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Opto-Electrical Characteristics of Polycrystalline Photovoltaic Materials

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Abstract: The optical and electrical properties of Copper-Indium-Selenium (CIS) thin films have been investigated using various experimental techniques. These compounds are extensively used in solar cell technology due to their exciting characteristics. CIS thin films have been grown onto glass substrates by a Stacked Element Layer (SEL) deposition technique in vacuum. 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 the films synthesised optimally. It is observed that p-type films have higher conductivity than n-type films. The reaction temperature of CIS formation is 250°C in vacuum. These properties are of great significance in manufacturing solar sell devices.

Key words: Solar cell materials, thin films

INTRODUCTION

Copper-Indium-Selenium (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 (Matsui *et al*., 2002; Brendel *et al*., 1997). Heterojunction solar cells with a wide band gap window and a narrow band gap absorber have been under investigation 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 (Lee and Joo, 1996; Chan and Chan, 2002). 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. A CIS absorber layer less than 1 μm thick can absorb more than 90% of the photon energy above its optical band gap. 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 (Jeurgens *et al*., 2002; Widenborg and Aberle, 2002).

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 550°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. The solar cells prepared from SEL technique and having $CuInSe_x$ as absorber material have shown efficiency up to 30.6% (Vetterl *et al*., 2002; Klein *et al*., 2002). $CuInSe_x$ polycrystalline thin films for solar cell devices were produced by Unold *et al.* (2000) on Corning 7059 glass substrates by vacuum evaporation at 5×10^{-7} torr by alternate elemental layer deposition followed by vacuum and air annealing. Shaukat *et al*. (1999) 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.

MATERIALS AND METHODS

Thin films of CIS are prepared at ambient temperatures by SEL technique on the glass substrates

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Table 1: The dependence of conduction type on $CuInSe_2$ ratios of CIS films

Sample No.	Atom (%) Cu	In	Se	Cu/In	Conduction type	Thickness after annealing (Å)
S1	18.19	35.76	46.05	0.509	n	650
S2	18.52	35.17	46.31	0.527	n	580
S3	19.52	33.70	46.78	0.576	n	500
S4	19.72	31.21	49.07	0.632	n	550
S5	21.63	32.71	45.66	0.661	n	600
S6	25.95	22.66	51.39	1.145	p	700
S7	26.93	28.08	44.98	0.958	p	913
S8	27.47	24.63	47.90	1.115	p	900
S9	31.08	23.77	45.15	1.307	p	893
S10	31.89	21.52	46.59	1.482	p	810
S11	32.45	19.85	47.70	1.635	p	630
S12	32.95	18.25	48.80	1.805	p	1000

of dimensions 3×1 cm. The films are annealed at temperatures ranging from 150-350°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 150-350°C for 5 to 10 min. All the samples have been annealed for 3 h 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.

Optical absorption and transmission has been recorded using the Perkin-Elmer UV/Vis/NIR Lambda 9 Spectrometer. 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 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.

RESULTS AND DISCUSSION

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 (Dalal and Erickson, 2000; Pangal *et al*., 2000). The electron-hole pairs created by the absorption of photons are thus 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 examined here in this research work has been 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.

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 transmission data in terms of absorbance is represented as:

$$\text{Transmission} = 10^{-\text{Absorption}} \times 100\%$$

The absorption coefficient (α) data for the CIS films is derived from transmission measurements with a Perkin-Elmer Lambda 9 Spectrophotometer on samples of 500-1000 Å, using the formula:

$$\text{Absorption Coefficient } (\alpha) = \frac{\text{OD} \times 2.303}{\text{Thickness of sample (mm)}}$$

where, OD-is the optical density [$\log_{10}(I_0/I)$] and 2.303-is the conversion factor into $\log_{10}$. The transmission plots for the samples reacted in vacuum exhibited large values of transmission. The transmission value increases continuously with the rise in reaction temperature. The compositional dependence of absorption coefficient has been measured at two wavelengths (1770 and 2550 nm) in the near infrared (NIR) region and the results are shown in Fig. 1. It is observed that the absorption coefficient (α), in the NIR region varies in a systematic manner with the Cu/In ratio.

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,

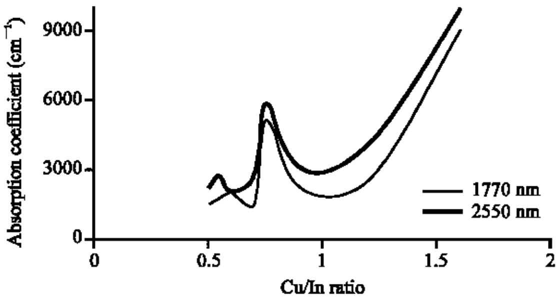

Fig. 1: The dependence of the absorption coefficient, α, on Cu/In ratios of CIS films in the NIR region

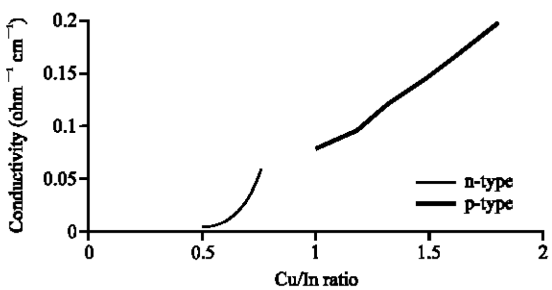

Fig. 2: The conductivity (at 300 K) of Cu/In ratios of CIS films

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 (Wenham and Nast, 2000).

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, 200, 250 and 300°C and reaction time of 5 min 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 250°C in vacuum.

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. It is evident from Fig. 2, that the formation of various types of defects, which give p-or n-type conductivities, depends on the Cu/In ratios. The type of conductivities of the films have been 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 Fig. 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.

The structure of CIS films prepared by the SEL technique was much improved as compared to the other deposition techniques. In these films, crystal growth was enhanced with crystallites of the order of 2 μm size as compared to the crystallites size less than 0.5 μm produced by the other technique. 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. This behaviour is of great significance in manufacturing the solar cell devices.

CONCLUSIONS

Thin films of CIS were prepared by SEL technique using resistive heating method. The films were then reacted in vacuum and air at ambient temperatures followed by annealing. The absorption coefficient data for the CIS thin films was derived from transmission measurements using Lambda 9 Spectrophotometer, with a sample of thickness 500-1000 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 varied in a systematic manner with the Cu/In ratio.

The Van der Pauw technique revealed 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 was increased. For air annealed samples, the conductivity decreases with increase in reaction temperature while conductivity was found high, when the samples were annealed in vacuum. 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

Brendel, R. and R.B. Bergmann *et al*., 1997. Ultrathin crystalline silicon solar cells of glass substrate. Applied Phys. Lett., 70: 390-392.

Chan, V.W.C. and P.C.H. Chan, 2002. An empirical model to determine the grain size of metal induced lateral crystallized film. IEEE Trans. Electron Devices, 49: 1399-1404.

Dalal, V.L. and K. Erickson, 2000. Microcrystalline Si solar cells. Mater. Res. Soc. Symp. Proc., pp: 609.

Jeurgens, L.P.H. and W.G. Sloof *et al*., 2002. Growth kinetics and mechanisms of aluminium-oxide films formed by thermal oxidation of aluminium. J. Applied Phys., 92: 1649-1656.

Klein, S. and F. Finger *et al*., 2002. High efficiency thin film solar cells with intrinsic microcrystalline Si prepared by hot wire CVD. Mater. Res. Soc. Symp. Proc., 715: 26-32.

Lee, S.W. and S.K. Joo, 1996. Low temperature poly-Si thin transistor fabrication by metal-induced lateral crystallization. IEEE Electron Device Lett., 17: 160-162.

Matsui, T. and M. Tsukiji *et al*., 2002. Influence of substrate texture on microstructure and photovoltaic performances of thin polycrystalline solar cells. J. Non-Cryst. Solids, 299-302: 1152-1156.

Pangal, K. and J.C. Sturm *et al*., 2000. p-channel thin transistor and complementary metal-oxide-silicon inverter made of microcrystalline silicon directly deposited at 320°C. J. Non-Cryst. Solids, 266-269: 1274-1278.

Shaukat, S.F. and K.J. McKinley *et al*., 1999. Optical and physical characteristics of HBLAN fluoride glasses containing cerium. J. Non-Cryst. Solids, 244: 197-204.

Unold, T. and R. Bruggemann *et al*., 2000. Anisotropy in the transport of microcrystalline silicon. J. Non-Crystl Solids, 266-269: 325-330.

Vetterl, O. and A. Brob *et al*., 2002. Changes in electric and optical properties of intrinsic microcrystalline silicon upon variation of the structural composition. J. Non-Cryst. Solids, 299-302: 772-777.

Wenham, S.R. and O. Nast, 2000. Elucidation of the layer exchange mechanism in the formation of polycrystalline silicon by aluminium induced crystallization. J. Applied Phys., 88: 124-132.

Widenborg, P.I. and A.G. Aberle, 2002. Surface morphology of poly-Si films made by aluminium induced crystallisation on glass substrates. J. Cryst. Growth, 242: 270-282.