepared by solution growth technique has been studied. The films annealed at 500–520°C in air, vacuum (10^{-4} torr), In-vapour and Se-vapour show polycrystalline chalcopyrite structure with orientation perpendicular to the (220) plane. Films annealed in Se-vapour at 500°C for 30 min have maximum grain size (560 Å), minimum optical energy gap, maximum absorption coefficient, lowest resistivity, maximum photosensitivity and thus are suitable for photovoltaic applications. Annealing in In-vapour or in vacuum changes *p*-type $CuInSe_2$ into *n*-type which possibly arises due to the increase in Se vacancies.

Keywords. Annealing effect; $CuInSe_2$.

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1. Introduction

$CuInSe_2$ has become an important semiconductor for solar cell applications (Mikelson and Chen 1982; Kazmerski *et al* 1983). The opto-electronic properties of $CuInSe_2$ polycrystalline thin films as well as single crystals have been studied extensively. It is known that chalcopyrite and sphalerite structure of $CuInSe_2$ films depend on the growth conditions of films (Piekoszewski *et al* 1980; Tomlinson *et al* 1980; Gorska *et al* 1980; Bates *et al* 1982). However, films prepared by spray pyrolysis (Dushan *et al* 1986; Mooney and Lamoreaux 1986) and laser irradiations (Laude *et al* 1986) were only single phase chalcopyrite in nature. Recently, Sharma and Garg (1989) studied the structural, optical and electrical properties of non-stoichiometric $CuInSe_2$ films and observed that opto-electronic properties are sensitive to Cu/In ratio and films of ratio equal to 0·9 have chalcopyrite structure, large grain size, low resistivity and high photosensitivity. According to Kazmerski *et al* (1983) the heat treatment of $CuInSe_2$ films in oxygen, nitrogen and argon at 200°C shows an improvement in absorption properties of the films. The effect of air annealing (200°C) on the spectral response of $CdS/CuInSe_2$ thin films solar cells were investigated by Noufi *et al* (1985) and found an increase in efficiency of the cells. Single crystals (Migliorato *et al* 1975; Masse and Redjai 1984) of $CuInSe_2$ were found to be *p*-type when annealed under Se-vapour, whereas crystals annealed under In-vapour or in vacuum were *n*-type. However studies on the post deposition heat treatment of non-stoichiometric films in different ambients are rarely found in the literature and are important both for device optimisation as well as temperature stability of ternary chalcopyrite phase.

In the present paper, we report the results of our investigations on the effect of annealing in different ambients on the opto-electronic properties of $Cu_{0.9}In_{1.0}Se_{2.0}$ films.

2. Experimental procedure

The solution growth technique used to deposit non-stoichiometric films of $CuInSe_2$ is described by Garg *et al* (1988). The process involves the reaction of Cu^+ with In^{3+} and Se^{2-} ions in deionized water solution. Elemental selenium (99·95%) is dissolved in an aqueous solution of sodium sulphite ($pH > 9$) at 90°C to form a partial unstable Na_2SeSO_3 compound. The solution is mixed with tetraamine copper and then added to a solution containing a complex ion of indium and citrate. In the solution, unstable Na_2SeSO_3 yields Se^{2-} and SO_3^{2-} ions. Sulphite ions reduce $Cu(NH_3)_4^{2+}$ and generate Cu^+ ions. The temperature of solution is held at 40°C for about 12 h, and uniform films of $CuInSe_2$ are obtained on glass substrates at 30Å min^{-1}. As deposited films (grown in same batch) were annealed in a vacuum tight chamber at 500–520°C in air, vacuum (10^{-4} torr), indium-vapour and selenium-vapour for 30 min separately, in identical sealed enclosures fitted with digital copper alumel thermocouple to record the temperature. Structural characterization of the films was carried out using XRD technique. The optical transmittance and reflectance of films at various wavelengths were measured using the Hitachi 330 spectrophotometer. The electical properties of the films were determined from d.c. Hall measurements using vander pauw geometry with evaporated indium ohmic contacts. To measure the photosensitivity of the films, current in dark and under illumination was measured by conventional method using digital multimeter (HIL). The temperature was determined by surface thermocouple probe with a digital indicator (HIL) of 1°C accuracy. The resistivity of the annealed films was measured by two probe electrical method.

3. Results and discussion

Figures 1(a) and 1(b) show the X-ray diffraction profile for films of $Cu_{0.9}In_{1.0}Se_{2.0}$ annealed in vacuum, air, In-vapour and Se-vapour respectively. The positions, relative intensities and identifications of the peaks indicate that all the films were polycrystalline and single phase chalcopyrite with the orientation perpendicular to the (220) plane. The lattice constants and grain size estimated from graphs are presented in table 1. The different values of c and a results from the shift of (220) peak and may be attributed to the change in the stoichiometry of films caused by Se deficiency through annealing. It can be seen from the above table that annealed Cu-deficient ($Cu_{0.9}In_{1.0}Se_{2.0}$) films irrespective of annealing ambients, have single phase chalcopyrite structure. Our earlier investigations (Sharma and Garg 1989) show that reduction of Cu: In ratio from one favour the formation of single phase chalcopyrite structure. Further, it is to be noted that films annealed in Se-vapour have maximum grain size. The present results are consistent with those reported by Kazmerski *et al* (1976), Varela *et al* (1985), Pamplin and Feigelson (1979) and Cammy *et al* (1984).

Figure 2 depicts transmittance spectra of samples annealed in air, vacuum, Se-vapour and In-vapour respectively. The observed sharp absorption edge in all the

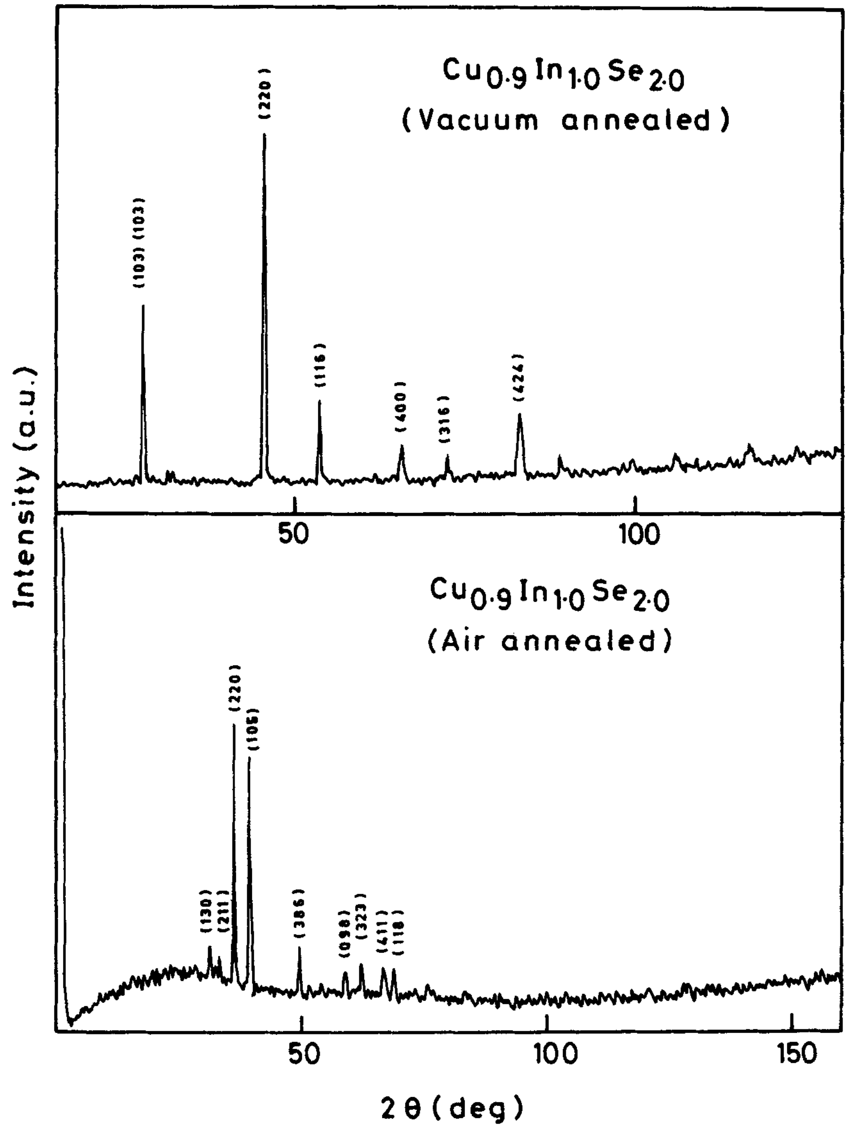

Figure 1a. X-ray pattern of $Cu_{0\cdot9}In_{1\cdot0}Se_{2\cdot0}$ films annealed in air and vacuum.

Table 1. XRD results of Cu_{09} $In_{1\cdot0}$ $Se_{2\cdot0}$ films annealed in different ambients.

Parameters	Vacuum	Air	In-vapour	Se-vapour
a (A°)	5·88	5·74	5·79	5·80
c (A°)	11·77	11·88	11·62	11·20
Grain size (A°)	499·00	502·00	541·00	560·00
Structure	Chalcopyrite	Chalcopyrite	Chalcopyrite	Chalcopyrite

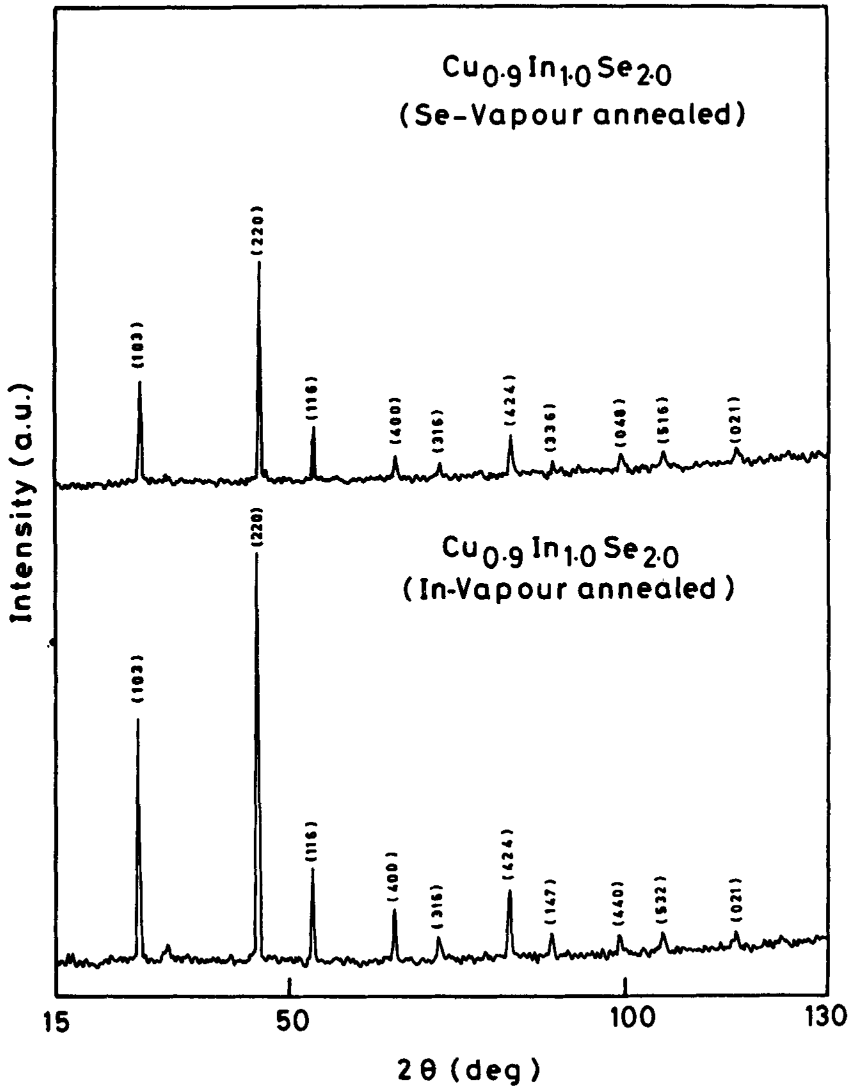

Figure 1b. X-ray pattern of $Cu_{0.9}In_{1.0}Se_{2.0}$ films annealed in In- and Se-vapours.

spectra suggest the presence of direct band gap and single phase. The optical absorption coefficient α of the films has been calculated at various wavelengths from the relation:

$$\alpha = \frac{4\pi K}{\lambda}, \tag{1}$$

where K is the extinction coefficient in the fundamental absorption region and λ is the wavelength in the same region. The value of K at different wavelengths has been computed from observed optical transmittance and reflection spectra and film thickness determined by interferometer technique, following the standard procedure reported by Rastogi and Salcalachen (1982), after applying necessary correction in observed transmission for attenuation by reflection behind the substrate (Berming

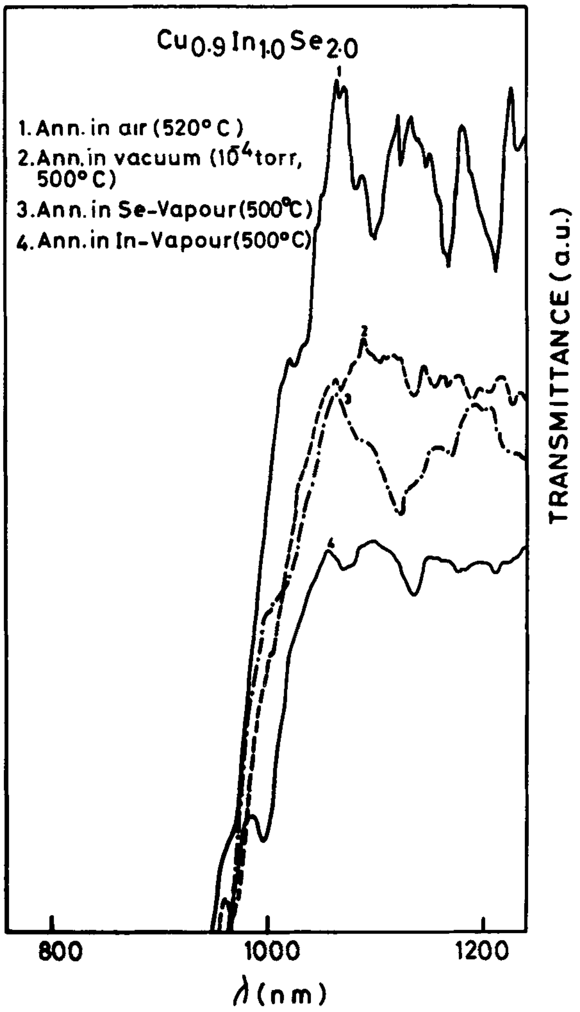

Figure 2. Transmittance spectra of $Cu_{0.9}In_{1.0}Se_{2.0}$ films annealed in air, vacuum, Se-and In-vapours respectively.

1963). The calculated values of α at wavelengths corresponding to absorption edge for films annealed in different ambients only are given in table 2. It can be seen that the films annealed in Se-vapour have highest absorption coefficient in comparison to vacuum and In-vapour annealed films. Since the films annealed in Se-vapour have maximum grain size, one may infer that annealing in Se-vapour results in improvement of the compositional uniformity both across and through polycrystalline thin films. On the other hand heating in vacuum/In-vapour, causes Se desorption near the film surface, causing a related degradation in the film absorptance (Kazmerski *et al* 1983).

The direct transition in a semiconductor is related by the relation:

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

where A is a constant, $h\nu$ is the photon energy and Eg is the optical band gap of the semiconductor. The band gap Eg of different samples has been deduced from the

Table 2. Properties of annealed $Cu_{0\cdot 9}In_{1\cdot 0}Se_{2\cdot 0}$ thin films at 300 K.

Annealing ambient	Annealing temperature T_A (°C)	Thickness t (μm)	Conductivity type	Structure	Resistivity ρ (Ωcm)	Carrier concentration h(cm^{-3})	Absorption coefficient α (10^4 cm^{-1})	Optical energy gap Eg(eV)	Absorption edge λ (nm)
As-deposited	50	2·0	p	Mixed	1600	4×10^{18}	1·25 ± 0·02	1·45 ± 0·02	800
Air	520	1·5	p	Chalcopyrite	500	6×10^{18}	1·30 ± 0·02	1·09 ± 0·02	1040
Se-vapour	500	2·0	p	Chalcopyrite	1·00	8×10^{19}	3·00 ± 0·03	0·96 ± 0·02	1060
In-vapour	500	2·2	n	Chalcopyrite	1·20	7×10^{17}	2·50 ± 0·02	1·14 ± 0·02	1010
Vacuum (10^{-4} torr)	500	1·6	n	Chalcopyrite	5·00	5×10^{17}	2·80 ± 0·02	1·00 ± 0·02	1030

intercepts obtained after extrapolation of the straightline section of $(\alpha h\nu)^2$ vs $h\nu$ curve. A curve $(\alpha h\nu)^2$ vs $h\nu$ for $Cu_{0\cdot9}In_{1\cdot0}Se_{2\cdot0}$ film annealed in Se-vapour is shown in figure 3 which is the representative of all the curves obtained in the present study. The calculated values of the optical band gap along with annealing ambients are presented in table 2. It is to be seen that film annealed in Se-vapour has lowest optical band gap and is a manifestation of better grain size i.e., improvement in the compositional uniformity of the film surface as suggested above.

The dependence of electronic properties of the films on the annealing ambients are presented in table 2. It can be seen from the table that films annealed in Se–vapour have *p*-type conductivity whereas films annealed in In-vapour-vacuum have *n*-type conductivity. Following Masse and Redjai (1984), the annealing in Se-vapour induces the disappearing of defects involving Se-vacancy, increases the concentration of cation vacancies and interstitial Se atoms, and may reduce the concentration of interstitial cations. The large conductivity observed in our Se-vapour annealed samples may therefore result from a decrease of Se-vacancies or interstitial cations or from an increase of cation vacancies or interstial Se atoms. Since interstitial cations are unstable, they are less probable in the process. Annealing in In-vapour/vacuum results in an increase in the Se-vacancies which in turn changes $CuInSe_2$ from *p*-type to *n*-type and decreases the conductivity. Further our results are consistent with those reported by Migliorata *et al* (1975), and Shih and Champness (1984) in single crystal stoichiometric $CuInSe_2$.

The photosensitivity of the films annealed in Se-vapour, is found to be maximum. Figure 4 depicts a plot of long photosensitivity(*s*) versus $10^3/T$ of the films annealed in Se-vapour and is a straight line whose slope yields a thermal activation energy $Ea = 0{\cdot}33 \pm 0{\cdot}01$ eV. To understand the thermal assisted conduction in polycrystalline $CuInSe_2$ films grain boundary trapping theory has been proposed by Seto (1975) and Baccarani *et al* (1978). According to them, trapping centres at the grain boundary

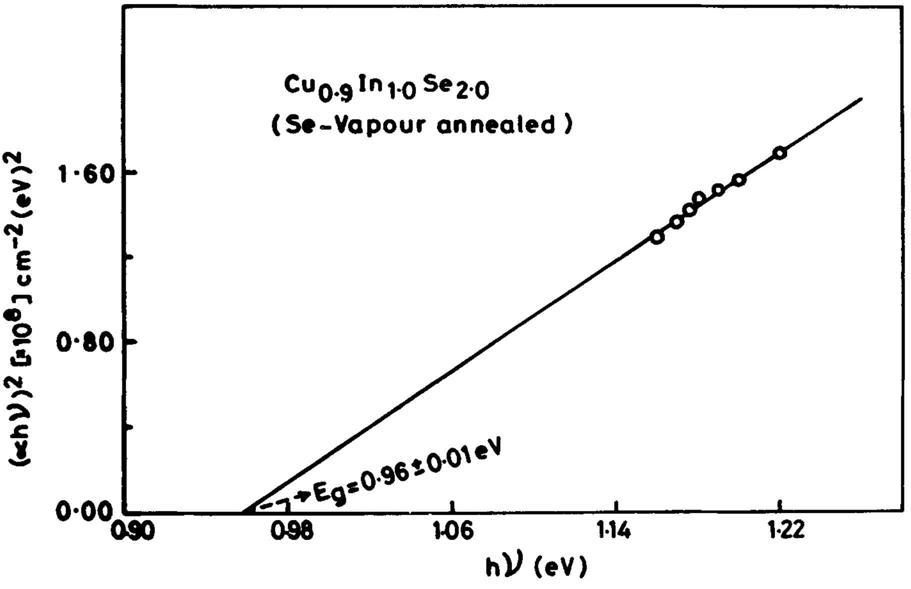

Figure 3. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for $Cu_{0\cdot9}In_{1\cdot0}Se_{2\cdot0}$ film annealed in Se-vapour.

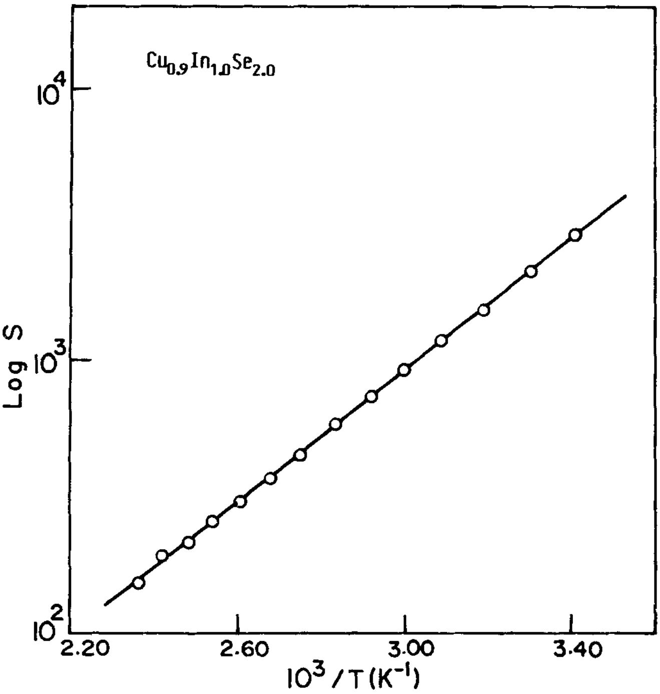

Figure 4. Plot of log photosensitivity versus $10^3/T$ for $Cu_{0.9}In_{1.0}Se_{2.0}$ film annealed in Se-vapour.

capture free carriers and these charged centres create barriers and carrier transport is influenced by these barriers.

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