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Deposition and characterization of copper indium gallium diselenide films by laser ablation and flash evaporation for use in solar cells

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Copper indium gallium diselenide (CIGS) thin films have shown considerable promise for use as an absorber layer in high-efficiency solar cells. The initial results obtained from the preparation of CIGS films via laser ablation and flash evaporation are presented along with a comparison of the two deposition processes. The as-deposited CIGS films have been characterized by a variety of techniques, namely Rutherford back scattering and energy dispersive analysis using X-rays for composition measurements X-ray diffraction and Raman spectroscopy for structure elucidation, SEM for surface examination, and the four-point probe for resistivity measurements. In essence, good-quality coatings of CIGS were produced from both deposition processes in terms of their stoichiometry, electrical and structural properties.

1. Introduction

For many years a wide variety of deposition methods including sputtering, evaporation and chemical vapour deposition (CVD) have been developed to deposit high-quality thin films of a broad range of materials for a number of different applications [1]. However, for the deposition of compounds such as $CuInSe_2$ and copper indium gallium diselenide (CIGS), most of these techniques have proved to be unreliable, mainly due to differences in vapour pressure of the various constituent elements and also the lack of availability of suitable combination(s) of chemical precursors for use in CVD [2]. Therefore, there is a commercial and scientific interest in developing new or existing deposition techniques to produce $CuIn_{0.75}Ga_{0.25}Se_2$ films with the desired electrical and optical properties on a large industrial scale for solar cells.

Laser ablation and flash evaporation appear to be two techniques which show considerable potential for growing CIGS films. Laser ablation was first employed over 30 years ago for the deposition of high-temperature superconductors, but has now become increasingly popular for the production of a diverse range of materials, including semiconductors, dielectrics, organometallics and chalcogenides [3, 4]. The process itself involves the interaction between sequential high-energy pulses and a target which consists of the material to be deposited. This interaction produces atoms and reactive species which then diffuse towards the substrate, which is located a short distance from the target; here they absorb and coalesce to form the desired film. The laser-ablation technique has the ability to deposit two-, three-, four-, five- or even six-element compounds without compromising the original stoichiometry, which makes it ideal for the production of CIGS photovoltaic materials.

The second method of interest here is flash evaporation, which was first reported for $CuInSe_2$ over 20 year ago. This method of deposition has been further refined to produce good-quality $CuInSe_2$ films, as well as CIGS materials [5].

In this paper we compare and contrast the deposition of CIGS thin film via laser-ablation and flash-evaporation techniques. Characterization of the as-deposited films suggests that good-quality films can be produced by both methods. In addition, we have elaborated upon key process parameters and probable mechanisms in order to ascertain a better understanding of these deposition technologies as well as their influence on the resulting film characteristics.

2. Experimental procedure

For the laser-ablation studies, Bridgman-grown single crystals of $CuIn_{0.75}Ga_{0.25}Se_2$ were used. The laser-ablation system itself has been described elsewhere

[6]. A focused laser beam (consisting of an XeCl excimer, wavelength = 308 nm, 40 mJ pulse, peak power density = 1×10^9 W cm^{-2}, pulse width less than 100 ns and a repetition rate of 25 Hz) was repeatedly scanned over a target area of 7.2 mm × 1.2 mm held at an angle of 45 °C to the beam. Typically, 5×10^4 laser pulses were used to obtain film thicknesses of 400 nm on either fused silica or single crystal $\{1\,1\,1\}$ substrates heated independently to 300 °C. The vacuum chamber was operated at a base pressure of 1×10^{-5} mbar and the target–substrate distance was maintained at 3 cm throughout all laser-ablation experiments. Typical deposition rates were of the order of 0.7 nm per pulse (18 nm s^{-1}).

For the flash-evaporation studies, the starting material was made by repeated grinding and sieving of polycrystalline $CuIn_{0.75}Ga_{0.25}Se_2$ prepared using pure elemental constituents (99.99%, Aldrich). A molybdenum twin-chimney boat was used as an evaporation source operated at a temperature of 1500 °C. The base pressure of the system was 1×10^{-5} mbar and the source–substrate distance was maintained at 12 cm throughout experiments. The films produced were characterized by X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDAX), Rutherford back-scattering (RBS), SEM and the four-point probe.

3. Results and discussion

X-ray diffraction patterns for films produced by laser ablation and flash evaporation showed a preferred $\{1\,1\,2\}$ orientation, i.e. parallel to the substrate (Fig. 1). However, only a single peak representing a $\{1\,1\,2\}$ orientation was observed for the flash-evaporated film. Conversely, the diffraction pattern for the laser-ablated film showed additional peaks at $\{1\,1\,6\}$ $\{3\,1\,2\}$, $\{2\,0\,4\}$ $\{2\,2\,0\}$ and $\{2\,1\,3\}$ $\{1\,0\,5\}$ which indicated a much more relaxed structure with a greater degree of structural disorder. The laser-ablated film showed a much broader $\{1\,1\,2\}$ peak than the flash-evaporated film, as well as having a greater intensity. A well-defined $\{1\,1\,2\}$ peak is associated either with high substrate temperatures ($>$ 350 °C) or, a film which is subjected to annealing following deposition.

Raman spectra of the as-deposited flash-evaporated and laser-ablated films are shown in Fig. 2. The A_1 mode of the lattice vibrations is indicated by a peak at 175 cm^{-1} and is commonly observed in the I–III–VI_2 chalcopyrite compounds [7]. A sharp A_1 peak is observed for the flash-evaporated film, whereas a much broader peak is seen for the laser-ablated film which is indicative of a much higher degree of disorder in the laser-ablated films. This hypothesis is reinforced by the XRD results already discussed. Typical full-width at half-maximum (FWHM) values were 10 and 13 cm^{-1} for the flash-evaporated and laser-ablated films, respectively.

EDAX analysis was used to investigate the bulk composition of the films produced by the two methods. The results of typical compositional analyses are shown in Fig. 3 which is, in fact, a compositional triangle normally employed for ternary compounds.

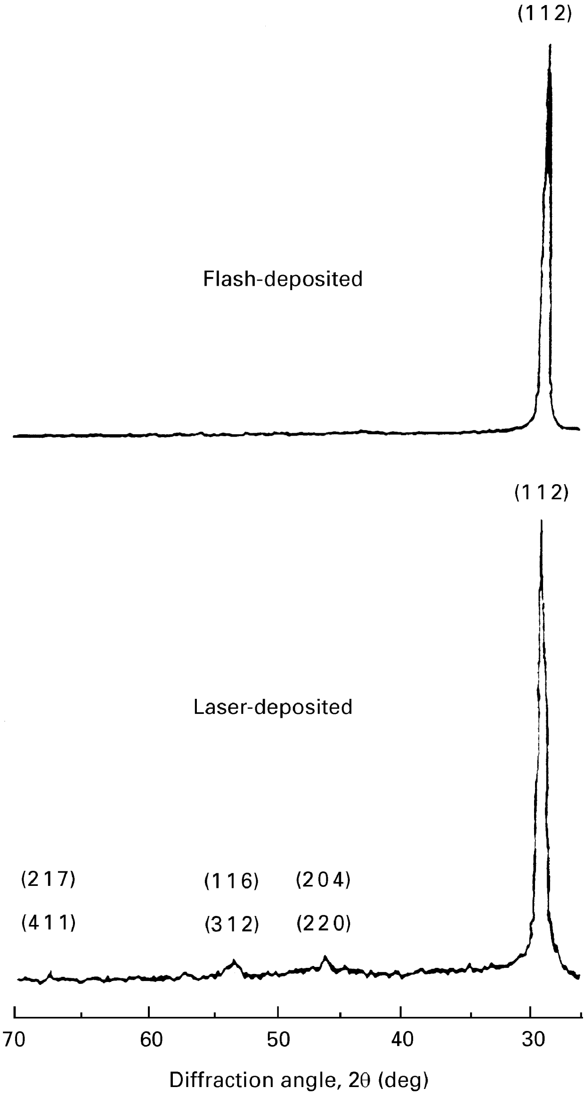

Figure 1 XRD pattern for flash-evaporated and laser-ablated CIGS films.

Because gallium is partially substituted for indium, these two elements are represented on the same axis. The as-deposited films revealed a selenium deficiency probably caused by a loss due to its high vapour pressure. However, selenium deficiency was much more pronounced in the laser-ablated films compared to the flash-evaporated films. For both deposition techniques, the copper and gallium contents were found to be close to those of the starting material.

The RBS technique was employed to determine the surface composition and depth dependence. The RBS spectra obtained from both deposition techniques are shown in Fig. 4. It is evident that the surface compositions for both techniques are nearly identical, apart from a slightly higher indium content for the flash-evaporated films which is again consistent with the EDAX analyses.

The electrical properties were measured using a four-point probe and hot-probe techniques. Both n- and p-type behaviour was observed not only between samples but also within the same sample. However, the films themselves were electrically inhomogeneous.

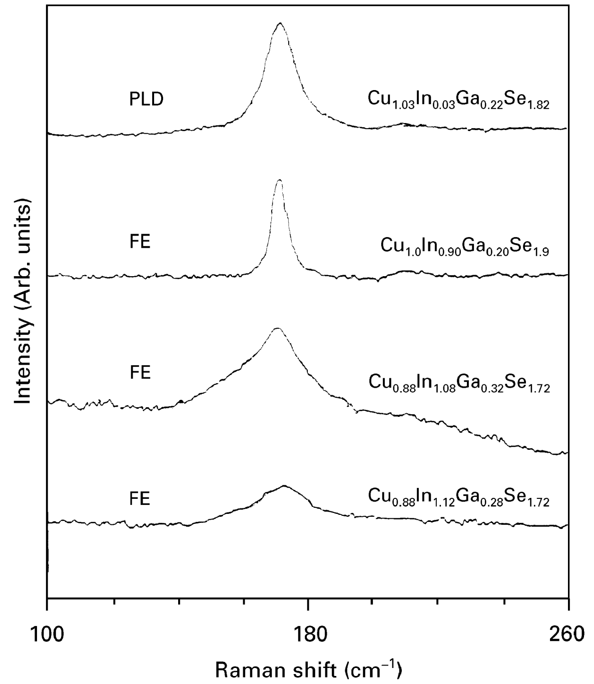

Figure 2 Raman spectra of the as-deposited flash-evaporated and laser-ablated CIGS films.

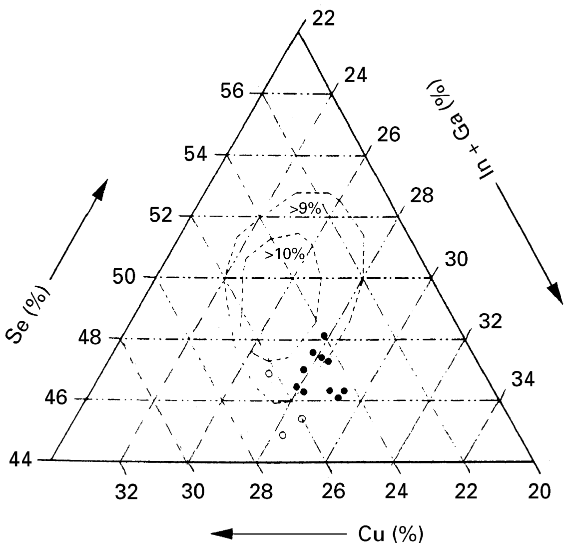

Figure 3 EDAX composition analysis of flash-evaporated and laser-ablated CIGS films.

For the as-deposited films, the resistivity was measured between 10^{-1} and 10^3 Ωcm. The high resistivity of the samples can be attributed to the presence of grain boundaries or other structural disorder which offer a highly resistive path for the movement of charge carriers. If these samples are annealed by heat treatment at 300 °C for 2 h in a selenium ambient, the resistivity drops from 1.34×10^2 to 0.20 Ωcm. However, if the ambient consists of a 9 : 1 mixture of $N_2 : H_2$ at 300 °C, then no noticeable change in the type of conductivity is observed, which indicates the presence of a selenium vacancy [8].

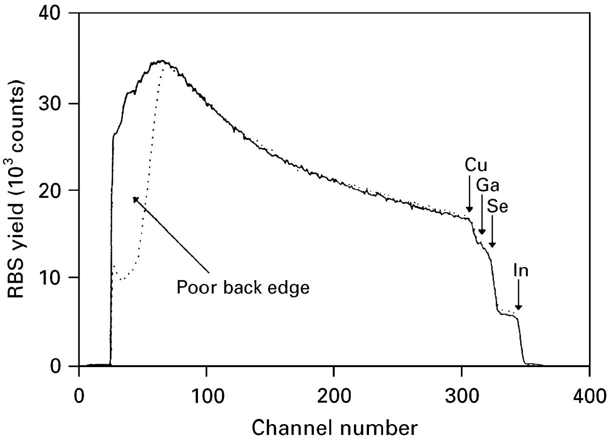

Figure 4 Depth dependence and surface composition of CIGS films deposited by (...) flash evaporation and (—) laser ablation.

4. Conclusions

Laser-ablation and flash-evaporation techniques were used for the deposition of copper indium gallium diselenide thin films. The resultant films were polycrystalline with a strong {1 1 2} preferred orientation, but a more relaxed structure was noticeable for the laser-ablated films. The broadness of the {1 1 2} peak indicated a structural disorder which could be attributed to small grain sizes of the order of 0.2 μm. Raman analyses showed the existence of an A_1 mode peak with the laser-ablated film showing decreased intensity of this mode, suggesting a poorer degree of crystallinity. Compositional analyses of the films revealed them to be close to the starting material, but a slight deficiency in the selenium content was common with both deposition methods.

We conclude that both flash evaporation and laser ablation may be employed to deposit CIGS films which have similar properties to each other. These films may be modified by annealing at 300 °C. It is envisaged that further improvements in the structural and electrical characterization could be achieved by optimizing the process and annealing parameters.

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