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Preparation and Study of the Structural, Optical and Electrical Properties of Cu(In,Ga)Se_2 Thin Films

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Abstract

Thin film samples of Cu(In,Ga)Se_2 (CIGS) were prepared at room temperature by physical vapor deposition (PVD) technique using resistive heating method onto soda lime glass substrates. Deposition conditions were same for all the samples. The prepared samples were annealed in vacuum at temperature of 200 °C for 5, 10, 15, 30 and 60 minutes and were characterized structurally, optically and electrically. The structural analysis indicate the partial formation of quaternary CIGS compounds for the samples which were annealed in vacuum at 200 °C for 30 and 60 minutes. XRD analysis indicate that there is a continuous growth and improvement in the structural formation of ternary ($CuInSe_2$ and $CuGaSe_2$) and quaternary CIGS compounds. The thin films after vacuum annealing show low values of transmission and suitable absorption in the wavelength range of interest. The band gap of CIGS absorber layer is estimated to be 1.32 eV by extrapolating the plot of $(\alpha h\upsilon)^2$ as a function of $h\upsilon$. The electrical resistivity of all the samples are calculated by using Van der Pauw technique and found to decrease with increase in annealing time. The resistivity of the samples is small; therefore the prepared samples can be used as an absorber layer in the fabrication of thin film solar cells.

Key Words: CIGS, thin films, absorber material, solar cell, optical properties, band gap, electrical properties.

1. Introduction

Polycrystalline chalcopyrite thin film solar cells based on Cu(In,Ga)Se_2 (CIGS) are regarded as promising candidates for thin film solar cell modules. CIGS compounds have a high potential for solar energy conversion because of their direct band gap and high absorption coefficient [1–2]. Devices based on absorber layers of these materials have shown efficiencies in excess of 17% [3–4] and have shown virtually no evidence of degradation with time [5]. However, a scalable, reproducible and low cost process for the preparation of high quality Cu(In,Ga)Se_2 has not been clearly established. The most successful deposition technologies thus for are co-evaporation of elements [6–7] and the selenization of elemental layers to form Cu(In,Ga)Se_2 [8]. In general, co-evaporation is difficult to control due to variations in the elemental fluxes resulting in lack of stoichiometric reproducibility. Selenization in H_2Se is also problematic due to the toxicity of materials used and non-uniformity of the layers produces. A number of deposition technologies for Cu(In,Ga)Se_2 have also been investigated, such as the laser annealing of elemental precursors [9] and flash evaporation [10]. However, neither of these processes were completely successful due to lack of good adhesion and sufficient electronic quality. It has also been demonstrated [11–12] that reasonable results can be obtained by the rapid thermal processing of electron beam evaporated and/or sputtered Ga/Cu/In/Se stacked elemental layers.

$Cu(In,Ga)Se_2$ based solar cells with higher efficiencies were realized by only using soda lime glass as substrate, in which sodium species are contained. Two reasons may be proposed to explain this observation: first, soda lime glass shows the excellent matching of its thermal expansion coefficient with that of $Cu(In,Ga)Se_2$ compared to other glasses such as corning 7059 and quartz glasses; and second, the sodium atom diffusing from the substrate improves grain growth and electrical property of thin films. On the later point, several reports have been published and the effects of sodium have been discussed [13–14].

In this study, device quality $Cu(In,Ga)Se_2$ absorber thin films are prepared by a relatively simple, fast and scalable four-stage technique. In this approach, precursor elements (Cu, In, Ga and Se) are thermally evaporated, each from separate source onto glass substrates in vacuum atmosphere and characterize structurally, optically and electrically for solar cell applications.

2. Experimental Detail

High purity (99.9999%) Cu, In, Ga and Se in appropriate proportions were weighed to prepare $Cu(In,Ga)Se_2$ (CIGS) thin films. CIGS thin films were prepared and characterized in the Centre for Solid State Physics, University of the Punjab, Lahore-Pakistan. CIGS thin films of thickness 0.15 μm are grown by physical vapor deposition (PVD) of the constituent elements under a vacuum of 10^{-6} Torr using an Edward 306 coating unit onto $1'' \times 3'' \times 1/20''$ soda lime silica (SLS) glass substrate. Single layer of the constituent elements of $Cu(In,Ga)Se_2$ were grown by resistive heating method in the sequence Cu-Se-Ga-In. Copper was evaporated from tungsten spiral while selenium, gallium and indium were evaporated from tantalum boats of sizes 1.7×1.3×0.5 cm, 1.5×1.3×0.5 cm and 1.7×1.5×0.5 cm, respectively. During evaporation the pressure in the chamber was maintained of the order of 10^{-6} Torr. Before deposition, the glass substrates were cleaned with Isopropyl alchol (IPA) and were dipped in a beaker containing acetone. The beaker was then placed in Kerry ultrasonic apparatus for at least 15 minutes to avoid contamination. Films were deposited on a pre-cleaned glass substrate at room temperature. Five samples were prepared under the same conditions. These samples were then annealed in vacuum at 200 °C for different time intervals (sample 1 for 5 min, sample 2 for 10 min, sample 3 for 15 min, sample 4 for 30 min and sample 5 for 60 min). The annealing was carried out in a 12 inch 306 Edwards coating unit. The thin film samples of CIGS were then characterized structurally, optically and electrically.

The X-ray diffraction (XRD) patterns were taken using a Rigaku Model XRD-D/MAX-IIA diffractometer operating at 35 kV and 25 mA. The experimental set up was: Cu K_α ($\lambda = 1.5418$ Å) radiation / Ni filter / 3 mm slit / primary collimator / 2 mm slit / sample / 4 mm slit / secondary collimator / 0.1 mm slit/ scintillation counter as detector. The diffractometer was calibrated using a standard Si powder sample. The samples were scanned with step width of 0.02° and preset time was 0.4 sec.

The optical properties were studied by taking the optical absorption and transmission plots. The optical absorption and transmission data were obtained using Shimadzu UV-240 double beam spectrophotometer [15], which automatically records the absorption and percentage transmission at different wavelengths. The measurements were carried out in wavelengths in the range 300 to 900 nm with 10 nm steps.

For measurement of electrical resistivity, Van der Pauw [16] technique was used. The CIGS samples were cut in square shape with the help of a diamond point. Then the ends of thin copper wire were cleaned with sand paper and connected at four corners of the sample with silver conducting paint. These contacts were sufficiently small and at the circumference of the sample. A current of 6.2 nA was applied through the contacts 1 and 3, and the voltage V_{24} was measured across contacts 2 and 4. The resistance $R_{13,24}$ was calculated by using the relation

$$R_{13,24} = \frac{V_{24}}{I_{13}}.$$

Similarly, a current of 6.2 nA was applied through contacts 2 and 4, while the voltage V_{13} was measured across points 1 and 3. The resistance $R_{24,13}$ was calculated from the relation

$$R_{24,13} = \frac{V_{13}}{I_{24}}.$$

The resistivity of the samples were calculated by using the relation [16].

$$\rho = \left(\frac{\pi t}{\ln 2}\right)\left(\frac{R_{13,24} + R_{24,13}}{2}\right) \times f,$$

where f is the correction factor and is equal to 1 when $R_{13,24} = R_{24,13}$; and t is the thickness of the CIGS thin film samples measured by Varians Å-scope using the relation [17].

$$t = \left(\frac{\text{Fringe Offset}}{\text{Fringe Spacing}}\right)\left(\frac{\lambda}{2}\right),$$

where $\lambda = 5892$ Å is the wavelength of the incident light.

3. Results and Discussion

3.1. Structural characterization

All annealed $Cu(In,Ga)Se_2$ (CIGS) thin film samples were analyzed structurally for the identification of different phases. This was done by taking the XRD patterns by using the XRD-D/MAX-II X-ray diffractometer. The XRD patterns of all CIGS samples are shown in Figure 1.

The reflecting planes and the corresponding phases of CIGS are indicated in these patterns. It is obvious from these patterns that the samples contained a mixture of CuSe, $CuSe_2$, Cu_2Se Cu_3Se_2, $CuGa_2$, Cu_9Ga_4, InSe, In_2Se_3,In_6Se_7, GaSe, Ga_2Se_3, $CuInSe_2$, $CuGaSe_2$ and CIGS. Sample 4, which was annealed at 200 °C for 30 minutes, exhibits only one peak corresponding to $CuInSe_2$, one peak corresponding to $CuGaSe_2$ and two peaks corresponding to $CuInGaSe_2$; while annealed sample 5 at 200 °C for 60 minutes exhibit two peaks corresponding to $CuInSe_2$ and $CuGaSe_2$ phase and two peaks corresponding CIGS phase. XRD analysis indicates that the reaction temperature of CIGS is greater than 200 °C. It is also observed from the XRD patterns that the samples annealed for longer duration at 200 °C showed continuous rise in intensity of the peaks. Intensity as a function of reaction time is shown in Figure 2, indicating continuous growth and improved structural formation of ternary ($CuInSe_2$ and $CuGaSe_2$) and quaternary CIGS compounds.

3.2. Optical characterization

All CIGS thin film samples were optically characterized by obtaining their absorption and transmission plots. The absorption and transmission plots for all the samples are shown in Figure 3 and Figure 4. The absorption edge could not be obtained in the absorption plots because the wavelength range of the Spectrophotometer used is from 190 nm to 900 nm. From the absorption and transmission plots it can be observed that as the samples are annealed for longer duration at temperature of 200 °C, the absorption increases and transmission decreases as can be seen from Figure 3 and Figure 4.

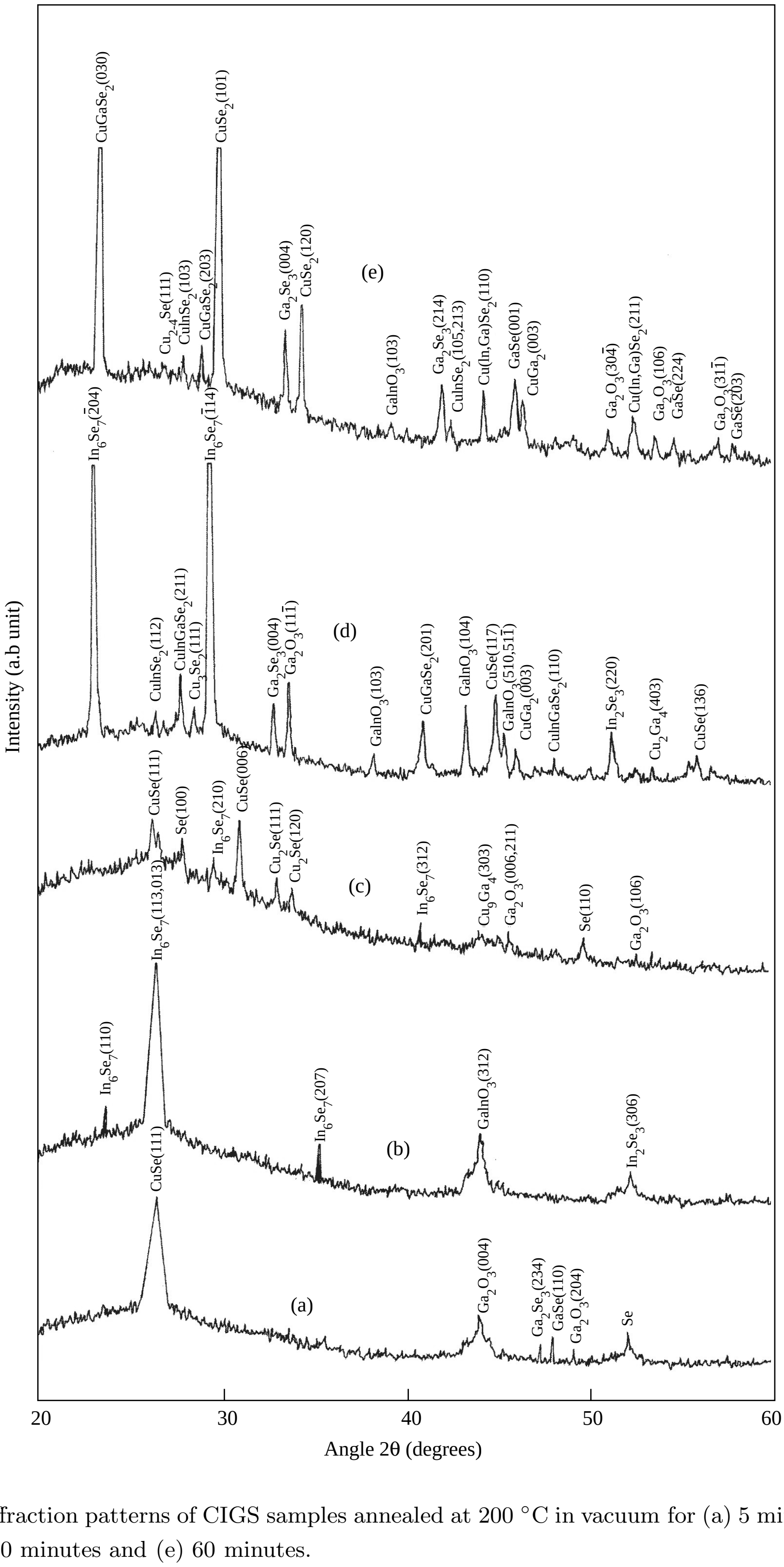

Figure 1. X-ray diffraction patterns of CIGS samples annealed at 200 °C in vacuum for (a) 5 minutes (b) 10 minutes (c) 15 minutes (d) 30 minutes and (e) 60 minutes.

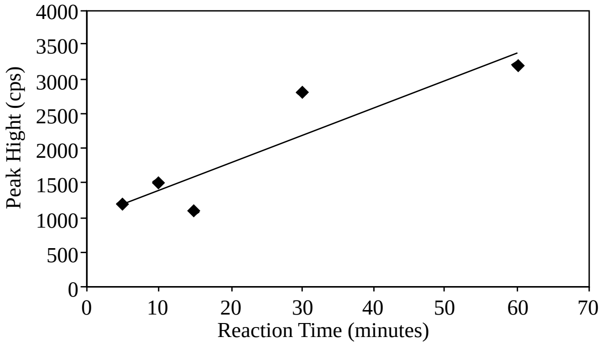

Figure 2. Dependence of peak intensity at reaction time for the CIGS samples annealed at 200 °C for different time intervals.

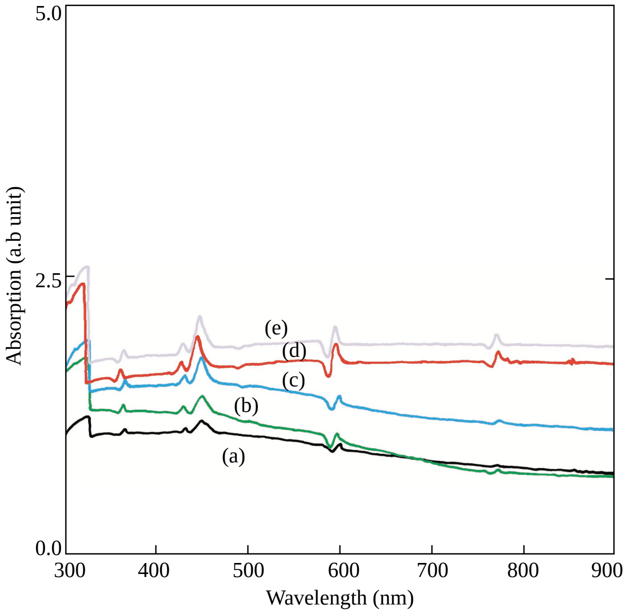

Figure 3. Absorption plots of CIGS samples annealed at 200 °C in vacuum for (a) 5 minutes (b) 10 minutes (c) 15 minutes (d) 30 minutes and (e) 60 minutes.

The dependence of absorption coefficient 'α' (in the region of absorption), on the wavelength can be used to determine the band gap. In the absorption process the photon of known energy excites an electron from lower to higher energy state. As CIGS is a direct band gap semiconductor, for direct transition, the absorption coefficient α is given by the following relation, obtained by Mott and Davis [18]:

$$(\alpha h\nu)^2 = A\left(\alpha h\nu - E_g\right)$$

Here, A is constant and E_g is the band gap energy. The usual method for determination of E_g involves plotting a graph of $(\alpha h\upsilon)^2$ as a function of photon energy $h\upsilon$ as shown in Figure 5. The linear straight line is clearly observed with an intercept on hυ axis, corresponding to the approximate value of 1.32 eV, which corresponds to the band gap of the prepared CIGS sample, which is annealed at 200 °C for 60 minutes.

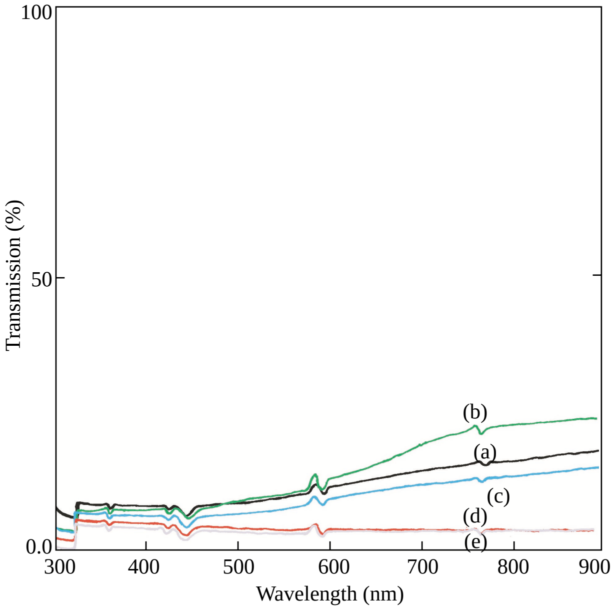

Figure 4. Transmission plots of CIGS samples annealed at 200 °C in vacuum for (a) 5 minutes (b) 10 minutes (c) 15 minutes (d) 30 minutes and (e) 60 minutes.

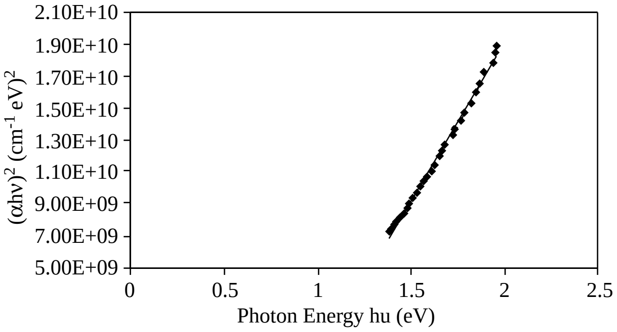

Figure 5. $(\alpha hv)^2$ versus $h\nu$ plot of selected CIGS sample.

3.3. Electrical characterization

In the electrical characterization of prepared samples, the electrical resistivity of the all the samples are calculated by using Van der Pauw technique. Figure 6 shows electrical resistivity as function of reaction time, from which it is clear that the sample resistivity decreases with increasing annealing time.

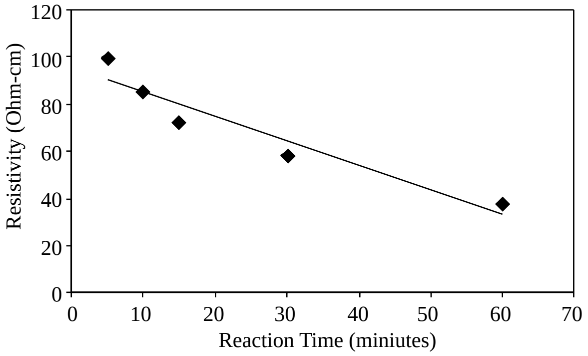

Figure 6. Dependence of electrical resistivity on the reaction time (annealing time).

4. Conclusions

CIGS is a I-III-VI$_2$ quaternary semiconductor compound whose band gap match with the solar spectrum and is a promising candidate for an absorber layer. Addition of small amount of gallium into CuInSe$_2$ increases its band gap, absorption and hence efficiency of the device. In this research work, thin film samples of Cu(In,Ga)Se$_2$ (CIGS) were prepared at room temperature by physical vapor deposition (PVD) technique using resistive heating method onto soda lime glass substrates. Deposition conditions were same for all the samples. The prepared samples were annealed in vacuum at temperature of 200 °C for 5, 10, 15, 30 and 60 minutes and were characterized structurally, optically and electrically. The structural analysis indicates the partial formation of quaternary CIGS compounds for the samples which were annealed in vacuum at 200 °C for 30 and 60 minutes. XRD analysis indicates that there is continuous growth and improvement in the structural formation of ternary (CuInSe$_2$ and CuGaSe$_2$) and quaternary CIGS compounds. The thin films after vacuum annealing show low values of transmission and suitable absorption in the wavelength range of interest. The band gap of CIGS absorber layer is estimated to be 1.32 eV by the extrapolation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ plot. The electrical resistivity of all the samples are calculated by using Van der Pauw technique and found to decrease with increase in annealing time. The resistivity of the samples is small; therefore the prepared samples can be used as an absorber layer in the fabrication of thin film solar cells.

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References

[1] T. Tanaka, Y. Demizu, A. Yoshida, *J. Appl. Phys.,* **81**, (1997), 7619.

[2] D. Haneman, *Crit. Rev. Solid State Mater. Sci.,* **14**, (1988), 377.

[3] J. Hedstrom, H. Ohlsen, M. Bodegard, A. Kylner, L. Stolt, D. Hariskos, M. Ruckh and H. W. Schock, *Proc. 23rd IEEE Photovoltaic Specialists Conf.,* Louisville (1993), p. 364.

[4] K. Zweibel, H. S. Ullal and B. von Roedern, *Proc. 25th IEEE Photovoltaic Specialists Conf.,* Washington (1996), p. 745.

[5] D. Tarrant, R. Gay, J. Hummel, C. Jensen and Al Ramos, *Sol. Cells,* **30**, (1991), 549.

[6] R. A. Mickelsen and W. S. Chen, Proc. 15th *IEEE Photovoltaic Specialists Conf.,* Orlando, (1981) p. 800.

[7] B. Dimmler, E. Gross, R. Menner, M. Powwalla, D. Hariskos, M. Ruckh, U. Ruhle, H. W. Schock, *Proc. 25th IEEE Photovoltaic Specialists Conf.,* Washington, (1996), p. 757.

[8] C. Fredric, R. Gay, D. Tarrant and D. Willet, *Proc. 23rd IEEE Photovoltaic Specialists Conf.,* Louisville, (1993), p. 437.

[9] L. D. Laude, M. C. Joliet and C. Antorniadis, *Solar Cells.,* **16**, (1986), 199.

[10] N. Benslim, A. Maasmi, L. Mahdjoubi and L. Gauskov, *Proc. 11th EC Photovoltaic Solar Energy Conf.,* Montreux, (1992), p. 890.

[11] F. Karg, V. Probst, H. Harms, J. Rimmasch, W.Riedl, J. Kotschy, J. Holz, R. Teichler, O. Eibl, A. Mittwalsky and A. Kiendl, *Proc. 23rd IEEE Photovoltaic Specialists Conf.,* Louisville (1993), p. 441.

[12] M. Bodegard and L. Stolt, *Proc. 11th EC Photovoltaic Solar Energy Conf.,* Montreux, (1992), p. 878.

[13] C. Heske, R. Fink, E. Umbach, W. Riedl and F. Karg, *Appl. Phys. Lett.,* **68**, (1996), 3431.

[14] M. Ruckh, D. Schmid, M. Kaiser, R. Schaffler, T. Walter and H. W. Schock, *Proceedings of the Ist World Conference on Photovoltaic Energy Conversion* (IEEE, New York, 1995), p. 156.

[15] Instruction Manual, Shimadzu UV-240, Spectrophotometer.

[16] J. Van der Pauw, *Phillips Research Report.,* **1**, (1958), 13.

[17] O. Wiener, *Wied Ann.,* **31**, (1887), 629.

[18] N. F. Mott and E. A. Davis, *Electronic Process in Non-crystalline Materials*, (Clarendon Press, Oxford, 1979).