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One step deposition of $Cu(In_{1-x}Al_x)Se_2$ thin films by RF magnetron sputtering

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$Cu(In_{1-x}Al_x)Se_2$ thin films were deposited by one-step RF magnetron sputtering. The target was composed of mixed binary selenides of CuSe, InSe and pure aluminum powder. Smooth films surfaces with good adhesion to the substrate were grown successfully. All of the films show strong (112) and (204/220) single phase $CuInSe_2$ peaks. Addition of Al to the target up to 6 wt-%, at the expense of indium, shifts the orientation peaks towards higher 2θ yielding films with an optical band gap between 1.05-1.7 eV. For the first time, this paper reports the application of a one step sputtering deposition process to grow $Cu(In_{1-x}Al_x)Se_2$ thin films for solar cell absorber applications.

Key words: Solar cells, thin films, $CuInSe_2$, sputtering, band gap.

Introduction

Solar cells based on thin film materials have been given much attention for their high efficiency, low material consumption and the ability to be implemented on large area substrates. $CuInSe_2$ (CIS) thin films and their quaternary compounds have been considered as one of the most promising material classes for absorber layers for solar cells mainly due to their high optical absorption coefficient and stability, approaching 20% laboratory efficiencies on $Cu(InGa)Se_2$ [1]. CIS has a 1.04 eV band gap which is rather low for optimum conversion efficiency and this can be improved by modification of the chemical composition as has been done by either replacing In with Ga or Se with S. Furthermore, there is also a need to reduce the manufacturing cost of solar cells by employing low cost technology and materials.

Addition of aluminum to the CIS films is a viable alternative to reduce the usage of expensive In and Ga as well as to improve the band gap of CIS solar cells by forming $Cu(In_{1-x}Al_x)Se_2$ (CIAS). This requires a relatively smaller amount of Al alloy concentration than Ga to achieve a comparable band gap. Although an efficcency as high as 16% has been recorded on CIAS using a co-evaporation method [2-5], there have been only a few reports on alternative production routes. This paper for the first time reports the possibility of using a one step sputtering deposition process from a mixed binary selenide target to grow CIAS thin films for solar cells applications. Compared to the selenization process applied in commercial CIS solar cells production, one-step RF magnetron sputtering is an inexpensive method to obtain a film with the desired stoichiometrical composition.

Experimental Details

CIAS films were deposited on corning glass 1737 substrates by RF magnetron sputtering from a 50 mm single target. Substrates were cut in 50×15 cm^2 and subsequently cleaned ultrasonically in soap water and organic solutions (acetone, ethanol) and de-ionized water prior to loading into the deposition chamber. The sputtering target was compacted from a mixture of binary selenides of CuSe, InSe and additional Al powders. Powders with at least 4 N purity were used as starting materials. After the initial chamber evacuation by a turbomolecular pump reached 1.33×10^{-3} Pa, depositions were carried out at a 5.33 Pa working pressure using Ar sputtering gas flowing at 2.2 sccm. The substrate-to-target distance was kept constant at 50 mm. To study the effect of deposition temperature, substrates were heated up to different temperatures from no-intentional heating (RT) to 200 °C. Films with different Cu/(In+Al) and In/Al as well as metal/Se ratios were obtained by varying the target compositions, mainly the InSe and Al (3 and 6 wt-%) content as the Al addition is designed to replace the part of In. To preserve the same condition for every deposition the target was remixed and pressed after every deposition process. The average film thickness was 1.5 μm resulting from 3 hours total deposition time using 75W RF power (deposition rate 1.38 Å/s).

All the deposited films were characterized to study their stoichiometry, structural and optical properties. An X-Ray diffractometer (Rigaku DMax 2500) was

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used to examine the films' crystallinity with Cu Kα radiation (λ=1.5405 Å). The surface morphology of the films was observed by a scanning electron microscope (Hitachi S-4100) while the chemical composition of the films were measured by energy dispersive X-ray spectroscopy (EDX) attached to the SEM equipment, in which the standard of the measurement was calibrated by wavelength dispersive spectroscopy [6]. A Cary Varian UV-Vis spectrophotometer was employed to observe the optical properties of the films.

Results and Discussions

Initial depositions were carried out to produce CIS films using a sputtering target composed of mixed CuSe and InSe powder (1:1 mole ratio) at different deposition temperatures i.e. RT, 125 °C, 150 °C and 200 °C. Depositions at the higher substrate temperatures were needed to improve the crystallinity of the films. The stoichiometry of these films was analyzed to provide the base parameters for deposition with Al-added targets at higher temperatures. As shown in Fig. 1, it can be seen that the ratio of Cu:In:Se in the films could be maintained near stoichiometry up to 125 °C deposition. Above that temperature, the In and Se content in the film decreased rapidly due to loss during deposition. Therefore all the subsequent depositions for producing CIAS thin films specimens were carried out at 125 °C.

Table 1 shows the chemical composition of films before and after Al addition observed by EDX bulk analysis. Apart from CIS films (marked as CIAS-0), two groups of specimens were prepared from targets with additions of 3 and 6 wt-% Al powder, denoted as CIAS-3 and CIAS-6, yielding films with x values of 0.17 and 0.25.

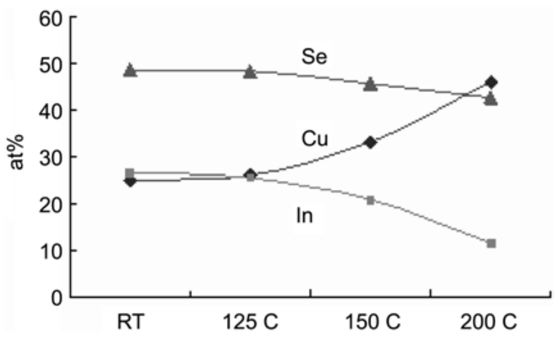

Fig. 1. EDX analysis of CIS films at different deposition temperatures.

Table 1. EDX analysis of CIAS films deposited at 125 °C (in atomic-%)

Element	CIAS-0	CIAS-3	CIAS-6
Cu	26.16	27.24	27.13
In	25.58	22.08	20.09
Se	48.26	46.26	46.14
Al	-	4.42	6.64

All of the observed films showed only a slight deficiency in Se between 46.14-48.26 at-%, which is found to be better compared to the similar films produced by selenization of sputtered metallic precursors [7]. Increasing the deposition temperature and the addition of Al increases the ratio of Cu/(In+Al) as well as the loss of Se. It is understandable since the Al is added in pure form, not in a binary selenide and at higher temperature In and Se are vaporized faster. A further selenization process could be employed to achieve a complete stoichiometric composition of CIAS films. The average amount of Cu in the films is 27 at-%, which seems relatively high compared to the one reported by Marsillac et al. [2] (around 23.5 at-%). This can be anticipated by adjusting the CuSe/InSe ratio in the target as the sputtering rate of Cu is higher than In.

The XRD spectra analysis for CIAS films is shown in Fig. 2. All of the films show strong CIS peaks, mainly shown by the (112), (204/220) and (312) orientations. From the spectra, the films were found to be single phase and of the polycrystalline chalcopyrite structure. Compared to RT deposition, the heating of the substrate during film deposition led to increased crystallinity of the films. One specific feature was the growth of the (301) orientation at higher substrate temperatures, which could not be seen in CIS film grown without intentional substrate heating. Although the variation is relatively small, the addition of Al in the films shifts the (112) peaks towards higher 2θ as previously reported by Itoh et al. [4] and Paulson et al. [3]. This is an indication that can result in a higher band gap as the lattice constant of the films decreased [3, 4].

The surface morphology and cross section of the films is given in Fig. 3. The surface was relatively smooth with an increase in the grain size with the addition of Al. Compared to films produced via co-evaporation or a two-stage process (precursors deposition and selenization), films produced by a one-step sputtering deposition method have a smaller grain size which is understandable as deposition took place at a lower temperature and also due to the nature of the sputtering process. Further annealing and/or a selenization process

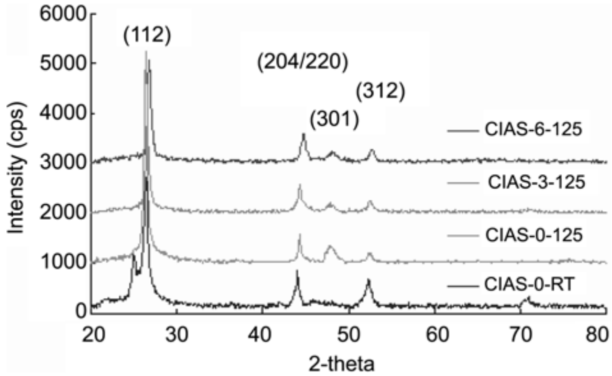

Fig. 2. XRD spectra of CIAS films with different Al contents and deposition temperatures.

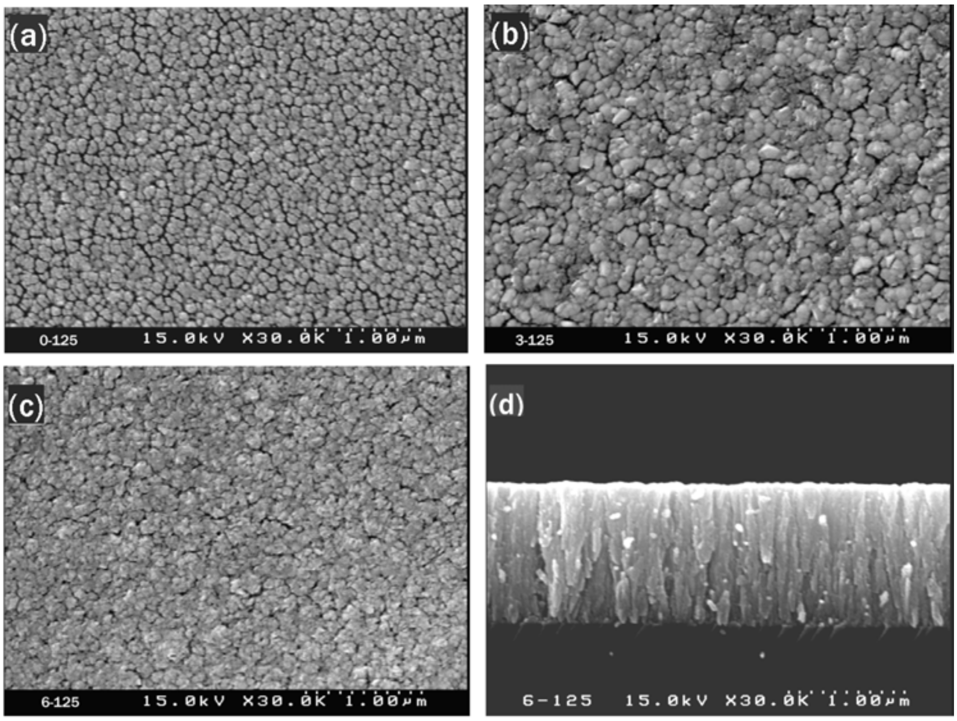

Fig. 3. Scanning electron micrographs of CIAS films deposited at 125 °C (a) CIAS-0 (b) CIAS-3 (c) CIAS-6 (d) cross section of CIAS-6.

may be employed to improve the grain size as well as the stoichiometry of the films. There is no sign of secondary phase presence in the surface as confirmed by XRD analysis. As can be seen in the cross sectional image in Fig. 3d, all of the films show uniform and clear columnar grains which are necessary to facilitate current transport across the films. A rather densely packed microstructure free of pinholes and micro-cracks was also observed from the cross sectional image. Generally, all of the films show strong adhesion to the substrates, which highlights the advantage of sputtering deposition over two-step (selenization) process.

The transmittance spectra of the films were determined by a UV-Vis spectrophotometer in the range 400-2500 nm wavelength as given in Fig. 4. The spectral transmittance data revealed that films with less Al content are more transparent. There is no significant shift observed in the fundamental absorption region of the films. The optical band gap was determined from the transmission spectra corresponding to the following equation:

$$\alpha = A\,(h\nu - E_g)^n / h\nu \qquad (1)$$

where A is a constant (which is equal to about 10^5 $cm^{-1}eV^{-1}$ at n=2). The exponent n (usually 1/2~3) depends on the nature of the optical transition whether direct allowed, direct forbidden, indirect allowed or indirect forbidden, respectively. Figure 5 shows the projected optical band gap of CIAS films deposited at a 125 °C substrate temperature. Films without the addition of Al show a 1.05 eV optical band gap, while films with an Al addition yield 1.35 eV for CIAS-3 and 1.7 eV for CIAS-6 respectively. These values are in good agreement with the optical band gap of CIAS

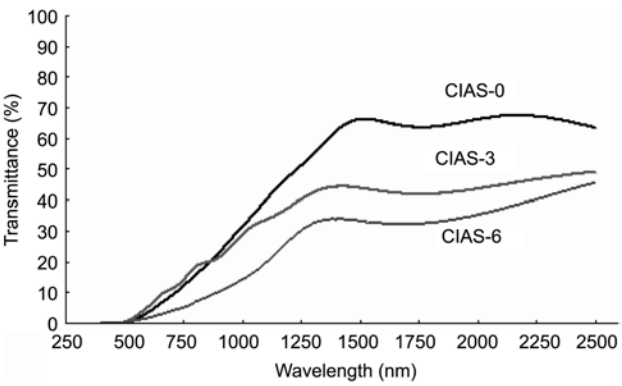

Fig. 4. Transmittance spectra of CIAS films deposited at 125 °C.

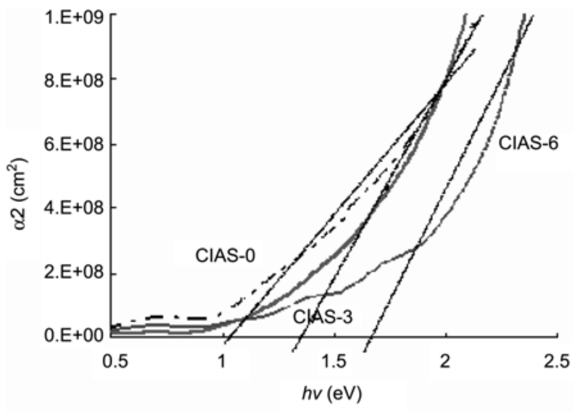

Fig. 5. Energy band gap of CIAS films deposited at 125 °C.

films produced by a co-evaporation method as reported by Reddy et al. [8].

Conclusions

CIAS thin films with Al content $x=0$, 0.17 and 0.25 were deposited on glass substrates using a one-step deposition by RF magnetron sputtering at 125 °C. Films with good substrate adhesion, smooth surfaces, a columnar structure and free from secondary phases were grown successfully. The films were found to be near stoichiometry, single phase and polycrystalline with the chalcopyrite structure, dominated by strong (112), (204/220) orientation peaks. As the Al content in the film increases from 0 to 25 at-%, the optical band gap of the films were estimated to be in the range 1.05-1.7 eV, which is suitable for applications as an absorber in solar cells.

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