Study of Cu/In/Se/Se thin films prepared by the Stacked Elemental Layer (SEL) technique

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Abstract : $CuInSe_2$ thin films have been grown on Corning glass and Si (100) substrates using stacked elemental layers (SEL) processing. The influence of substrate's nature and substrate's temperature were studied. X-ray diffraction and SEM measurements have shown that the films exhibit an excellent crystallinity and crystallize in a tetragonal structure. Scanning electron microscopy investigations have shown that the films consist in a structure with large grains in the range 80 – 200 nm. Increasing the deposition temperature from room temperature to 300 °C has lead to a change in the composition and morphology of the films. Characteristic peaks of the chalcopyrite structure such as (101), (211) and (311) were clearly observed for both layers upon annealing at 450°C as evidenced by X-ray diffraction study. The determined lattice parameters were a = 0.57725 (6) nm, b = 1.1621 (2) nm for sample prepared at room temperature and a = 0.57770 (4) nm, b = 1.1602 (1) nm for Ts = 300°C. The crystallographic structure of the $CuInSe_2$ sample was analyzed by Rietveld analysis using X-ray powder diffraction data. UV-Vis-NIR Spectrophotometry was used to investigate the optical characteristics of different Cu/In/Se/Se thin layers in the spectral range between 300 – 2000 nm. The optical band-gap of our materials increases from 0.98 to 1.01 eV.

Key words: chalcopyrite, (CISe), X-Ray diffraction, optical properties.

I. Introduction

$CuInSe_2$ (CISe) ternary compounds and their alloy with gallium (SIGSe) have been and are still some of the most extensively studied photovoltaic materials due to their high value of absorption coefficient (10^4-10^5 cm^{-1}) within the visible and near infrared, its near-optimum band gap Eg and an excellent outdoor stability [1]. Thin film solar cells based on such materials have produced a record efficiency of 19.5% [2, 3]. The CIGSe absorber materials were grown by coevaporation from elemental sources. Record conversion efficiency of about 20.3%, based on such process, was recorded recently on small (0.5 cm2) cells by the Zentrum fuer Sonnenenrgie-und-Wasserstoff–Forschung of the Fraunhofer Institute for Solar Energy Systems. Thus such process is expected to compete with crystalline silicon based technology.
Concerning $CuInSe_2$ thin films, various techniques were used to prepare such material. The best results were obtained for the layers grown using the coevaporation from elemental sources technique. However, such process is difficult in upscaling and involves high vacuum and thus high cost. Reducing the cost is the challenge of research groups around the world. In this way several studies were undertaken to deposit good quality thins films using vacuum and non vacuum cost effectives processes. Electrodeposition is one of the most studied processes [4]. Stacked elemental layer (SEL) processing is one of the most promising one [5]. Compared to other deposition methods, SEL offer some advantages, such as a precise control of the composition, a high homogeneity, and the ability to deposit large area films on complex substrates. In this study, we report some results on the synthesis, structure, and optical properties of the $CuInSe_2$ thin films as well as the results of effect of substrate temperature and substrate on these properties.

II. Experimental

Elemental layers of Cu, In and Se were thermally evaporated sequentially onto glass and on Si (100) substrates at room temperature and at T_S = 300°C under ~ 10^{-3} Pa. The Cu, In and Se thickness were chosen of about 14nm, 28nm and 63nm respectively. After a heat treatment at 250°C for 30 min, a layer of 30 nm Se was deposited (figure 1). Samples were then subjected to annealing at 450°C under Ar flow. In this work, structural analysis of the samples have been performed using grazing incidence X-Ray diffraction (GIXRD), XRD and SEM. Compositional analysis was made by EDS Spectroscopy and optical properties were studied with UV-Vis-NIR SpectrophometryFor Transmission Electron Microscopy (TEM) investigation, the starting

materials were evaporated directly on carbon film supported by Ni grids.

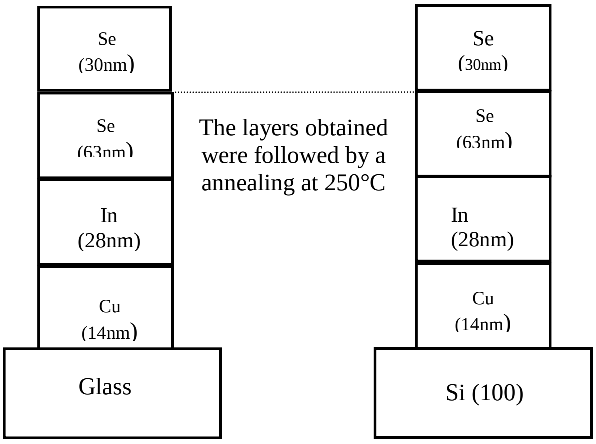
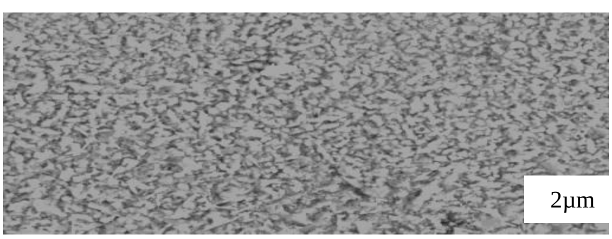


Figure 1: Schematic diagram of the elemental layers

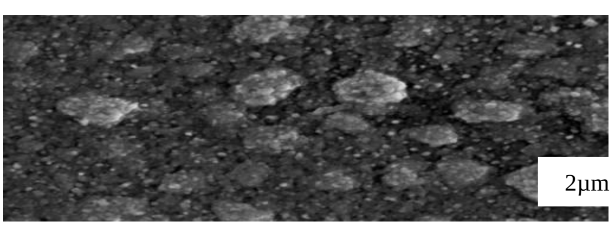
III. Results and discussion

3.1 Cu/In/Se/Se on glass substrate

The SEM photograph of the CIS produced by SEL technique, with Cu/In ratio of (a) 1.16, (b) 0.82, is shown in figure 2. The TEM photographs of the starting elements Cu, In and Se on Ni grids are also shown for reference. SEM studies (figure 2a) revealed smooth amorphous-like structures with an almost complete absence of defined grain structure. An increase to 300°C resulted in a significant improvement in crystalline quality on a morphological level. SEM studies (figure 2b) revealed a dense and compact structure of well-defined grains with typical sizes between 0.4 and 1.6μm. This morphology was also observed by several authors [6, 7]. Many studies have investigated the effect of temperature substrate and have suggested that increasing the temperature during film growth increases the grain sizes [8] and reduces the number of defects inside the CIS grains [9].

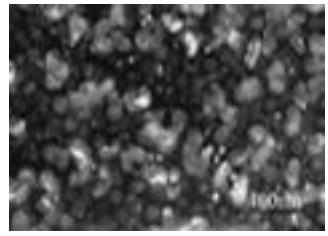


2a) Room temperature

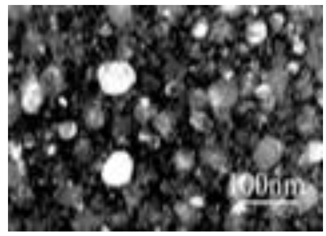


2b) Ts = 300°C

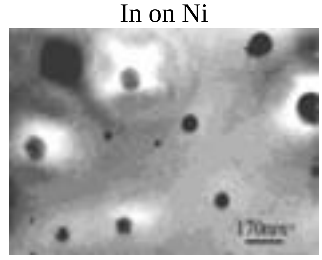
Figure 2: SEM micrographs, illustrating the surface morphology of Cu/In/Se/Se film produced by the SEL technique at different substrate temperature after annealing.



Cu on Ni



In on Ni



Se on Ni

Figure 3: TEM photographs of the starting materials Cu, In, and Se are also shown for reference.

The films were examined using X-ray diffraction (XRD) to check the structure in the overall samples. It revealed that the thin films are of the chalcopyrite structure (figure 4). This is confirmed by the presence of the main diffraction peaks in their XRD spectra. Thus, XRD indicates that the film contains no secondary phase. Although substrate temperature had a dramatic influence over morphology as described above, it had little impact on the orientation. Both samples were polycrystalline and displayed a high degree of (112) orientation. At the temperature of 300°C the FWHM becomes smaller and the signal from the (112) orientation is the strongest as shown in figure 4.

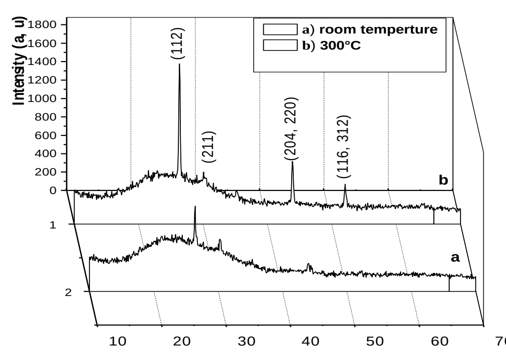


Figure 4: XRD 2□/□ scan of a $CuInS_2$ film grown on glass substrate after annealing

Figure 5 depicts the glancing incident x-ray diffraction (GIXRD) scans at incident angles of 0.2º, 0.5° and 1.5º of the (112) peak for the best layer (300°C). The set of GIXRD patterns reflect the uniformity of the film. The scattering volume decreases with decreasing incidence angle. The main feature in the patterns is therefore a decreasing intensity for smaller incidence angle, besides these, no significant changes and no additional peak are found in the scans.

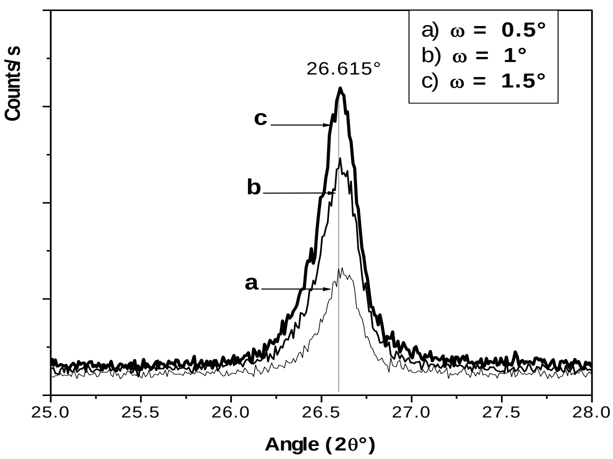


Figure 5: Grazing-Incidence X-Ray Diffraction (GIXRD) patterns of the (112) peak of the sample prepared by SEL method at Ts= 300°C.

The optical characteristics of the layers were obtained by means of transmittance measurements at room temperature. To estimate the energy gap Eg we have plotted $(\alpha h\nu)^2$ versus hν and extrapolated the linear part of the curves to an intercept on a photon energy axis, yielding the band gap of CIS layer crystals. Figure 6 shows the variation of band gaps with the substrate temperature onto glass. The figure depicts that values increase with increasing substrate temperature. The values obtained for $CuInSe_2$ films at room temperature (empty triangles) and T_S = 300°C (empty squares) are 0.98 and 1.01 eV, respectively, which is in good agreement with the reported range of values for $CuInSe_2$ [10, 11].

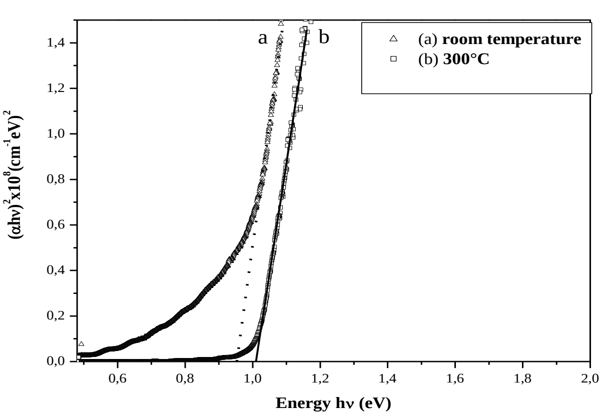


Figure 6: Plot of $(\alpha h\nu)^2$ vs incident photon energy hν of $CuInSe_2$ layers: (a) at room temperature and (b) at 300°C after annealing at 450°C.

3.2 Cu/In/Se/Se on Si (100) substrate

The X-ray diffraction pattern of the CIS sample prepared by the SEL method on Si (100) substrate is shown in figure 7. X-ray patterns were analysed by MAUD program [12], which is based on the Rietveld method [13]. The strongest peak is (112) followed by (204), (220), (312), (116) and with (101), (211), (105) and (301) characteristic peaks with lower intensity can be indexed on a basis of a tetragonal unit cell having lattice parameters listed in table I. These values are a little smaller than the reported lattice constants of a chalcopyrite-type CIS of JCPDS number 40 - 1487, a_c=0.5782(1) nm and c_c=1.1619(1) nm. As expected, the substrate temperature during evaporation critically influenced the structural properties of the thin film and showed that the annealing process reduced the FWHM value from 0.24 to 0.16° indicating a change in both film composition and microstructure. We remark that there is a striking difference between the XRD of non stoichiometric layers grown on Si (figure 7) and those grown on glass substrate (figure 4). Additionally, the XRD spectra observed from CIS on Si substrate is practical identical to those reported in [14] prepared with the same technique and without excess of Se.

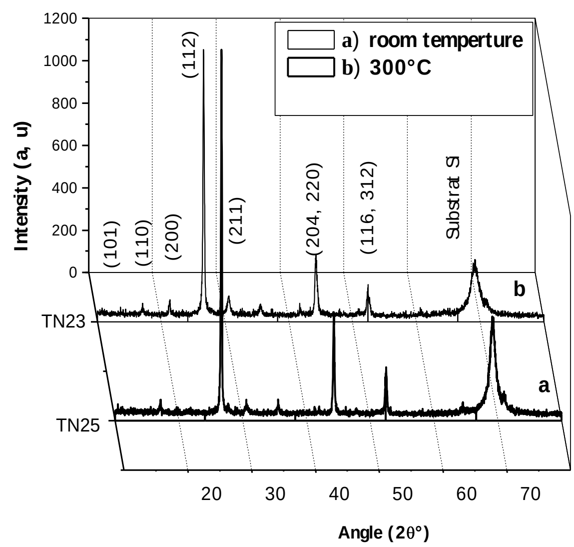


Figure 7: XRD 2□/□ scan of a $CuInSe_2$ epitaxial film grown on [100] Si Substrate.

Table I: Crystallographic parameters of CIS on Si (100) substrate from the Rietveld analysis (Maud program).

Sample	a(nm)	b(nm)	c/a	thickness (nm)	Structural formula	Grain size (nm)	Cu/In
Room temperature	0.57725 (6)	1.1621 (2)	2.01317	609 (580)	$Cu_{0.73(7)}In_{0.85(5)}Se_{2.34(7)}$	37.5 (8)	0.64
T_S=300°C	0.57770 (4)	1.1602 (1)	2.0083	946.8 (811)	$Cu_{0.80(4)}In_{0.85(3)}Se_{2.50(7)}$	78.5 (2)	0.91

IV. Conclusion

We have demonstrated in this work that the control of substrate's temperature Ts can be used to obtain $CuInSe_2$ thin films after annealing, produced by SEL technique, with suitable properties. The results indicate also that the CIS samples prepared by the SEL method on Si (100) substrate exhibit a good crystalline quality like their counterparts synthesized by the conventional methods. It has also shown, from the analysis of chemical composition, that SEL technique could be used to prepare $CuInSe_2$ thin films with controlling the non-stoichiometry of such compounds.

References

[1] U. Rau, W. Schock, Appl. Phys. A. Mater. Sci. Process. 69 (1999) 131.
[2] M.A. Contreras et al., Prog. Photovolt: Res. Appl. 13 (2005) 209.
[3] K.R. Ramanathan, M.A. Contreras, C.L. Perkins, S. Asher, F.S Hasoon, R. Noufi, Prog. Photovolt. Res. Appl. 11 (2003) 225.
[4] A. Ihlal, K. Bouabid, D. Soubane, M. Nya, O. Ait-Taleb-Ali, Y. Amira, A. Outzourhit and G. Nouet. Thin Solid Films, 515 (2007), 5852.
[5] K. Mitchel, In Soar Cells and their applications, Edited by L. D. Partain, Wiley, New York (1995).
[6] G. Neelkanth, M. Dhere, C. Lourenco and R.G. Dhere, Solar Sells, 13 (1984) 59.
[7]. N. Benslim, A. Maasmi, L. Mahdjoubi, and L. Gouskov, 11th European Photovoltaic Solar Energy Conference, Switzerland, Montreux, 12-16 0ctober (1992) 890.
[8] E. R. Don, R. Hill and G. J. Russell, Solar Cells 15, (1986) 131.
[9] W. N. Shafarman, J. Zhu, in Mat. Res. Soc. Symp. Proc., 668, H2. (2001) 3
[10] J.E. Jaffe, A. Zunger, Phys. Rev. B 29 (1984) 1882.
[11] S.B. Zhang, Su-Huai Wei, A. Zunger, H. Katayama-Yoshida, Phys. Rev. B 57 (1998) 9642.
[12] L. Lutterotti, MAUD CPD, Newsletter (IUCr) 24 (2000).
[13] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[14] L. Bechiri, M. Benabdeslem, N. Benslim, A. Djekoun, A. Otmani, L. Mahdjoubi, R. Madelon, P. Ruterana and G. Nouet, Catalysis Today 113 (2006) 226.