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# Physical Properties of Stacked $CuInSe_2$ Thin Films

A. ASHOUR
*Physics Department, Faculty of Science, El-Minia University, El-Minia, EGYPT.*

ABSTRACT. Semiconducting thin films of $CuInSe_2$ have been grown by thermal annealing in air of evaporated layers of Cu, In and Se on glass substrates. The structure of the films has been studied using the X-ray diffraction (XRD). The films were polycrystalline and showed mixture phases (ternary and binary) depending on the annealing temperature. The electrical properties revealed resistivity range of $10^1$-$10^4$ Ω cm respectively. The resistivity influenced with the annealing temperature and decreased with increasing temperature. The films have been analyzed for optical band gap.

Keywords: Evaporation; Electrical resistivity; Stacked elemental Layer (SEL); $CuInSe_2$

## 1. Introduction

Copper indium diselenide (CIS) thin film solar cells are one of the most promising photovoltaic devices for large area terrestrial applications. Several researches demonstrated greater than 18% efficiency using alternative lower cost methods (Nancheva *et al.*, 2002). The high absorption coefficient of $CuInSe_2$ material ( $\alpha \approx 10^5$ $cm^{-1}$) makes thin-film solar cells practical, even though the rather low optical hand gap of 1.05 eV is low for optimum conversion efficiency (Onuma *et al.*, 2001). $CuInSe_2$ can be made either n- or p-type depending on the preparation conditions, which permits the formation of homo- and hetero- junctions and has electrical properties, which are compatible with photovoltaic device fabrication. It also has excellent thermal stability in air. A variety of techniques have been devised to deposit $CuInSe_2$ thin films (Kavcar *et al.*, 1992). They include flash evaporation, R.F. and ion beam sputtering, molecular beam epitaxy, spray pyrolysis, co-evaporation and stacking elemental layer (SEL). The former method has proven to be promising from the viewpoint of high efficiency, and therefore some recent studies have focused on this. However, the stacking elemental layer (SEL) is an attractive method, because large-area films with good uniformity can be grown at low cost (Ashour *et al.*, 2004).

The present study focuses on the relationship between the properties of the $CuInSe_2$ films and the film-preparation conditions. $CuInSe_2$ films have been deposited on the glass substrate by SEL and have been characterized with respect to X-ray diffraction, resistivity, and optical absorption.

## 2. Experimental details

The ternary compound semieonduetor CIS thin films have been produeed by thermal air annealing of stacked elemental layers. The experimental method has been deseribed elsewhere (Kavcar *et al.*, 1992; Ashour *et al.*, 2004). Spec-purc elements of Cu, In and Se (99.999%) with the proper weights, according to the mole ratio 1:1:2 were vacuum deposited onto glass substrates by thermal evaporation. A quartz thickness monitor (Edwards Model FTM3) was used to control both film thickness and deposition rate inside the vacuum chamber. The thieknoss of the deposited $CuInSe_2$ films were measured accurately after deposition by utilizing multiple-beam Fizeau fringes at refleetion. The individual layer thicknesses were gencrally chosen to be in the ratios 1.0:2.2:4.6 to achieve a 1:1:2 stoichiometrie ratio for copper, indium and selenium, respeetively. Figure 1 shows the schematic representation of the total thickness of each sandwich was approximately 500 nm.

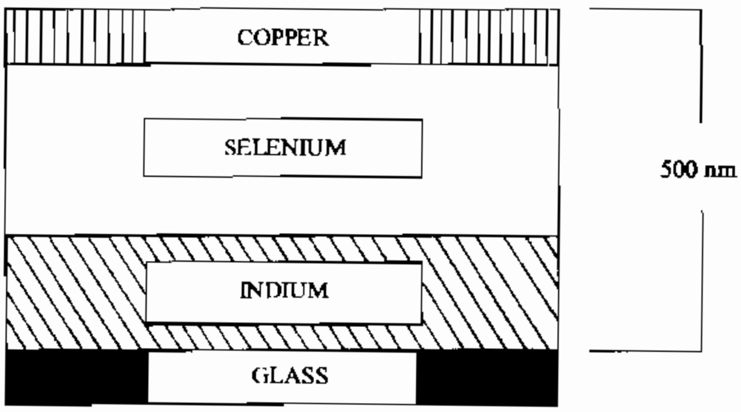


Fig. 1. The Schematic representation of the sandwich.

Annealing in air was performed at 200, 300 and 350 °C for 1h (60 min.), to study the effect of annealing on the structure and phases. After annealing, the temperature was decreased gradually to room temperature with 50 °C/min. The structural aspect of the films was investigated by X-ray diffraction (model JEOL 60PA) using the Mo-kα radiation in range of 20° to 60° with slow scanning speed (2°/min) and step width of 0.02°.

The electrical resistivity of the prepared films was measured by the four-point probe method of Van der Pauw (1958) in conjunction with the corresponding correction tables (Ramadan *et al.*, 1994). The potential difference and the current were measured by a Keithly electrometer (model 616). Four small aluminum contacts were deposited at room temperature on the $CuInSe_2$ films, which were arranged symmetrically around the circumference. Copper wire was attached to the contacts using silver paste and the leads were shielded to minimize induced currents.

The optical transmittance measurements through the films, referenced to the glass were carried out in the wavelength range from 500-2000 nm with an UV/visible spectrophotometer (Shimadzu 3101 PC).

### 3. Results and discussion

The optimization of the physieal properties of polycrystalline $CuInSe_2$ absorber films is an important prerequisite for the successful fabrieation of high-ternary phase of $CuInSe_2$ films. The information gained from this study established a basis for the fabrication of high-ternary phase thin films in our laboratory. In this study, the sequenee of In/Se/Cu for the sandwieh system of SEL is chosen, because the previous studies (Ashour *et al.*, 2004; Akl, 1997) revealed that the best one is In/Se/Cu to get ternary phase of $CuInSe_2$ thin films.

The sandwich structures of the elemental layers in the ratio to give a stoichiometrie eompound were deposited and a thermal annealing step was carried out. Therefore a series of experiments to determine the anneal temperature and time for optimum properties were earried out. The annealing took place within the furnace. The anneal temperature was determined to be 350 °C for 1h in air for optimum condition.

The structural, electrical and optical properties of thin films prepared by SEL were investigated. The XRD studies showed the films to be polyerystalline and the speetra (Figure 2) indieated a mixture of $CuInSe_2$ and binary compound of CuSe phase. However, upon annealing the heating processed sample in air, an improvement resulted. Films annealed below 350 °C were also polyerystalline. However, as the annealing temperature was increased, more structure of ternary phase was observed. The annealed samples were subjeeted to a thermal anneal at 350 °C for 1h after which the $CuInSe_2$ phase was produced without binary products as shown in Figure 3. Subsequent investigation for the films gave X-ray diffraction spectra showing only $CuInSe_2$ phase being present. The results confirm the findings of other workers (Kavcar *et al.*, 1992; Ashour *et al.*, 2004; Akl, 1997; Akl *et al.*, 2001; Saehan & Meakin, 1993).

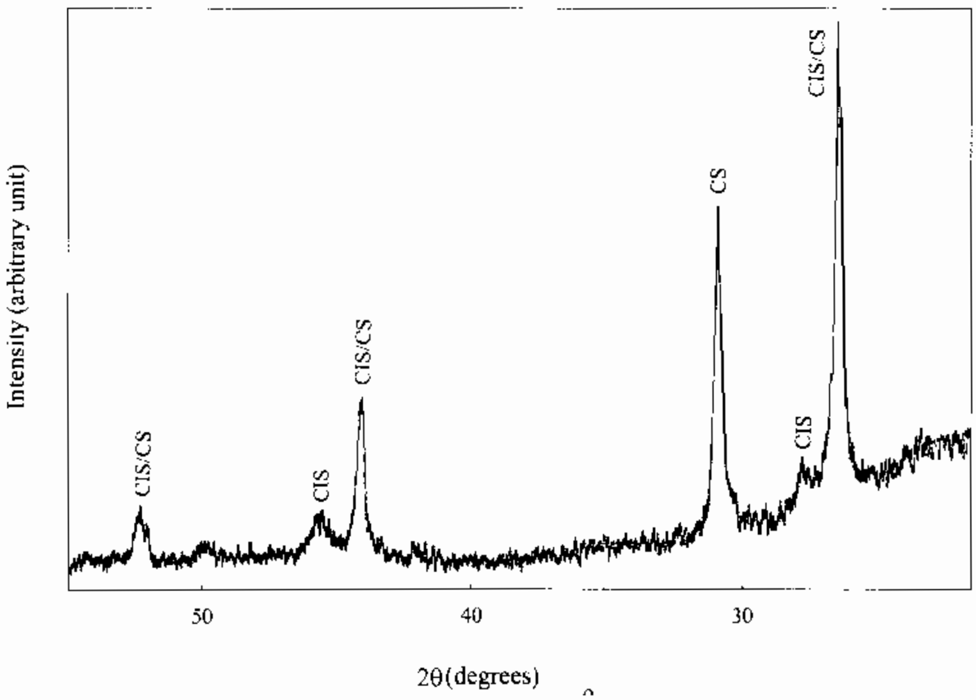


Fig. 2. X-ray diffraction pattern of the film after annealing at 200°C for 1h in air (CIS: $CuIoSe_2$ , CS: CuSe phase)

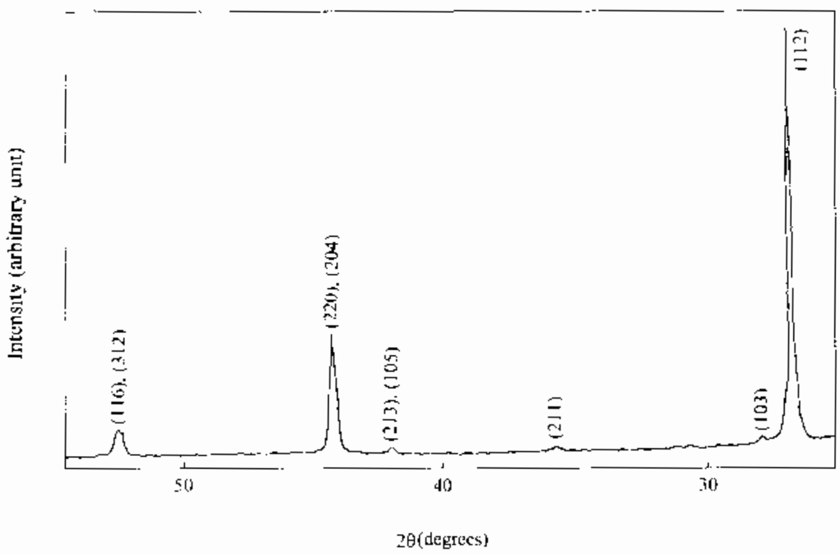


Fig. 3. X-ray diffraction pattern of the tenary phase of $CuInSe_2$ film after annealing in air at 350°C for 1h.

The eleetrical properties were measured and the resistivity influenced with the annealing temperatures in air. All films with sequence In/Se/Cu exhibited semiconducting behaviour with the resistivity, p, ranging from $10^1$ - $10^4$ Ωcm. The electrical resistivity decreases with the increase in air annealing temperatures. This is probably attributed to the increasing in the amount of ternary phase ($CuInSe_2$) present and the optimnm parameters were 350 °C for 1h as proved hy the XRD study. The depeudence of film resistivity is on the anncaling temperature in air as reported elsewhere (Akl, 1997; Sachan & Meakin, 1993).

Optical measurements of the films at room temperature showed a sharp absorption edge at a wavelength of 1250 nm indicating $CuInSe_2$ formation. However, after annealing the film in air, an improvement resulted. The optical transmission is shown in Figure 4. The optical transmission for these films with lower annealing temperature (200 °C for 1h) was ahout 30%. As one would expect, the highest transmission (80%) was found for the chalcopyrite $CuInSe_2$ annealed at a temperature of 350°C for 1h. The absorption coefficient, α, was fonnd with the order $10^4$ $cm^{-1}$, indicating the material is the direct-band-gap type and the transition is allowed (Bhattacharya & Pramanik, 1982; Pawar *et al.*, 1984).

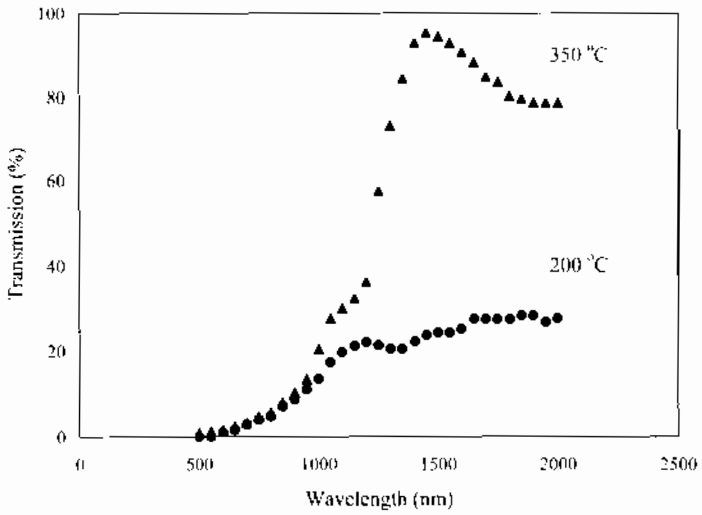


Fig. 4. Transmission spectra of the In/Se/Cu sandwich after annealing at 200 and 350°C for 1h in air.

The absorption coefficient (α) is determined from the transmission (T) and reflection (R) spectrum based on the following relation (Cho et al., 2001):

$$T = [(1-R)^2 \exp(-\alpha d)] / [1 - R^2 \exp(-2\alpha d)]$$

Where d is the film thickness. The absorption coefficients were determined as a function of wavelength at various annealing temperatures. As it is seen from Fig. 5, the annealing temperatures in air influenced the absorption coefficients. The highest absorption coefficient was found for the chalcopyrite $CuInSe_2$ annealed in air at a temperature of 350 °C for 1h. The values of α in the neighborhood of the energy gap are similar to those obtained by others (Kavcar *et al.,* 1992; Stratieva *et al.,* 1997; Akl, 1997). Kazmerski *et al.,* (1983) have demonstrated the effect on the absorption characteristics of thin films by annealing. Air annealing increases the absorption coefficients, this influence was not due to an oxide formation, but to an improvement in compositional uniformity (Kavcar *et al.,* 1992).

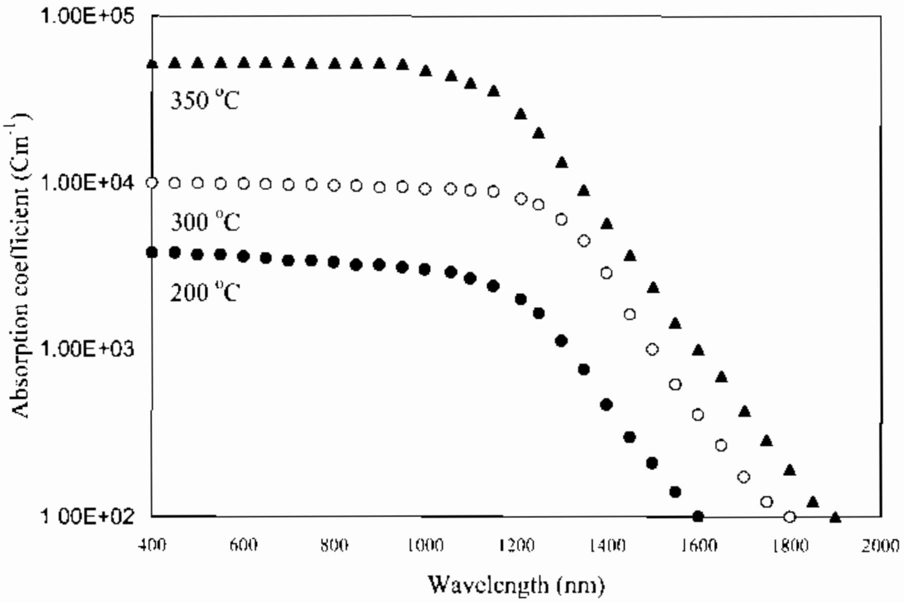


Fig. 5. Absorption coefficients after annealing at 200, 300 and 350°C in air for 1h.

The absorption coefficient, α, of a direct transition is related to the energy bandgap as (Ashour *et al.,* 1995):

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

Therefore, from the plot of direct band gap $(\alpha h\nu)^2$ versus hν as shown in Fig. 6, the gap energy can be defined by extrapolating the linear portion of the curve to the intercept of the photon energy axes. The band gaps ($E_g$) values for the films are very close to 1.0 eV, which near the accepted value of 1.05 eV. The range of band gap energy (0.90-1.0 eV) obtained is in good agreement with previously published data for $CuInSe_2$ thin films prepared by other methods (Kavcar et al., 1992; Akl, 1997; Stratieva et al., 1997; Hill et al., 1988; Neumann et al., 1982; Yamaguchi et al., 1992). Since the optical properties of the films were greatly improved by the annealing step, it was decided that the production of $CuInSe_2$ films by thermal annealing of stacked elemental layer structures should be investigated further.

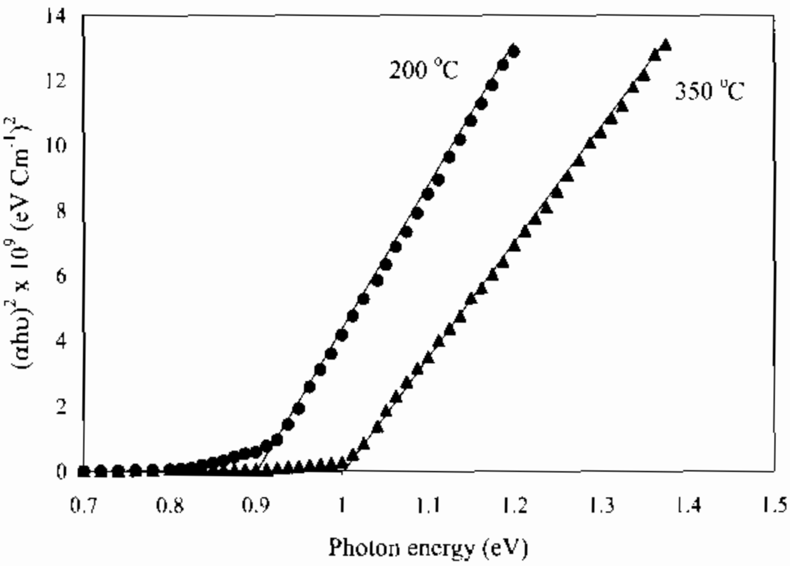


Fig. 6. Relation between $(\alpha h\upsilon)^2$ and photon energy of the films after annealing at 200 and 350°C in air for 1h.

On the other hand, the optimum value of $E_g$ (~ 1.0 eV) is due to the formation of single phase of ternary CIS as shown for the best In/Se/Cu sequence, which annealed at 350 °C for 1h. This conclusion is confirmed by the X-ray diffraction.

## 4. Conclusions

$CuInSe_2$ thin films have been synthesized by SEL. The structural, electrical and optical properties have been studied. All the deposited films were polycrystalline exhibited the chalcopyrite structure with a strong (112) orientation. The phase of the films was influenced with the annealing temperature. The ternary phase ($CuInSe_2$) increased with increase of annealing temperature. The electrical resistivities of the films were in the range of $10^1 - 10^4$ Ωcm. From the optical measurements, the energy band gaps of the range of 0.9 – 1.0 eV were obtained. The formation of single phase of ternary CIS can be obtained by the annealing of the best In/Se/Cu seqnence at 350 °C in air for heating time of 1h.

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# الخواص الفيزيائية لشرائح رقيقة من ثاني سلينات النحاس والإنديوم المتلاصقة

**عادل عاشور**

*قسم الفيزياء، كلية العلوم، جامعة المنيا، المنيا، مصر*

*المستخلص.* تم تحضير شرائح رقيقة لأشباه الموصلات من ثاني سلينات النحاس والإنديوم بطريقة التخمير (التسخين) الحراري في الهواء لشرائح متبخرة من النحاس، الإنديوم والسيلينيوم على شرائح زجاجية ، ولقد تمت دراسة التركيب للشرائح باستخدام تشتت الأشعة السينية ، وكانت الشرائح متبلّرة وخليط من الطور الثنائي والثلاثي ويعتمد ذلك على درجة حرارة التخمير ، ولقد أظهرت الخواص الكهربية مدى المقاومة النوعية من ١٠–$١٠^{٤}$ أوم سم والتي تتأثر بدرجة حرارة التخمير وتتناقص المقاومة النوعية مع زيادة درجة حرارة التخمير ، ولقد تم تحليل الشرائح ضوئيا لدراسة نطاق الفجوة الضوئية.