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Fabrication and characterisation of $CuInSe_2$/Si(1 0 0) thin films by the stacked elemental layer (SEL) technique

L. Bechiri [a,*], M. Benabdeslem [a], N. Benslim [a], A. Djekoun [a], A. Otmani [a], L. Mahdjoubi [a], R. Madelon [b], P. Ruterana [c], G. Nouet [c]

[a] Laboratoire des Cristaux et des Couches Minces, Institut de Physique, Université de Annaba, BP. 12, 23200 Sidi Amar, Algeria
[b] Laboratoire d'Etude et de Recherche des Matériaux, FRE 2149 CNRS, Institut des Sciences de la Matière et du Rayonnement ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen cedex, France
[c] Equipe Structure et Comportement Thermodynamique des Matériaux—Laboratoire de Cristallographie des Matériaux, UMR 6508 CNRS, Institut des Sciences de la Matière et du Rayonnement, 6 Boulevard du Maréchal Juin, 14050 Caen cedex, France

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Abstract

Thin films of (Cu/In/Se) were fabricated by evaporated elemental layers of Cu, In and Se on Si (1 0 0) and on glass substrates at $T_S = 250$ °C. Films with phase chalcopyrite structure and strong (1 1 2) preferred orientation were produced. EDX showed uniform compositional properties of the films over a substrate area of 1 cm^2. The optical energy band gap of 0.984 eV was obtained and photoluminescence measurements have been carried out in as-deposited polycrystalline Cu/In/Se thin films deposited onto (1 0 0) oriented Si wafers doped with 10^{15} cm^{-3} of boron. The PL spectra of $CuInSe_2$ show emission peaks at 0.87 eV ranging from 0.75 to 0.98 eV. The broad emission band is ascribed to donor–acceptor pair (DAP) transition.

Keywords: $CuInSe_2$; Chalcopyrite; SEL; Defects

1. Introduction

Thin film $CuInSe_2$ solar cells have the potential to achieve the goals of higher efficiency and low cost, necessary for large scale applications. Different methods have been used to fabricate $CuInSe_2$ thin film absorbers as reported in literature reviews [1–4]. Device efficiencies greater than 14% over small areas have been achieved using the coevaporation of the elemental materials [5]. Although various methods have been used successfully to produce $CuInSe_2$, there is no commercial manufacturing operation for the present moment.

The stacked elemental layer (SEL) is a technique suitable for large area development because of its simplicity to control the deposition parameters. The SEL technique has been used to produce $CuInSe_2$ materials and low efficiency devices have been reported [6]. However, no detail characterisation has been undertaken to identify the various defects associated with SEL based $CuInSe_2$ thin films. In this work, the origin of the luminescence transitions is further probed by intensity and temperature dependent measurements.

2. Experimental

Elemental layers of Cu (99.999% from Balzers), In (99.999% from Balzers) and Se (99.999% from Balzers) were sequentially deposited on (1 0 0) oriented Si wafers doped with $10^{15}cm^{-3}$ of boron and Càrning 7059 glass substrates of size 1 cm × 1 cm at $T_S = 250$ °C by thermal evaporation in the vacuum chamber at about 10^{-5} Torr. The layer thicknesses of Cu, In and Se were 20, 40 and 90 nm, respectively. The typical thickness of the obtained films was approximately 150 nm for a 15 min deposition time. Cu and In were evaporated from W boats, while Se was evaporated from a graphite effusion source. A quartz crystal monitor was used to record the evaporation rate.

All films were characterised for morphological, compositional and structural properties using the scanning electron

* Corresponding author. Fax: +213 38 87 28 86.
E-mail address: bechiri@hotmail.com (L. Bechiri).

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microscopy (SEM), energy dispersive X-ray analyser (EDX) and X-ray diffraction (XRD), respectively. The optical and electrical properties were studied using the optical a Perkin-Elmer λ9 (UV-VIS-NIR) double beam spectrophotometer (500–3000 nm) and Hall measurement. Jeol transmission electron microscopy, operating at 200 kV was used to evaluate the cystallinity of the Cu/In/Se samples.

PL spectra were recorded using a standard Lock-in technique with a Jobin-Yvon HR1000 grating monochromator and a North Coast EO-817 germanium detector. An oxford closed cycle He cryostat cooled the sample to 7 K and Ar^+ ion laser excited the PL by the 514.5 nm.

3. Results and discussion

The In-rich samples have uniform shiny grey colour. Optical measurements of the films at room temperature showed low transmission (20%) with a sharp absorption edge at a wavelength of 1250 nm. The absorption coefficient, α, was calculated as $3 \times 10^5\ \mathrm{cm}^{-1}$ from the equation,

$$\alpha = -\frac{1}{t}\ln\left[\frac{T}{(1-R)^2}\right]$$

where T is the transmittance, R the reflectance and t is the film thickness.

The absorption coefficient (α) of a direct transition is related to the energy band gap [7,8] as $\alpha h\nu = \sqrt{h\nu - E_g}$. Plot of $(\alpha h\nu)^2$ against $h\nu$ is shown in Fig. 1. The value of E_g obtained by extrapolating the fundamental absorption edge of the $CuInSe_2$ on the $h\nu$ co-ordinate, at room temperature, is 0.984 eV, which agrees with the value reported in the literature by Kazmerski et al. [9].

Electrical parameters were derived from Hall measurements using Van der Pauw method at room temperature, the contacts used were a wire of platina (Pt). Films were p-type with electrical resistivity (ρ) of 0.02 Ω cm, mobility of 45.27 cm^2/V/s, and carrier concentration of $2.70 \times 10^{19}\ \mathrm{cm}^{-3}$.

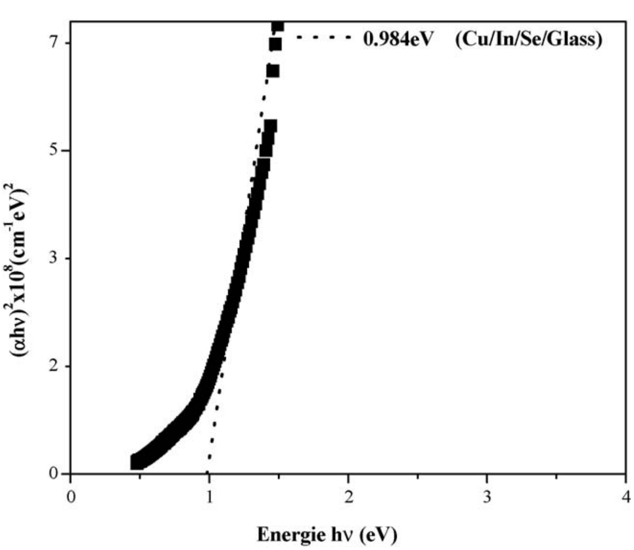

Fig. 1. Dependence of $(\alpha h\nu)^2$ on photon energy for thin films grown at T_S = 250 °C.

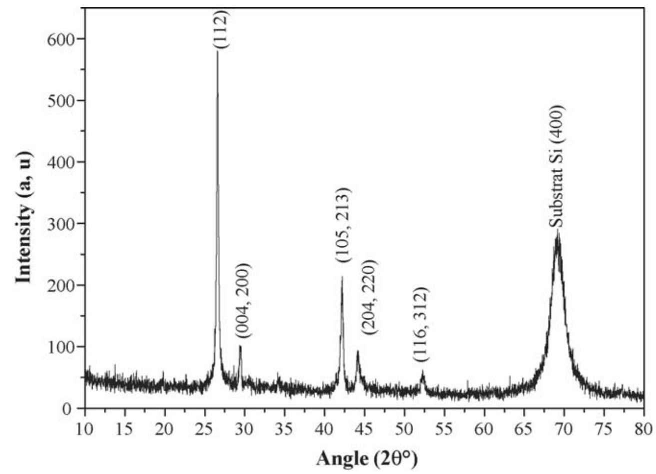

Fig. 2. X-ray diffraction patterns of sequentially deposited Cu/In/Se layers.

The XRD profiles spectra of the CIS thin films deposited at 250 °C substrate temperature is shown in Fig. 2. We can identify diffraction peaks associated with (1 1 2), (0 0 4)/(2 0 0), (1 0 5)/(2 1 3), (2 0 4)/(2 2 0) and (1 1 6)/(3 1 2) reflections. The XRD patterns of the films clearly demonstrate the diffraction reflections typical to the chalcopyrite. The diagrams do not present any characteristic line (1 0 1), (2 1 1) and (1 0 3) of chalcopyrite structure as the films deposited at this temperature are nanocrystalline [10]. Additional reflexions at 2θ = 65–73° are those of Si (1 0 0) substrate. From Scherrer's formula we estimate the average crystallite size to be 40 nm.

SEM studies (Fig. 3) indicated that the prepared In-rich films were characterised by poor morphological properties with no apparent grain structure. This observation was also confirmed by planar view transmission electron microscopy (TEM) studies, indicating the presence of small (120–140 nm), highly defected grains TEM studies also showed (see Fig. 4) that the most common type of crystalline defects in In-rich films were planar defects (i.e. microtwins). A significant amount of microtwins (indicated by X) were also detected in these films. The average composition (at.%) of film, given by EDS analysis using a spot size of 25 nm, was: Cu = 22.28, In = 33.83 and

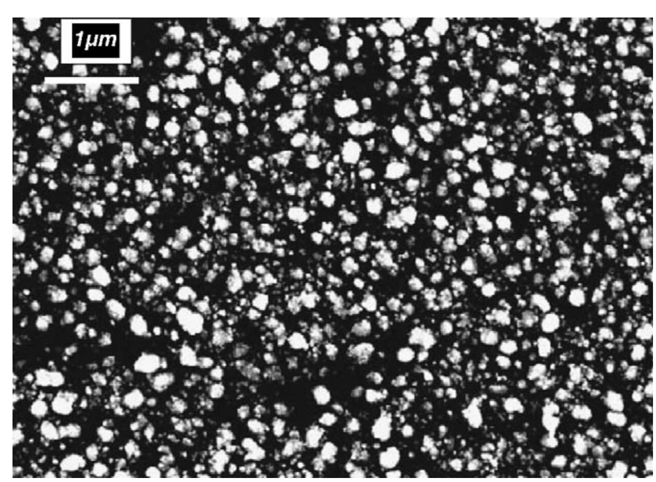

Fig. 3. SEM micrograph of $CuInSe_2$/Si(1 0 0) thin films deposited at 250 °C.

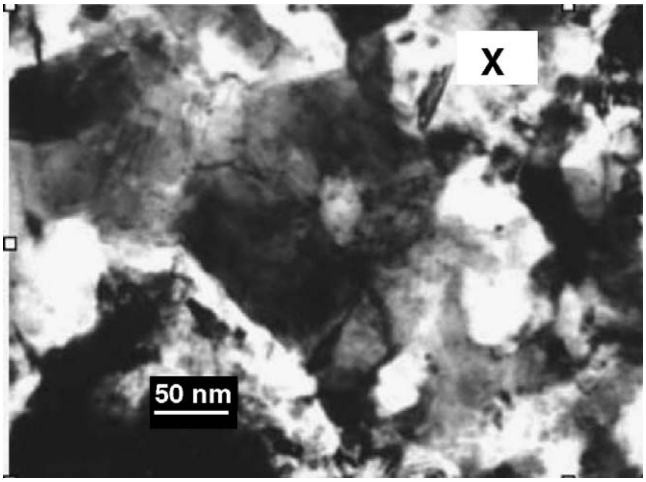

Fig. 4. Bright field planar view TEM micrograph of typical In-rich sample.

Se = 43.89. Rapid EDS analysis of the layer cross-section showed that the Cu concentration was relatively higher in the layer region close to the substrate while the In and Se concentrations were lower.

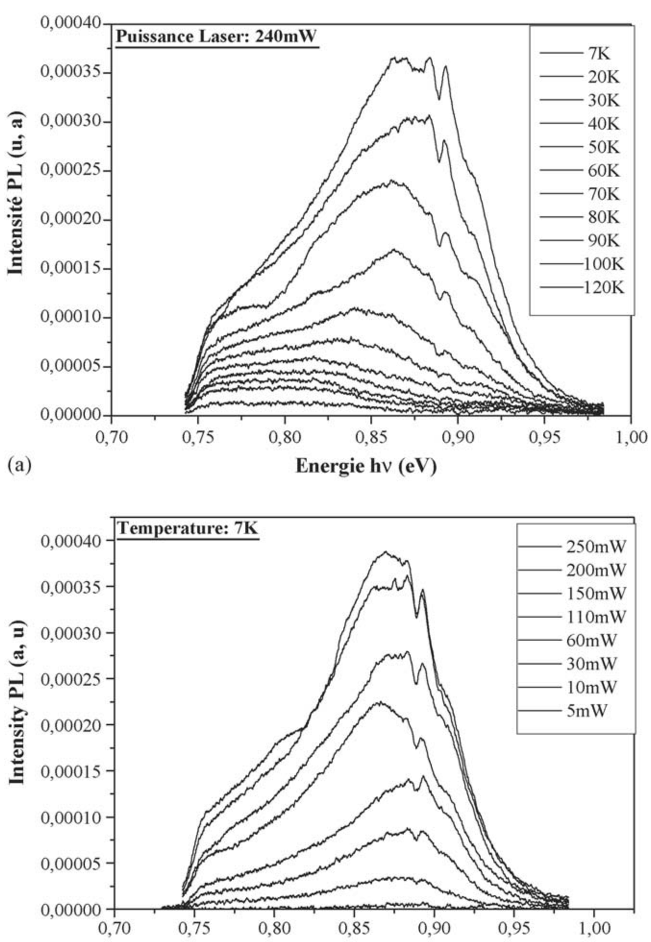

Fig. 5. Typical example of the effect of temperature (a) and excitation intensity (b) on the emission peaks from sample.

Fig. 5a shows emission spectra excited with a constant intensity for as-grown p-type crystal as a function of temperature. The band peak shifts to lower energy and becomes broader with an increase in temperature. The effect of excitation intensity on the broad-band emission peaks was also evaluated at 7 K (Fig. 5b). With increasing excitation power the emission shifts to higher energies. This behaviour is usually taken as an indication of DAP recombination.

The PL emission energy for D–A transition will be given by [11]

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{4\pi\varepsilon\varepsilon_0 r}$$

where E_g is the band gap, E_A and E_D are the acceptor and the donor levels, ε the dielectric constant and r is the separation of the donor–acceptor pair.

Fig. 6 shows the Arrhenius plots for PL peaks. Employing the appropriate formula after the work of Bimberg et al. [12], we can fit the peak intensity I to the illumination intensity I_0 by

$$I = \frac{I_0}{1 + A\exp\left(\frac{-E_a}{k_B T}\right)}$$

where E_a is the activation energy associated with the recombination route. This yields activation energies of 24 meV for the 0.87 eV emission line.

This value of activation energy is very close to the one that has been measured by several groups and attributed to Cu-vacancy V_{Cu} [13,14]. This defect will be an acceptor in $CuInSe_2$. The donor level could result from the antisite defect In_{Cu}, which is likely to be present in In-rich material. It may also be due to Se-vacancy V_{Se} which is likely to occur in Se-deficient material. Assuming a band gap of 0.984 eV and $h\nu = 0.865$ eV at low excitation power (5 mW) $h\nu = E_g - (E_A + E_D)$, we find $E_D = 81$ meV.

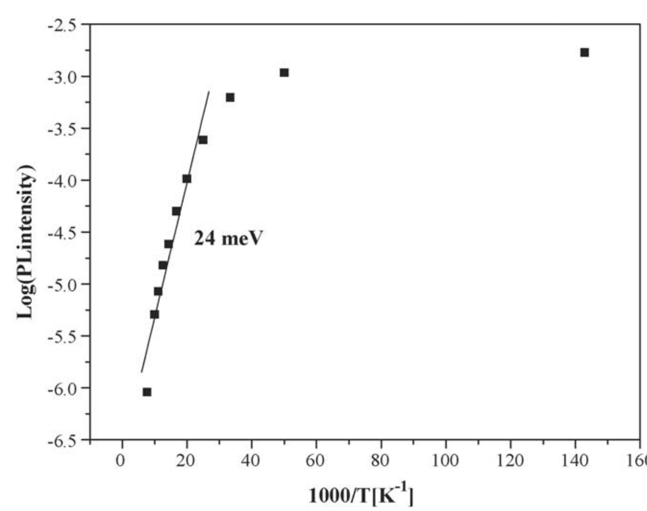

Fig. 6. Dependence of the emission intensity on reciprocal temperature of $CuInSe_2$.

4. Conclusion

$CuInSe_2$ thin films were fabricated by thermal evaporation of Cu, In and Se elemental layers. Studies of the micro structural properties revealed single phase chalcopyrite structure with strong (1 1 2) preferred orientation. EDX analysis shows In-rich films. An energy band gap of 0.984 eV was obtained from the optical measurements. p-Type films produced at $T_S = 250\,^{\circ}C$ do not have high structural quality. PL spectra contain only one broad PL emission. Results indicate that donor–acceptor pair (DAP) transition from a donor level lying approximately 81 meV below the conduction band, to an acceptor level laying 24 meV above the valence band, dominates.

References

[1] A. Rockett, J. Appl. Phys. 70 (7) (1991) R81–R97.
[2] M.V. Yakushev, A.V. Mudryi, V.F. Gremenok, V.B. Zalesski, P.I. Romanov, Y.V. Feofanov, R.W. Martin, R.D. Tomlinson, J. Phys. Chem. Solids 64 (2003) 2005.
[3] V. Alberts, J.H. Schon, E. Bucher, J. Appl. Phys. 84 (12) (1998) 6881.
[4] A.G. Chowles, J.A.A. Engelbrecht, J.H. Neethling, C.C. Theron, Thin Solid Films 361/362 (2000) 93.
[5] J. Hedestrom, H. Ohlsen, M. Bodegard, A. Kylner, L. Stolt, D. Harisos, M. Ruckh, H.W. Schock, in: Proceedings of the 23rd IEEE Photovoltaic Specialist Conference, Louisville, Kentucky, 1993, p. 364.
[6] H. Oumous, A. Knowles, M.H. Badawi, M.J. Carter, R. Hill, 21st IEEE Photovoltaic Specialist Conference, Institute of Electrical Electronics Engineers Inc., Kissimimee, Florida, 1990, p. 479.
[7] J.L. Shay, J.H. Wernick, Ternary Chalcopyrite Semi-Conductors: Growth, Electronic Properties and Applications, Pergamon Press, Oxford, 1975, p. 3.
[8] W. Horig, H. Neumann, H. Sobotta, Thin Solid Films 48 (1978) 67.
[9] L.L. Kazmerski, M. Hallerdt, P.I. Ireland, R.A. Michelsen, W.S. Chen, J. Vac. Sci. Technol. A1 (1983) 395.
[10] L. Béchiri, N. Benslim, M. Benabdeslem, L. Mahdjoubi, J. Chen, P. Ruterana, G. Nouet, Ann. Chim. Sci. Mat. 27 (2) (2002) 45.
[11] D.G. Thomas, J.J. Hopfield, W.M. Augustyniak, Phys. Rev. 140 (1965) A202.
[12] D. Bimberg, M. Sondergeld, E. Grobe, Phys. Rev. B 4 (1971) 3451.
[13] G. Dagan, F. Abou-ElFotouh, D.J. Dunlavy, R.J. Matson, D. Cahen, Chem. Mater. 2 (1990) 286.
[14] J.H. Schon, E. Bucher, Sol. Energy Mater. Sol. Cells 57 (1999) 229.