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Laser Annealing of Flash-Evaporated $CuInSe_2$ Thin Films

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In this paper, the impact of laser annealing on the structural, electrical, and optical properties of $CuInSe_2$ (CIS) thin films has been investigated. The films were deposited using a modified flash evaporation system onto glass substrates. Structural analysis using x-ray diffraction (XRD) showed that the films have a strong preferred growth direction in the ⟨112⟩ plane. After laser annealing with a diffused beam of 20 ns width, the structure was relaxed and an increase in the intensity of ⟨112⟩ diffraction line was observed. A gas-microphone-type, high-resolution, near-infared (IR) photoacoustic spectrometer was used for the analysis of nonradiative defect states in as-grown and laser-annealed CIS thin film samples at room temperature. The absorption coefficient has been derived from photoacoustic spectra to establish activation energies for several defect-related energy levels. The calculated intrinsic defect ionization energies were also compared with the existing data available in the literature. The changes in the optical properties of the films have been explained in terms of the variations in the structural characteristics within the material.

Keywords annealing, $CuInSe_2$, flash evaporation, photoacoustic spectroscopy, photovoltaic, thin films

1. Introduction

Compound semiconductors are leading candidates among photovoltaic materials mainly because they have a wider range of physical, optical, and electrical properties than elemental materials. Among the polycrystalline materials, I-III-VI_2 ternary and quaternary chalcopyrite semiconductors have attracted considerable interest due their potential for use in solar cells, in light-emitting diodes, and in various nonlinear optical devices (Ref 1-3). The most commonly investigated material is $CuInSe_2$ (CIS), which has a number of desirable properties particularly for use in solar cells. For example, it is a direct band gap material with the highest absorption coefficient of any known semiconductor, a moderate surface recombination velocity and radiation resistance to both electron and proton particles (Ref 4). Thin film solar cells based on a polycrystalline CIS absorber layer have already displayed efficiencies in excess of 19% (Ref 5), and if this can be increased further, then potential applications currently being researched will become more economically feasible for industrial production.

A variety of deposition methods for thin films of CIS have been investigated in pursuit of high efficiency solar cells. These include electron beam evaporation, laser ablation, molecular beam epitaxy, and spray pyrolysis (Ref 6-9). So far none of the technologies have been entirely satisfactory when considered from a production perspective. Therefore, it is highly likely that further advances will come from using either deposition followed by postdeposition treatment or hybrid deposition technologies or a combination of both. Mooney et al. (Ref 10) in a systematic study using rapid thermal annealing for the recrystallization of coevaporated CIS thin films observed an enhancement in grain growth within the film structure. It has been reported (Ref 11, 12) that two-stage postdeposition thermal annealing improves the composition, grain size, electrical and optical properties of flash-evaporated $CuIn_{0.75}Ga_{0.25}Se_2$ thin films considerably.

Surface modification of compound semiconductors with lasers is well known. Lasers have been used for the synthesis of multicomponent compounds in thin film form on various thermally insulating substrates (Ref 13). The deposited films can also be annealed with laser irradiation. The process involves the interaction of laser radiation with the surface of the sample. This effectively reorganizes the original film structure into an ordered crystalline form. Post processing of several layers of the same or different materials to form a superior integrated layer is also a feasible process. Laude et al. (Ref 14) synthesized polycrystalline CIS films using laser irradiation of vacuum evaporated multilayer sandwiches of copper, indium, and selenium. They observed only the chalcopyrite phase. Hill and co-workers (Ref 15) have made stoichiometric compound films of CIS in a similar process employing lasers.

In this paper, results obtained from initial studies of the effects of laser annealing on the properties of CIS thin films are reported. The samples were deposited using a modified flash evaporation technique. The samples were irradiated with a diffused excimer laser in pulsed mode (5 pulses of 20 ns time period) with energy of 170 mJ. The as-grown and laser-annealed samples were characterized with x-ray diffraction (XRD) and photoacoustic spectroscopy (PAS).

2. Experimental Procedures

The flash evaporation technique was used to deposit thin CIS films onto glass substrates. The substrate temperature was varied between room temperature and 200 °C. Fine-grain (150

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to 250 mm) starting material was made by repeatedly grinding and sieving of polycrystalline CIS ingots, prepared from 99.999% pure constituent elements by vacuum fusion. Preparation details of the starting material have been given elsewhere (Ref 16). A Mo twin chimney boat held at a temperature of 1500 °C was used as the evaporation source. A source-to-substrate distance of 12 cm and a pressure below 10^{-5} mbar were used during evaporation. A diffused beam excimer laser in pulsed mode was used to anneal flash-evaporated CIS thin films. Five pulses of 20 ns pulse width were used. The structural and optical properties of the as-grown and laser-annealed samples were investigated using XRD and PAS. Film compositions were determined by energy dispersive x-ray analysis (EDAX). The results were complemented with Rutherford backscattering (RBS), which used a 2 MeV He^+ ion beam from a Van de Graff generator in conjunction with a multichannel energy analyzer with a resolution of 5 keV/channel. The electrical parameters, including resistivity and conductivity type, were determined by using four-point and hot-point probe techniques. The photoacoustic spectrometer used in this study has been described in detail elsewhere (Ref 17). Briefly, a 300 W Xe 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 onto a specimen in the photoacoustic cell. The microphone output was phase-sensitively detected using a lock-in amplifier. Finally, the photoacoustic 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 of the spectra were recorded at room temperature at a modulating frequency of 112 Hz.

3. Experimental Results and Discussion

All of the as-grown CIS films were uniform, smooth, and strongly adherent to the substrate surface. EDAX analysis indicated that the as-grown films were stoichiometric and the composition in the films was close to that of the starting prereacted material. RBS analysis, however, showed a number of humps in the central plateau region of the spectrum, indicating nonuniformity in the film composition throughout the film thickness. Electrical measurements exhibited both n- and p-type conductivities with resistivity values in the range of 10^{-1} to 10^{3} Ω cm.

Figure 1 shows the XRD spectra of both the as-grown and laser-annealed CIS samples. An intense ⟨112⟩ diffraction line was observed, in the as-grown CIS thin films, for the range of substrate temperature used. However, this peak was broader 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. This apparent contradiction can be understood by considering the nature of radiative effects likely to be operating in the experiments performed. Although there was not any active heating of the substrate due to the small distance between the substrate and the heated source, some heating of the substrate is inevitable from radiative transfer of energy. It is thus highly likely that these nonintentionally elevated substrate temperatures are responsible for the strong ⟨112⟩ orientation observed in this work.

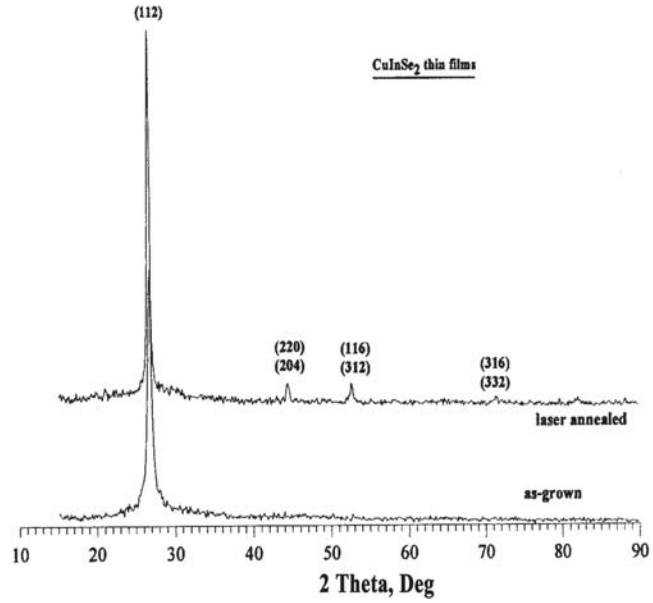

Fig. 1 XRD spectra of the as-grown and laser-annealed CIS thin films

The intensity of the ⟨112⟩ diffraction line was enhanced after laser annealing along with the appearance of other CIS related peaks, which could be attributed to the relaxation in the preferred orientation of the film structure. From observation of the ⟨112⟩ peak full width half-height (FWHF), it appears that the as-grown films are more structurally disordered than the laser-annealed films. The values of FWHF for as-grown and laser-annealed films were 56° and 40°, respectively.

The RBS technique was used to determine the elemental surface composition as well as to obtain a compositional depth profile of both the as-grown and laser-annealed CIS thin films. This is a very useful technique for gaining the qualitative information about the compositional uniformity (through the film) of the films and the quantitative information about surface composition. Figure 2 shows the effect of a laser anneal on the composition as determined by RBS. It can be seen that the spectrum of the as-grown sample is non-homogenous in composition throughout its thickness, with a number of humps being identified on the central plateau region of the spectrum. After the laser anneal, there is a significant change in the central plateau region of the spectrum, which became smoother. On the front edge of the spectra, the peak heights corresponding to In, Se, and Cu are the same. It appears that the laser anneal has significantly improved the homogeneity of the film composition with respect to thickness of the film without disturbing the surface composition. This is as expected, because annealing helps to redistribute the constituent atoms into their most stable states.

Figure 3 shows an example of the normalized PA spectra of laser-annealed thin film compared with the as-grown flash-evaporated CIS thin film. In both cases the PAS spectra exhibited two clear regions separated at approximately 1.02 eV, the fundamental band edge of CIS. After laser annealing, significant changes are observed not only near the fundamental absorption edge but also in the tail of the spectrum between 0.7 and 1.00 eV. An overall decrease in the minimum of the PA amplitude is evident. This could be caused by a change in the nonradiative quantum yield of the material (Ref 18). It was also

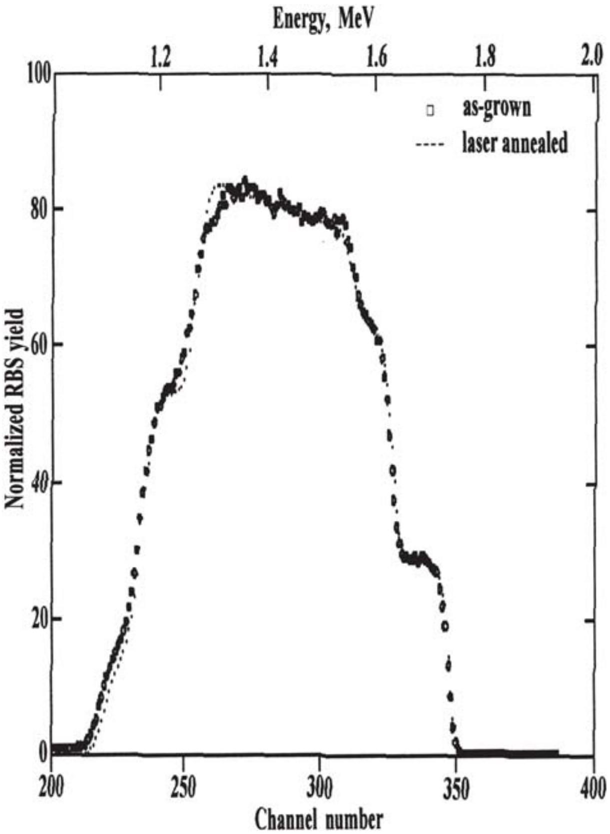

Fig. 2 RBS spectra of the as-grown and laser-annealed CIS thin films

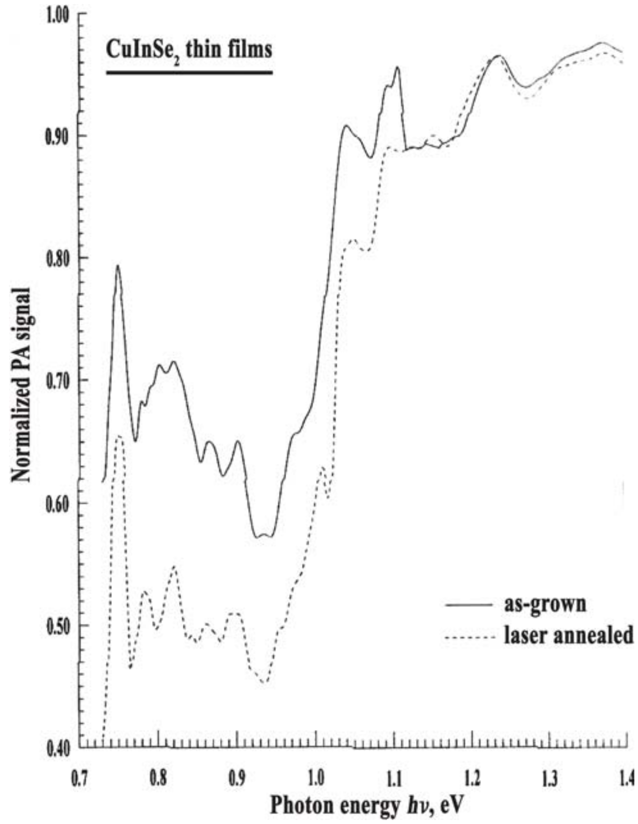

Fig. 3 Comparative plot of the normalized photoacoustic amplitude signal for the as-grown and laser-annealed CIS thin films

noted that a shallow defect level at 1.00 eV was introduced by the laser annealing process.

For a comparison of deeper state transitions appearing in the tail of the spectra (0.7 to 1.00 eV), Fig. 4 was constructed. It shows the absorption coefficient (α) below the energy gap, derived from the respective sections of the PA spectra of the as-grown CIS thin film (dashed line) and the laser-annealed CIS thin film (dotted line). The absorption coefficient of standard p-type CIS single crystal (full line) is also included in the same figure; although, the minimum level of the absorption curve in the photon energy range for the single-crystal sample was lower than those for thin films. For ease of comparison, it has been placed above the thin-film spectra. As expected, the deeper level states, labeled by E_1 to E_5 are very clear and well resolved in the case of the single crystal. The same deeper states are also evident in thin films; however, in the as-grown sample these states are not well resolved. In particular, the E_2 and E_3 peaks overlap, resulting in a single broad peak. In contrast, the spectrum obtained from the laser-annealed sample revealed that all the peaks from E_1 to E_5 are clear and well resolved and are comparable to those obtained from the single-crystal sample. If one compares the observed changes in the PA spectrum of laser-annealed CIS thin film with the respective XRD spectrum, a good correlation is found, as expected. The XRD spectrum of the laser-annealed sample showed a slight relaxation in the structure compared with that of the as-grown thin film. Similar effects were observed in the laser-annealed $CuIn_{0.75}Ga_{0.25}Se_2$ (CIGS) thin films. The film homogeneity was also improved as the RBS spectrum of the latter sample demonstrated a smooth central plateau region of the spectrum. As expected, the composition of the sample remained unaffected. The resistivity value was slightly decreased from 10^3 to 10^1 Ω cm. The scanning electron micrographs, however, showed no conclusive evidence of the modification in the grain structure with both the as-grown and laser-annealed films having similar grain structures.

In laser annealing, the rate of structural regrowth from the original phase to the crystalline phase is determined by the temperature at the reordering interface. The crystal orientation can also have some effect on the regrowth rate, and because the complete process involves nonequilibrium heating, it is not a simple task to quantify the total procedure. However, it appears from the comparison of the PA spectra that laser annealing has redistributed the atoms within the sample and changed the crystal structure. To correlate the observed effect with the fundamental properties a more detailed study is required. The energy band gap value of the as-grown and laser-annealed samples were calculated from the room temperature plots of $(\alpha h\nu)^2$ versus the photon energy $h\nu$, shown in Fig. 5. Analysis of the experimental data showed that the near-vertical portion of the $(\alpha h\nu)^2$ curves is due to an allowed direct band-to-band transition. By extrapolating the linear portion of the curves to $(\alpha h\nu)^2 = 0$, the band gap energies were determined. The measured band gap value of the as-grown sample is found to be approximately 0.996 eV. However, in the case of laser-annealed sample, the observed band gap value is slightly higher at 1.015 eV. The energy band gap values of both the as-grown and laser-annealed films are in good agreement with those measured by PAS (Ref 19, 20). It appears that the new defect levels observed on the portion near the fundamental band edge are the probable cause of the band gap shift to this higher value.

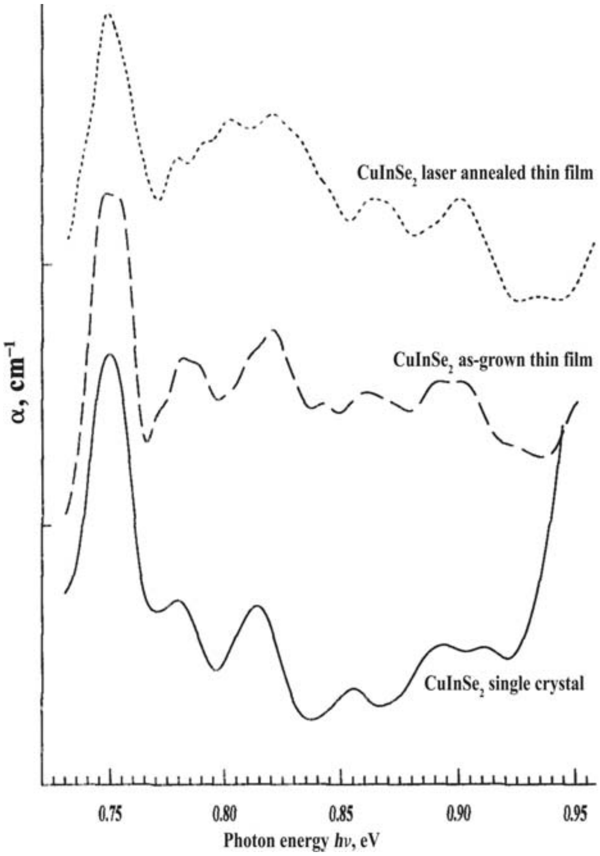

Fig. 4 Comparative plots of the absorption coefficient of (a) a single crystal, (b) laser-annealed, and (c) as-grown CIS thin films

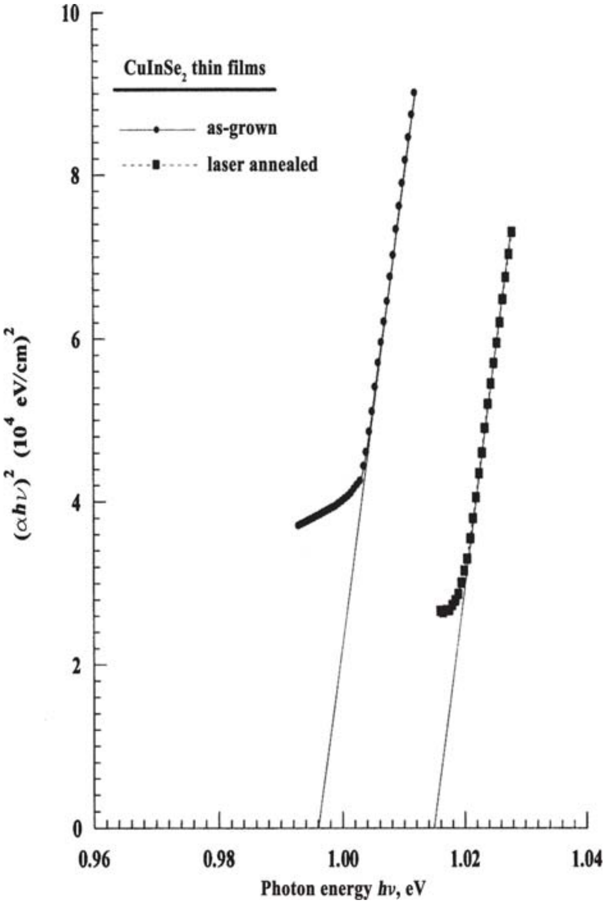

Fig. 5 Plot of $(\alpha h\nu)^2$ against the photon energy to calculate the band gap of CIS thin films, before and after laser annealing

It should be noted that the sample was not processed under any atmosphere (Se/CIS powder) before laser annealing.

The ionization energies of the deeper defect levels from the appropriately determined values of the gap energy are derived for both thin-film and single-crystal samples of CIS and are tabulated in Table 1.

The proposed electrical activities (D, donor; A, acceptor) have also been indicated. The strongest peak appearing at 263 meV is an acceptor state and is in good agreement to that reported from DLTS studies on CIS single crystal at 250 meV (Ref 21) and on thin films at 260 meV (Ref 22). The peak at 235 meV is due to an intrinsic donor state, reported by Neumann (Ref 23), with an activation energy in the range of 220 to 225 meV.

The ionization energy of the peak E_3, 191 meV, could be either an acceptor or a donor state. An acceptor with ionization energy of approximately 190 meV has been observed in p-type CIS thin films (Ref 24) but DLTS measurements confirmed that this defect is a hole and electron trap with ionization energies of 186 and 182 meV, respectively (Ref 21). The energy E_4, 151 meV, can be ascribed to an acceptor state. Within the measurement error, this value agrees with an acceptor activation energy of 160 meV determined in In-rich CIS (Ref 25) and with 140 to 160 meV observed in the PAS (Ref 26). In the case of energy E_5 the electrical activity can again be ascribed to either an acceptor or a donor. In the literature it is reported to be an acceptor state with energy in the range of 110 to 120 meV (Ref 23), determined by electrical measurements on p-type CIS single crystals. In most cases, the proposed electrical activity agrees with that reported in literature.

Table 1 Fundamental energy gap E_g and different defect ionization energies (E_1 to E_5) of p-type CIS thin films and single crystal

Peak number	Peak energy, eV		Proposed electrical activity
	Thin film	Single crystal	
E_g	1.015	1.008	…
E_1	263	256	A
E_2	235	228	D
E_3	198	191	A/D
E_4	158	151	A
E_5	128	120	A/D

In another report by Abou-Elfotouh et al. (Ref 27), this state has been described as a donor state with the same energy of 115 meV, deduced from the photoluminescence spectra. In most of the cases, the proposed electrical activity agrees with the reported ones. However, the nature of the defect levels (E_3 and E_5) is still questionable, and to be sure about their electrical activity, a range of samples differing in their structural and compositional properties should be analyzed using the PAS technique.

4. Conclusions

The effects of laser annealing on the structural and optical properties of flash-evaporated CIS thin films have been investigated. Comparison of data from different analytical techniques showed a good correlation. The as-grown CIS thin films were shown to have a strong ⟨112⟩ preferred orientation. After laser annealing, the film crystallinity improved and the preferential orientation along the ⟨112⟩ direction was enhanced along with the appearance of other CIS-related peaks.

The optical properties of the as-grown and laser-annealed CIS thin films, characterized using a high-resolution photoacoustic spectrometer, revealed a complex nonradiative defect structure that comprised a set of five deep-level states. After laser annealing, these defect levels were more distinguishable than in the as-grown films. The position and intensity of these defect levels was comparable to that observed from standard CIS single crystal. After laser annealing a decrease in the minimum level of the PA signal along with the introduction of a new shallow defect level near the fundamental band edge, as compared with the as-grown sample, was also observed. The intrinsic defect ionization energies of the deeper defect levels have been calculated and possible activity levels have been assigned on the basis of the comparison with the existing literature.

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