Turk J Phys
31 (2007) , 265 – 269.

Opto-Electrical Properties of Copper-Indium-Selenium Thin Films

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Received 05.05.2006

Abstract

Copper-Indium-Selenium (CIS) thin films have been characterised using various experimental techniques. These compounds are extensively used in solar cell technology as absorber layers due to their exciting characteristics.

Optical transmission measurements on different compositions of CIS films are observed and the absorption coefficient is determined. The Van der Pauw technique is used to divulge the electrical characteristics of these films. The electrical conductivity is found relatively high for the films annealed in vacuum but decreases for films synthesised optimally. It is observed that p-type films have higher conductivity than n-type films. The grain size, composition, structure and the spacing of the elements of CIS thin films are revealed by XRD. The reaction temperature of CIS formation is 270 °C in vacuum. These properties are of great significance in manufacturing solar cell devices.

Key Words: Solar cell devices, thin films.

1. Introduction

Copper-Indium-Selenium (CIS) is used in the solar cell industry in single crystal and polycrystalline forms. CIS single crystal homojunction and heterojunction solar cells have been used by different researchers but the polycrystalline heterojunction cells have been found to give greater efficiency [1, 2]. Heterojunction solar cells with a wide band gap window and a narrow band gap absorber have been under investigations due to their advantageous features. Elements, binary compounds as well as ternary compounds have been used in homojunction solar cells and as absorber or transmitter materials in heterojunction solar cells. Photovoltaic energy conversion is being used today for both space and terrestrial solar energy conversion [3, 4].

A CIS absorber layer less than 1 μm thick can absorb more than 90% of the photon energy above its optical band gap. CIS with a direct band gap of 1.04 eV and a high optical absorption coefficient greater than 10^5 cm^{-1} is well suited for solar cell absorber applications. CIS forms heterojunctions with materials such as ZnO, CdS and CdZnS. The maximum efficiencies achieved as yet are of 22.6% to 28.9% for CIS-based solar cells fabrication [5, 6].

The Stacked Elemental Layer (SEL) technique is characterized by the physical deposition of metallic layers on a substrate and the semiconducting absorber is then synthesized by thermal processing (up to about 500 °C). In this way, the chemical reaction pathways of the SEL-synthesis of the chalcopyrites can be determined. The subsystems of $CuInSe_2$ and $Cu(In,Ga)Se_2$, respectively, can be examined by dynamic scanning calorimetry, X-ray diffraction and in-situ conductivity measurements. The solar cells prepared from SEL technique and having $CuInSe_x$ as absorber material have shown efficiency up to 30.6% [7, 8]. $CuInSe_x$ polycrystalline thin films for solar cell devices were produced by Kavcar et al [9] on Corning 7059 glass substrates by vacuum evaporation at 5×10^{-7} torr by alternate elemental layer deposition followed by vacuum and air annealing. Omous et al [10] prepared $CuInSe_2$ thin films by alternate elemental layer deposition on substrates of Corning 7059 glass and on cheap microscope glass slides at ambient temperature by thermal evaporation under vacuum at 10^{-6} torr.

2. Experimental Details

SEL technique has been used to prepare thin films of CIS, at ambient temperatures on the glass substrates of dimensions 4 cm × 2 cm. The films are annealed at temperatures ranging from 200–375 °C for different time intervals in air and in vacuum. Cu, In and Se films with varying ratios of the contents are deposited and selenized. Film quality was improved by incorporating Se into the film and annealing in a Se ambient. Edwards 306 coating unit is used to deposit the materials at ambient temperature by thermal evaporation under vacuum at 10^{-6} torr. Once the base pressure is reduced, the coating unit is heated to a temperature near the melting point of the evaporant, i.e, from 200–375 °C for 5 to 10 minutes. All the samples have been annealed for 3 hours at temperature from 100–150 °C. In case of vacuum annealing, the samples are kept in vacuum chamber and the substrate temperature was raised to the required level. The percentage ratio of the CIS film components, the conduction type and the thickness after annealing the samples are given in Table 1.

Perkin-Elmer UV/Vis/NIR Lambda 9 Spectrometer has been used to measure optical absorption and transmission. The dual machine is designed for measurements of absorption and transmission of liquid and solid samples over the wavelength range from 1600 nm to 8 μm. The spectrometer has a double monochromator to select the wavelength of the probe beam but the transmitted light is detected directly. The system is controlled by a PC which automatically stores absorbance data to an output file.

The structure of CIS thin films has been determined by Philips θ-2θ diffractometer. In this diffractometer, the reflection technique and the Ni filtered Cu Kα radiation at 36 kV and 26 mA at a wavelength of 1.54 E has been used. The focussing Bragg-Brentano geometry with 1° divergent beam is employed because the absorption correction is relatively simple and independent of scattering angle for a flat thick sample. The CIS films have been electrically characterized by Van der Pauw technique, using two probe method. Two Ag contacts have been made by high-conductivity silver paint (Electrodag 915, UK). Copper leads have been attached to the contacts and the electrical conductivity has been measured by the standard dc method.

3. Results and Discussion

The electron-hole pairs created by the absorption of photons are encouraged to drift to the front and back of the solar cell. To enhance the drift velocity of the solar cell, the back of the cells were covered by a metallic contact that removes charges to the electric load. An anti-reflective coating has been applied on the top of the cell in order to absorb maximum light incident on it. A solar cell consists of a junction of two semiconductor materials and two electrical contacts on both sides. When the junction is exposed to light, the photons with energy smaller than the band gap make no contribution to the output of the cell. However, the photons of energy greater than the band gap are absorbed, raising the electrons in energy from the valence band to the conduction band, creating electron hole pairs. If the band gap is low, more photons will be absorbed causing a large number of electron-hole pairs to be formed [11, 12].

Table 1. The dependence of conduction type on $CuInSe_x$ ratios of CIS Films

Sample #	Atom (%)			Cu/ In	Conduction type	Thickness after annealing (Å)
	Cu	In	Se			
S1	32.74	18.44	48.82	1.805	p	900
S2	32.45	19.85	47.70	1.635	p	885
S3	31.89	21.52	46.59	1.482	p	810
S4	31.08	23.77	45.15	1.307	p	893
S5	27.47	24.63	47.90	1.115	p	900
S6	26.93	28.08	44.98	0.958	p	913
S7	25.95	22.66	51.39	1.145	p	786
S8	21.63	32.71	45.66	0.661	n	670
S9	19.72	31.21	49.07	0.632	n	550
S10	19.52	33.70	46.78	0.576	n	767
S11	18.52	35.17	46.31	0.527	n	580
S12	18.23	35.65	46.12	0.509	n	650

The transmission plots for the samples reacted in vacuum exhibited large values of transmission which continuously increased with rise in reaction temperature. The compositional dependence of absorption coefficient has been measured at two wavelengths (1350 and 2130 nm) in the near infrared (NIR) region and the results are shown in Figure 1. The shape of the solar spectrum is such that at a certain wavelength there are maximum number of photons available whilst none or very few at other wavelengths. The band gap of the material to be used as absorber in the fabrication of solar cells is thus to be matched with the spectrum. The optimum band gap of CIS films has been found 1.5 ± 0.2 eV, and the maximum light is absorbed. The absorption coefficient data for the CIS films is derived from transmission measurements with a Perkin-Elmer Lambda 9 Spectrophotometer on samples of 550–900 Å. It is observed that the absorption coefficient (α), in the NIR region varies in a systematic manner with the Cu/In ratio. This plot also shows that near-stochiometric films had the minimum Sub-Band Gap (SBG) absorption. It can further be seen that the SBG absorption increases with increasing or decreasing copper concentration beyond perfect stochiometry. However, as the Cu/In ratio becomes less than 0.6, the SBG decreases.

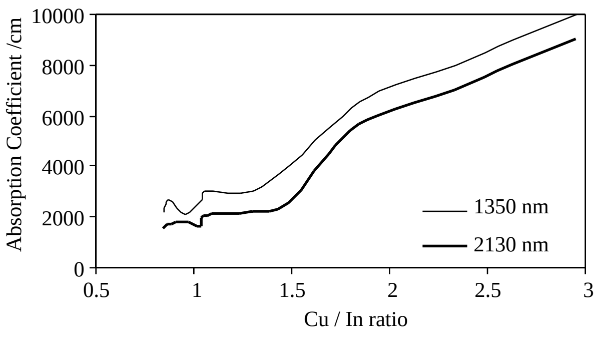

Figure 1. The dependence of the absorption coefficient, α, on Cu/In ratios of CIS films in the NIR region.

The presence of any imperfect phase of any kind in solar energy materials have many deleterious effects like reduction in the photoactive volume of the material, impediment of photon penetration, hindrance of carrier transport, etc. Therefore, care must be taken to choose the composition of CIS thin films with a view to utilize them as solar energy-absorbing materials [13]. The SBG absorption in CIS films is believed to be related to the presence of a secondary phase at grain boundaries. The transmission plots for each sample show that some samples reacted in vacuum exhibited large values of transmission; the reason probably being that the films peeled off during initial sintering/annealing step, resulting in very thin films, which showed high values of transmission. It is also observed that during vacuum annealing, the transmission value increased continuously with the rise in reaction temperature (reaction temperatures 150 °C, 200 °C, 250 °C and 300 °C, and reaction time of 5 minutes each). This is due to increased structural formation. For increased reaction duration at 300 °C, the transmission values started to decrease, therefore, it is evident that the reaction temperature for the CIS formation is 270 °C in vacuum.

It is evident from figure 2, that the formation of various types of defects, which give p- or n-type conductivities, depends on the Cu/In ratios. Figure 2 shows room temperature (≈300 K) electrical dc conductivities (σ) of different samples of CIS thin films having different Cu/In ratios. It is noted that (i) indium-rich films have n-type conductivities and near-stochiometric and copper-rich films have p-type conductivities; (ii) p-type films have higher conductivities than those of n-type films; and (iii) in each type of films, the conductivities increase with Cu/In ratios. Type of film conductivities is summarized in Table 1. It is observed that the electrical conductivities at 300 K of n-type and p-type films are 2.15×10^{-3} and 1.6×10^{-1} $(\Omega\ \mathrm{cm})^{-1}$, respectively, as Cu/In ratio varies between 0.509 and 1.805. Therefore, it is evident that p-type films have higher conductivities than n-type films. In fact, n-type films have higher mobilities but lower charge densities in contrast to the p-type films. However, the extent of the decrease of charge densities in p-type films is much greater than the increase of the mobilities in n-type films. Further observation from figure 2 shows that, for each type of films, either p- or n-type, the conductivities increase as Cu/In ratio increases. This may be explained as follows: as the Cu/In ratio increases, the charge-carrier concentrations increase almost exponentially while the mobilities decrease at an almost linear rate. Therefore, as the Cu/In ratio increases the hole-concentration increases and hence the conductivity increases.

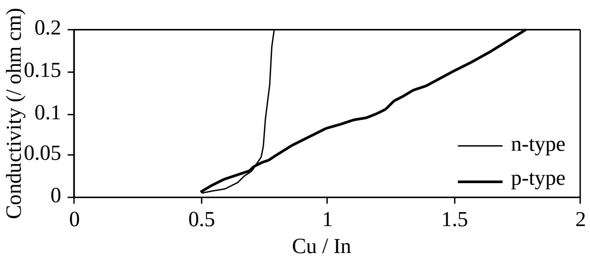

Figure 2. The conductivity at 300 K of Cu/In ratios of CIS films.

In the CIS films, crystal growth is enhanced with crystallites on the order of 3 μm compared to the crystallites size less than 0.4 μm produced by the other technique. XRD scans show that the structure of the CIS films prepared by the SEL technique is much improved compared to the other deposition techniques. Films deposited with a large Se content resulted in better quality than old SEL technique. Samples produced with no Se content had loosely packed crystallites, whereas those containing a small amount of Se tended to produce films with tightly packed grains. XRD analysis reveals that the samples contained a mixture of CuSe, InSe, $CuInSe_2$ and $CuSeO_4$ compounds. It is observed that, the samples reacted in vacuum at a temperature above 270 °C completely transform to the chalcopyrite $CuInSe_2$. Whereas, at temperatures below 270 °C there are a number of un-reacted indium peaks. This clearly leads us to the conclusion that the reaction temperature for CIS films is 270 °C. This behaviour is of great significance in manufacturing solar cell devices.

4. Conclusions

CIS thin films prepared by SEL technique are reacted in vacuum and air at ambient temperatures, followed by annealing. The absorption coefficient data for the CIS thin films is derived from transmission measurements using a Lambda 9 Spectrophotometer, with a sample of thickness 550–900 Å. The transmission plots for the samples reacted in vacuum exhibited large values of transmission and the transmission value increases continuously with the rise in reaction temperature. The absorption coefficient (α), in the NIR region varies in a systematic manner with the Cu/In ratio. The Van der Pauw technique reveals that in CIS films the p-type films have higher conductivities than n-type films at room temperature, as the ratio of the p-type is increased. For air annealed samples, the conductivity decreases with increase in reaction temperature while conductivity is high, when the samples are annealed in vacuum.

Philips θ-2θ diffractometer, using the reflection technique and the Ni filtered Cu Kα radiation has been used to characterise the structure of the CIS thin films. XRD scans confirmed the improvement in quality, structure and grain size for the samples prepared by the SEL technique. It has also been revealed that the reaction temperature for CIS films is 270 °C. These characteristics of CIS thin films suggest that, the stoichiometric or slightly copper-rich CIS films have optimum properties for their application in fabricating solar cells.

References

[1] H. M. Hubbard, *Science*, **2**, (1989), 297.

[2] S. F. Shaukat, K. J. McKinley, P. S. Flower, P. R. Hobson, J. M. Parker, *J. Non-Crystalline Solids*, **244**, (1999), 197.

[3] M. A. Green, *Solar Cells: Operating Principles, Technology and Systems Applications*, Prentice Hall, NJ, USA, 1982.

[4] A. J. Nelson, A. B. Swartzlander, J. R. Tuttle and R. Noufi, *J. Appl. Phys.*, **74**, (1993), 5757.

[5] A. J. Nelson, S. P. Frigo and R. Rosenberg, *J. Appl. Phys.*, **73**, (1993), 8561.

[6] J. R. Tuttle, M. Contreras, D. S. Albin and R. Noufi, *Proc. 22^{nd} IEEE Photovoltaics Specialists Conference*, Las Vegas, NV, USA, 1991.

[7] A. Knowles, H. Oumous, M. J. Carter and R. Hill, *Proc. 20^{th} IEEE Photovoltaic Specialists Conference*, Las Vegas, NV, USA, 1988.

[8] A. Knowles, H. Oumous, M. J. Carter and R. Hill, *Semicond. Sci. Technology*, **3**, (1988), 1143.

[9] N. Kavcar, M.J. Carter and R. Hill, *Solar Energy Materials and Solar Cells*, **27**, (1992), 13.

[10] H. Omous, A. Knowles, M.H. Badawi, M.J. Carter and R. Hill, *Proc. 9^{th} EC Photovoltaic Solar Energy Conference*, Freiburg, Germany, 1989.

[11] Y. Sudo, S. Endo and T. Irie, *Jpn. J. Appl. Phys.*, **32**, (1993), 1562.

[12] J. R. Tuttle, D. S. Albin and R. Noufi, *Solar Cells*, **30**, (1991), 21.

[13] J. R. Tuttle, D. S. Albin, J. P. Goral, R. Noufi, *Proceedings of the 21st IEEE Photovoltaic Specialists Conference*, vol. **1**, 21–25, Kissimimee, Florida, USA, (1990), 748.