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Effects of H^+ Ion Implantation and Annealing on the Properties of $CuIn_{0.75}Ga_{0.25}Se_2$ Thin Films

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In this paper the effects of post-deposition annealing followed by hydrogen ion-implantation on the properties of $CuIn_{0.75}Ga_{0.25}Se_2$ thin films have been investigated. The samples were grown by flash evaporation onto glass substrates heated at temperature between room temperature and 200 °C. Selected samples were subsequently processed under several sets of conditions, including vacuum, selenium, inert (argon) and forming gas (a 9:1 mixture of N_2:H_2) followed by hydrogen ion-implantation. A high-resolution near-infrared photoacoustic spectrometer (PAS) of the gas-microphone type was used for room temperature analysis of non-radiative defect levels in the as-grown, annealed and hydrogen implanted thin films. The absorption coefficient has been derived from the PA spectra to determine the gap energy and to establish the activation energies for several defect-related energy levels. The changes observed in the PA spectra following annealing and ion-implantation has been directly correlated with the compositional and structural properties of the samples.

Keywords Solar Cells, Copper alloys, Thin Films, Heat Treatment, Spectroscopy, Electrical Conductivity

1. Introduction

The potential application of $CuInSe_2$ (CIS) and $CuIn_xGa_{1-x}Se_2$ (CIGS) semiconductor compound in the development of high efficiency photovoltaic devices for both space and terrestrial applications (Ref 1) has long been recognised. Thin film heterojunctions based on absorber layers of these materials have demonstrated efficiencies in excess of 19% (Ref 2). Studies on CIGS thin films are more attractive as this system allows tailoring of the band gap and other material properties (Ref 3). As x in CIGS is reduced from 1 to 0 the band gap increases approximately linearly (Ref 4) from 1.02 to 1.68 eV. By choosing an appropriate value of ‚x' along with a suitable window layer, this material can be matched to the solar spectrum where the photovoltaic conversion efficiency has a maximum value (Ref 3). The composition $CuIn_{0.75}Ga_{0.25}Se_2$ having a band gap of about 1.20 eV presents a useful compromise between the optimum band gap of 1.5 eV and ease of film preparation (Ref 3).

Although, thin film solar cells based on CIS/CIGS absorber layers have realized higher efficiencies, there is a fundamental lack of understanding the origin of the complex intrinsic defect states. Many of the physical properties of CIGS are dominated by various types of electrically active intrinsic defects associated with deviations from the ideal stoichiometry of the compound (Ref 5). Of particular importance are the deep states which act as trapping centres for minority charge carriers and limit the ultimate efficiency of devices. The efficiency of the device can be enhanced by reducing the defect population either by carefully controlling the deposition parameters of thin film process or by using a post-deposition treatment to alter the film properties. The doping of semiconductors to alter their electrical characteristics is an alternative process, which is normally achieved by adding small amount of impurities to the semiconductor using an appropriate method. One of the most widely used methods is that of ion-implantation (Ref 6). Following ion-implantation, high temperature annealing is necessary to activate the dopants and remove surface damage introduced by the ions entering the crystal lattice.

This paper reports a study of the effect of annealing and ion implantation on the properties of flash-evaporated CIGS thin films. The structural, compositional, optical and electrical information was obtained using a range of analytical techniques. The changes observed in the photoacoustic spectra following annealing and ion implantation were directly correlated with the compositional and structural properties of thin film samples.

2. Experimental Apparatus

Thin $CuIn_{0.75}Ga_{0.25}Se_2$ films were deposited by the flash evaporation technique onto glass substrate, the temperature of which was varied between room temperature and 200 °C. Various annealing regimes were employed to investigate their effect on the structural, compositional and electro-optical properties of the as-grown CIGS thin films. Selected samples

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were heat treated in vacuum, selenium, inert and forming gas atmospheres. The influence of different times and temperatures in the range 200-400 °C was also investigated. Two stage annealing was then developed including selenium followed by an inert and selenium followed by forming gas ambient.

The ion-separator at the University of Salford was used to implant H^+ ions, at room temperature, into the processed/annealed CIGS thin film samples with different energies and doses at a current density of 2-5 μA/cm^2. The composition of the as-grown, annealed and implanted samples was determined by Energy Dispersive Analysis with X-ray (EDAX). These results were cross-examined using X-Ray Fluorescence (XRF) and Rutherford Backscattering Spectroscopy (RBS) techniques. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were used to ascertain the structural properties. The electrical parameters, including the resistivity and conductivity type were determined by using the four-point and hot-point probe techniques respectively.

The improvements in the structural and compositional properties followed by post-deposition annealing and implantation were confirmed utilizing non-destructive photoacoustic spectrometer (PAS). The gas-microphone type PAS is described elsewhere (Ref 7) and only a brief description is given here. A 300 W Xenon short-arc lamp was used as the radiation source. The light beam after being modulated by a servo-controlled mechanical chopper was dispersed through f/4 Spex Minimate monochromator. Modulated light was thereafter directed by an f/0.7 off-axis elliptical mirror onto a specimen placed inside the photoacoustic cell. The cell made of stainless steel was designed to give a non-resonant cavity configuration. A Knowles Electronics BT 1753 microphone was used as the acoustic detector, the output of which was phase-sensitively detected by using a lock-in-amplifier. The final output was read by a personal computer which was also configured to control the monochromator. The spectra were corrected for the spectral distribution of the optical system, the microphone and the cell by normalizing the response of the specimen to that of a fine powder of carbon black. All the spectra were recorded at room temperature using a modulating frequency of 112 Hz.

3. Experimental Results and Discussion

All of the as-grown CIGS films deposited were found to be uniform, smooth, strongly adherent to the substrate surface and free from pinholes. XRD revealed a very strong ⟨112⟩ preferred orientation in the as-grown CIGS thin films deposited for the range of substrate temperature used. However, this peak was broader and less intense than that from the starting material. Contrary to the reported work, amorphous films were not observed even when deposited at room temperature and only crystalline films with a strong preferred orientation of ⟨112⟩ were seen. EDAX analysis indicated a slight excess of indium and a small deficiency of selenium. The percentage of copper and gallium were found to be very close to that of the starting pre-reacted material. These results of film composition were in good agreement to those obtained from XRF and RBS techniques (Ref 8). The resistivity of as-grown and processed films was in the range of 10^{-1}-10^7 Ωcm.

Figure 1 shows normalized photoacoustic spectra of CIGS thin film sample annealed under maximum selenium vapour pressure at 300 °C for 2 h followed by an anneal under forming gas ambient at 200, 300 and 400 °C each for half an hour. It can be seen that the annealing has affected the spectra both near the fundamental band edge and in the tail. However, the changes are more significant in the photon energy range from 0.75 to 1.00 eV where deeper defect related levels (E_1-E_5) were observed. In addition, a new shallow level at approximately 1.10 eV appeared which consistently raised the minimum level of the photoacoustic signal in the lower photon energy range. Otherwise, the position of the five major peaks (E_1-E_5), also observed in the as-grown films, was approximately the same. A number of new defect levels between 0.94 and 1.02 eV gradually appeared with increased annealing temperature. An annealing temperature of 400 °C showed the worst photoacoustic spectrum in that an increased defect levels intensity and population is evident. This could be due to the effect of high annealing temperature causing a thermal stress at the surface and or the interface between film and substrate.

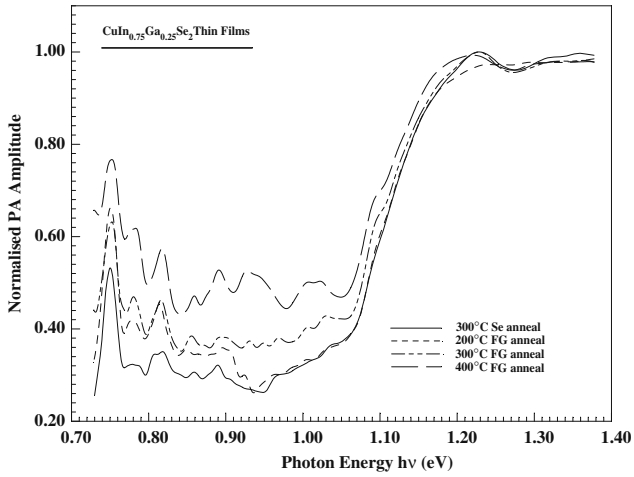

Fig. 1 Normalized photoacoustic spectra of representative polycrystalline CIGS thin films annealed under selenium and forming gas ambient at different temperatures

The effect of the inert atmosphere (argon) anneal at temperatures in the range of 200-400 °C on the photoacoustic spectra is shown in Fig. 2. It can be seen that at annealing temperatures up to 300 °C there is hardly any change in the spectra. However, at 400 °C there is a significant change in the photoacoustic spectral response. Once again a new shallow level at approximately 1.10 eV is mainly responsible for the increased minimum level of the absorption curve. In addition, a number of new defect levels are introduced in the photon energy range $h\nu < 1.05$ eV. The position of the original peaks (E_1-E_5) within the experimental error of ±5 meV is approximately the same. Some of the peaks are resolved into two separate peaks and some are joined to show the combined effect. For example, the defect level represented by peak label E_2 is gradually resolved into two peaks and the E_3 is now combined with its nearest neighbour, producing a single resolved peak. The structural and compositional properties of the respective samples showed no change after annealing. Qualitatively, the electrical properties also remained the same. The comparison of the two ambient at 400 °C anneal revealed that this temperature is not suitable for the flash-evaporated samples prepared in this study. However, the visual appearance of the annealed samples was good. This could be due to the fact that the samples were annealed for shorter times with slower

ramp rates. Other comparisons of the various ambient on the electronic structure showed that the deeper states are less affected in argon than in forming gas. This is not surprising as argon is an un-reactive gas and should not affect the film surface chemically. On the other hand, the forming gas is known to be reactive with semiconductors and several reports are available on the hydrogen passivation of semiconductor (Ref 9).

The band gap energies were calculated from the room temperature plots of $(\alpha h\nu)^2$ against the photon energy hν, and representative spectra of the polycrystalline CIGS thin films are shown in Fig. 3 as well as in Table 1. For most of the processed

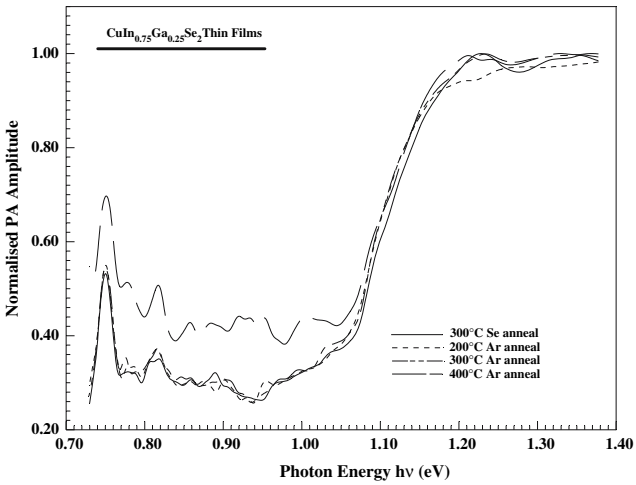

Fig. 2 Normalized photoacoustic spectra of representative polycrystalline CIGS thin films annealed under selenium and argon gas ambient at different temperatures

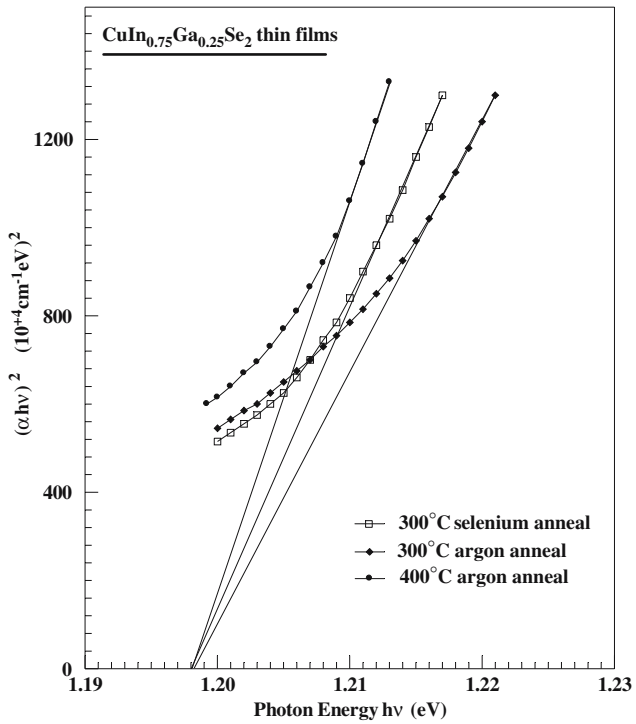

Fig. 3 Plot of $(\alpha h\nu)^2$ versus photon energy for selenium and argon annealed polycrystalline CIGS thin films at different temperatures

Table 1 Band gap energies of the CIGS thin films annealed under various ambient at different temperatures

	E_g(eV)			
Process	**30 Hz**	**112 Hz**	**185 Hz**	**312 Hz**
300 °C Se anneal	–	1.197	1.200	–
200 °C Ar anneal	–	1.197	1.197	–
300 °C Ar anneal	1.196	1.196	–	–
400 °C Ar anneal	–	1.196	1.181	–
200 °C FG anneal	1.197	–	1.180	1.196
300 °C FG anneal	1.195	1.195	1.174	–
400 °C FG anneal	–	1.196	–	–

CIGS thin films, an average value of 1.197 eV was observed which is in good agreement to those reported in the literature (Ref 10). Few samples, however, revealed slightly lower band gap value of 1.180 eV when analyzed with a chopping frequency of 185 Hz. There could be several possible reasons for this observation. Since the thermal diffusion lengths at modulating frequencies of 30, 112, 185 and 312 Hz are 232, 120, 93 and 72 μm respectively and in most of the cases the film thickness was in the order of 1 μm, all the light can pass directly through the sample. It is therefore not possible for the deviated values of band gap to be due to the variations in composition with sample depth. The second possibility is that of measurement error which in this study is about 0.5%. The most probable cause for the observed change in band gap is due to the inclusion of shallow levels as discussed earlier.

The incorporation of hydrogen into CIS single crystals using both proton implantation and diffusion from a plasma source has been found to be considerably modify the electrical properties of the compound (Ref 11). Thin film samples of CIGS already processed under various post deposition heat treatments were implanted with hydrogen species (10 keV, 10^{15} ions/cm^2) at room temperature. Figures 4 and 5 shows the normalized photoacoustic spectra of H^+ implanted CIGS thin films together with the spectra obtained after the last anneal. It can be seen that for the argon annealed sample, the implantation has improved the structure of the deep states with the defect related peaks being well resolved. An enhanced shoulder at

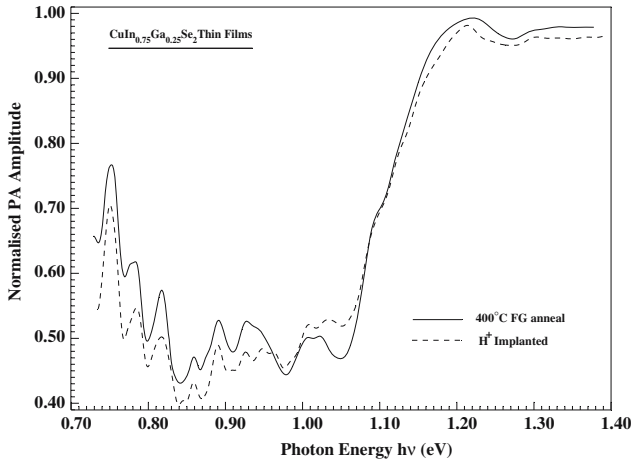

Fig. 4 Normalized photoacoustic spectra of CIGS thin films annealed under forming gas ambient at 400 °C followed by an implantation of H^+ ions

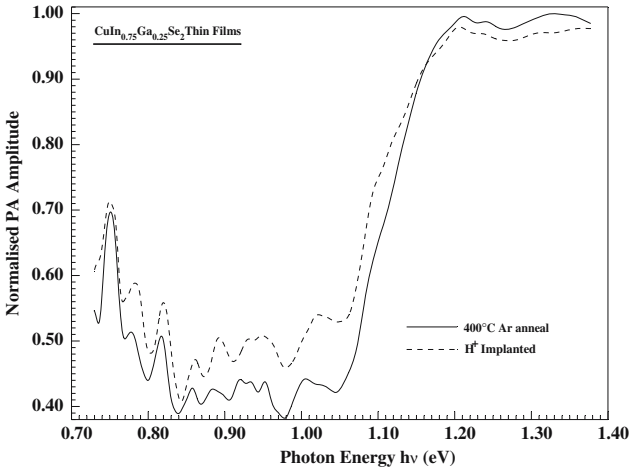

Fig. 5 Normalized photoacoustic spectra of CIGS thin films annealed under argon gas ambient at 400 °C followed by an implantation of H^+ ions

approximately 1.10 eV has raised the minimum level of the photoacoustic signal. In case of the forming gas annealed sample, the implantation effect is not so significant in the low energy range. This could be due to the fact that the sample was already stable in terms of the usual observed deeper state defect population. However, in case of argon annealed sample, the situation was exactly opposite. The sample before implantation showed a number of extra defect states and therefore the effect of hydrogen implantation is more pronounced. Hydrogen has a tendency to interact with other intrinsic or extrinsic defects and induce defects in semiconductors (Ref 9). It is well known that all hydrogenation techniques produce some lattice damage (Ref 11), which affects the native defect concentrations and thus the electrical and photo-thermal properties. However, post implantation heat treatments can alter these defects. While studying the influence of proton implantation on the electrical properties of p-type CIS single crystals, it has been observed that the implantation induced modifications become thermally unstable at temperatures close to or even below 100 °C (Ref 11). It will be interesting to expand this study to ascertain the post-implantation annealing effects on properties of CIGS thin films.

4. Conclusions

Photoacoustic spectrometer of the gas-microphone type was used to evaluate the effects of post-deposition processing on the properties of flash-evaporated CIGS thin films. The samples annealed in selenium, argon, forming gas ambient and implanted with hydrogen species revealed significant changes both near the fundamental band edge and in the low photon energy range. The photoacoustic spectra were found to be highly influenced by high annealing temperatures of 400 °C. Both in forming gas and argon ambient, this high temperature annealing has produced some shallow levels near the fundamental band edge and ultimately altered the band gap values. The changes observed in the photoacoustic spectra of the processed thin films were found to be in good agreement with the improvements noticed in their physical properties. The gap energy of CIGS thin films being 1.197 eV has been found to be in good agreement to that reported in the literature.

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