

## Flash-evaporated thin films of $\text{CuInSe}_2$

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**Abstract.** Flash-evaporated technique has been developed for deposition of  $\text{CuInSe}_2$  thin films. A control over the stoichiometry and chemical composition of the films has been obtained by varying the deposition parameters. Single phase chalcopyrite structure films with optical gap  $\sim 1.15$  eV have been obtained. The electronic properties of the films have been tailored for solar cell applications.

**Keywords.** Flash evaporation; copper; indium; selenium.

### 1. Introduction

The attainment of conversion efficiency, greater than 10% using  $\text{CuInSe}_2$  as an active material in all thin film solar cell has led to considerable research interest in this material (Mickelsen *et al* 1984). Thin film heterojunction  $p\text{-CuInSe}_2/n\text{-CdS}$  and  $p\text{-CuInSe}_2/n\text{-Zn}_x\text{Cd}_{1-x}\text{S}$  cells have yielded efficiencies around 9.5 and 11.5%, respectively. A number of investigations have since been undertaken to understand the properties of  $\text{CuInSe}_2$  relevant to photovoltaic conversion (Kazmerski 1978; Kazmerski *et al* 1981; Sobotta *et al* 1980; Naufi *et al* 1984; Abernathy *et al* 1984). It has been established that Cu to In ratio and metal (Cu + In) to selenium ratio in the films are critical parameters affecting the film properties (Shay and Wernick 1975; Masse and Redjai 1984). As a consequence, only three source evaporation techniques for deposition of  $\text{CuInSe}_2$  films have succeeded for solar cell applications. However, with an increased understanding of the dependence of the properties of  $\text{CuInSe}_2$  on stoichiometry and structure, newer techniques for film deposition have been used which yield properties comparable to those of films prepared by the three-source technique. These techniques include spray pyrolysis (Pamplin and Feigelson 1979; Gorska *et al* 1980; Abernathy *et al* 1984), sputtering (Piekoszewski *et al* 1980; SERI Report 1981), chemical vapour deposition (SERI Report 1981) and screen printing (Pachori *et al* 1985).

Flash evaporation technique has been used earlier for the deposition of  $\text{CuInSe}_2$  films but discarded due to the difficulty of producing films of reproducible quality (Horig *et al* 1978; Durny *et al* 1980). We have revived this technique due to its simplicity and potential to deposit multi-component films with widely varying vapour pressure constituents. Further, with a vastly improved knowledge of the properties of  $\text{CuInSe}_2$ , we have succeeded in producing  $\text{CuInSe}_2$  films with excellent and reproducible photovoltaic properties. Since our objective is to fabricate thin film  $\text{CuInSe}_2/\text{CdS}$  solar cells,  $p$ -type  $\text{CuInSe}_2$  films have been studied in greater detail. This paper describes the preparation and properties of  $\text{CuInSe}_2$  films obtained by the flash evaporation technique. Preliminary results on  $\text{CuInSe}_2/\text{CdS}$  junction are also given.

## 2. Experimental details

Ingots of  $\text{CuInSe}_2$  were prepared from its constituent elements, viz copper, indium and selenium. The elements weighed in the stoichiometric proportion were sealed in a quartz ampoule under vacuum ( $\sim 10^{-5}$  torr) and homogenized at  $\sim 1000^\circ\text{C}$  for 48 hr in a furnace. The ingots were then powdered to a mean particle size  $\sim 150\ \mu\text{m}$ . The  $\text{CuInSe}_2$  powder was gradually dropped onto a closed molybdenum boat heated to  $\sim 1400^\circ\text{C}$  in vacuum ( $\sim 10^{-5}$  torr). The substrate temperature was maintained at  $450 \pm 10^\circ\text{C}$  using a temperature controller. The thickness and rate of deposition were monitored by a quartz crystal thickness monitor. After deposition, the films were annealed at  $\sim 475^\circ\text{C}$  for 30–45 min in vacuum. The selenium concentration in the films was varied by controlling the concentration in the powder itself. For Se-deficient cases, the starting alloy was prepared in a non-stoichiometric manner with pre-determined Se deficiency. Se-excess films were prepared by mixing a weighed amount of free selenium powder with the stoichiometric  $\text{CuInSe}_2$  powder before evaporation. It may be noted that the Se concentration mentioned in the text refers to the concentration in the powder before evaporation and not in the final film. Auger analysis was, however, used to determine the chemical composition of the films. In the text the Se-deficient films have been indicated with negative Se at.wt. % concentration whereas Se excess films are denoted by positive concentration.

The thickness of the films was measured by the Taylor-Hobson Talystep instrument. The electronic properties of the films were determined from d.c. Hall measurements using van der Pauw geometry. The optical transmittance at various wavelengths was measured using Hitachi 330 Spectrophotometer. Solar cells were fabricated by evaporating 2–3  $\mu\text{m}$  thick CdS layer on top of the annealed  $\text{CuInSe}_2$  films at a substrate temperature  $200^\circ\text{C}$ . The resistivity of CdS layer was in the range of 1–20 ohm-cm. Silver paste was used for taking contacts from both materials.

## 3. Results and discussion

The structural properties of the films were studied using x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD results show that the films are polycrystalline and the as-deposited flash-evaporated films are multiphase containing sphalerite  $\text{CuInSe}_2$  and excess-free selenium distributed throughout the films. By vacuum annealing of the as-deposited films, single phase chalcopyrite  $\text{CuInSe}_2$  films with lattice constants  $a = 8.70\ \text{\AA}$  and  $c = 11.70\ \text{\AA}$  have been obtained. The values of lattice constants for annealed  $\text{CuInSe}_2$  films are quite close to the reported values (Kazmerski *et al* 1976). Annealing of as-deposited films in vacuum produces two important changes in the films, namely, structural transformation from sphalerite to chalcopyrite and reevaporation of excess-free selenium. No traces of indium oxide and copper oxide have been found. The average grain size of the as-deposited and the annealed films, as determined by TEM, are  $\sim 60$ – $80\ \text{nm}$  and  $\sim 90$ – $120\ \text{nm}$ , respectively.

Figure 1 shows the transmittance spectra of the as-deposited (+ 17 at. wt. % excess Se) and the corresponding vacuum-annealed films. For the as-deposited films, two distinct slopes corresponding to the absorption edges of  $\text{CuInSe}_2$  and free selenium are discernible. On vacuum annealing, the slope corresponding to free selenium absorption

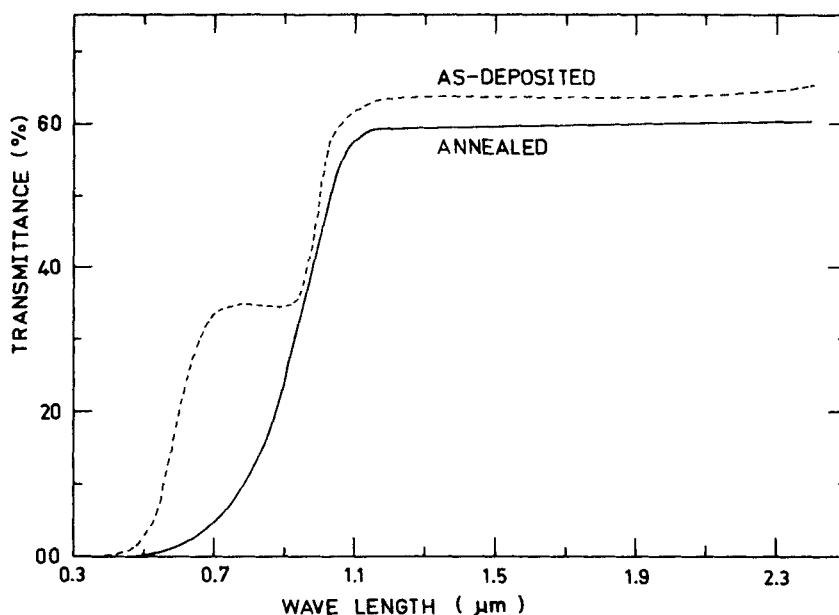


Figure 1. Transmittance of flash-evaporated CuInSe<sub>2</sub> films (+ 17 at. wt. % Se).

edge disappears. This suggests that the as-deposited films are multiphase in nature containing CuInSe<sub>2</sub> and free selenium. The undesirable excess Se is removed in the vacuum annealing step.

The optical absorption coefficient of the films has been calculated at various wavelengths from the transmittance values of two films of different thickness using the formula

$$\alpha = \frac{\ln [T_1/T_2]}{(t_2 - t_1)},$$

where  $\alpha$  = absorption coefficient,  $T_1$  and  $T_2$  are the transmittance of the films of thickness  $t_1$  and  $t_2$  respectively. Figure 2 shows a plot of the variation of  $\alpha^2$  with  $h\nu$ . The straight line behaviour establishes that the films have a direct bandgap of  $\sim 1.15$  eV. The value of  $\alpha$  at  $0.55 \mu\text{m}$  is  $\sim 10^5 \text{ cm}^{-1}$  for the annealed films and compares well with reported data (Sun *et al* 1978).

The chemical composition and metal-to-Se ratio for various vacuum-annealed films as determined from Auger results are shown in table 1. The analysis shows that the Se that is evaporated is not entirely incorporated in the film which is attributed to the high vapour pressure and low sticking coefficient of Se. The metal-to-Se ratio is less than unity for films prepared from excess Se concentration powder and greater than unity for deficient Se concentration powder.

The dependence of the electronic properties of the films on the Se concentration in the powder is shown in figure 3. Three different regions can be identified in the figure (1) *n*-type (left side), (2) *p*-type (right side), and (3) high resistivity intrinsic-like behaviour (central region). Correlation with Auger results (see table 1) shows that the conductivity type of the films is governed by the metal-to-Se ratio. The films are *n*-type if the ratio is greater than one and *p*-type if the value is less than one. Figure 3 shows that as the Se

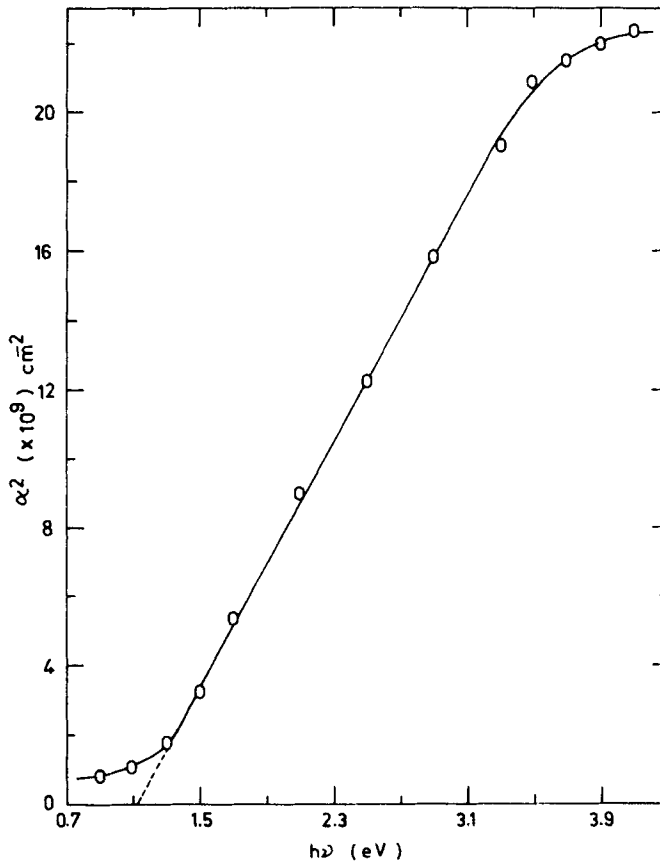
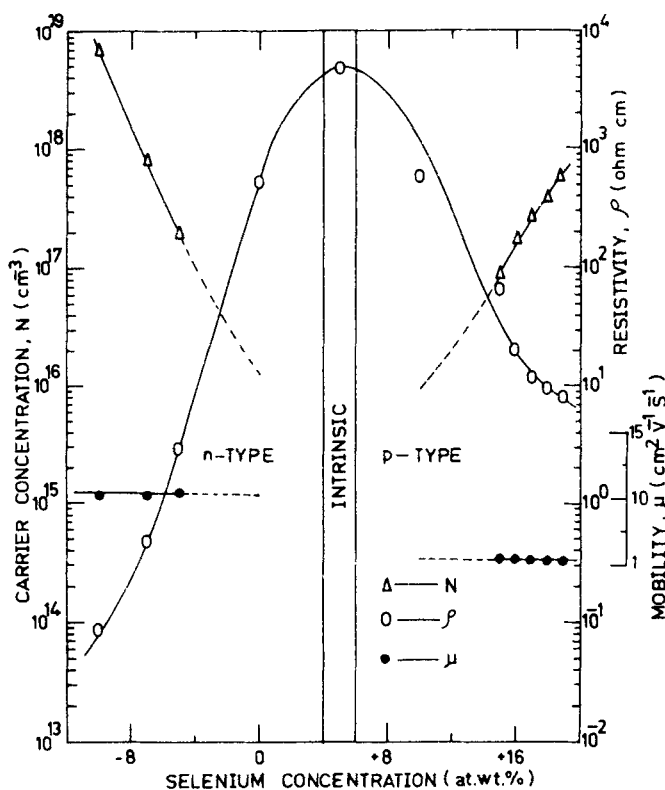


Figure 2. Variation of  $\alpha^2$  with  $h\nu$  of vacuum-annealed  $\text{CuInSe}_2$  films (+17 at. wt. % Se).

Table 1. Auger composition analysis of flash-evaporated  $\text{CuInSe}_2$  films

Selenium concentration in powder (at. wt. %)	Copper (at. %)	Indium (at. %)	Selenium (at. %)	Metal/selenium ratio
-10	25.2	31.6	43.2	1.32
-5	24.0	30.3	45.7	1.19
0	22.3	30.2	48.5	1.08
+5	22.0	26.8	51.2	0.95
+10	20.2	26.5	53.3	0.88
+15	19.0	25.2	55.8	0.79
+16	18.8	24.8	56.4	0.77
+17	18.5	24.5	57.0	0.76
+18	18.0	24.5	57.7	0.74
+19	17.7	24.3	58.0	0.72



**Figure 3.** Variation of carrier concentration ( $N$ ), mobility ( $\mu$ ) and resistivity ( $\rho$ ) of vacuum-annealed CuInSe<sub>2</sub> films with deficit/excess selenium in powder.

concentration is increased or decreased beyond the stoichiometric composition, the resistivity decreases as the films become more and more of  $p$ -type or of  $n$ -type respectively. Further, the decrease in resistivity is almost entirely due to an increase in the free electron or hole concentration as the case may be. Mobility essentially remains constant at  $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  for  $n$ -type films and  $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  for  $p$ -type films. The films with Se concentration +20 at. wt. % are of  $p$ -type but multiphase in nature containing both CuInSe<sub>2</sub> and Se.  $p$ -type films with carrier concentration of  $\sim 3 \times 10^{17} \text{ cm}^{-3}$ , resistivity of  $\sim 1.2 \times 10^1 \text{ ohm cm}$  and mobility of  $\sim 1.0 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  have been used to fabricate junctions of  $p$ -CuInSe<sub>2</sub>/ $n$ -CdS. The CdS films have been deposited on the CuInSe<sub>2</sub> films by vacuum evaporation. The junction has exhibited an open circuit voltage of the order of 350–375 mV. Having established the feasibility of using the CuInSe<sub>2</sub> films for making junctions, present efforts are directed towards attaining high conversion efficiencies.

#### 4. Conclusions

The feasibility of using a flash evaporation technique for the deposition of thin films of CuInSe<sub>2</sub> has been established. The properties of the films can be tailored by control of

the stoichiometry of the films, and vacuum-annealing treatments. CuInSe<sub>2</sub>/CdS junctions fabricated using these films have shown high  $V_{oc} = 350\text{--}375$  mV.

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