Effects of Sb-doping on the grain growth of CIGS thin films fabricated by electrodeposition*

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$Cu(InGa)Se_2$ (CIGS) solar cells become one of the most important thin film photovoltaic devices thus far. The doping of Sb has improved the grain size of CIGS thin film and therefore led to the enhancement of solar cell efficiency. Various approaches have been used for the Sb doping. Not many reports of electrodeposition of In, Ga and Sb alloy have been reported. In this work, the Sb thin film was coated over Cu film surface prior to the In and Ga deposition in order to form a Cu/Sb/In/Ga metal precursor. After selenization, the Sb doped CIGS film was prepared. The structure and morphology of Sb doped CIGS films were investigated compared with the undoped CIGS reference samples. A modified selenization method was proposed, which improved the grain size. Finally, the conversion efficiency of Sb doped CIGS based solar cells has been improved by 1.02%.

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$Cu_2InGaSe_4$ (CIGS) solar cells with high efficiency and long-term stability are considered to be one of the most promising photovoltaic devices[1,2]. Up to date, the highest efficiency of 23.35% of CIGS solar cell has been obtained by vacuum deposited method[3]. However, CIGS solar cells fabricated by this method require large scale investment for industrial applications. One approach to further reduce cost is to develop alternative deposition techniques for thin film CIGS solar cells using non-vacuum coating processes. CIGS thin films prepared by electrodeposition can reduce the cost, improve the utilization of raw materials and are suitable for large-scale industrial production[4]. Up to now, this method has been used successfully to prepare CIGS absorber layer and the highest efficiency is 15.9%[5].

Despite this progress, the performance of CIGS solar cells fabricated by this method remains far lower than that by the co-evaporation method. One reason is that the grain size of CIGS films fabricated by electrodeposition is always smaller than that by other methods. As is known, the grain boundaries in absorber can act as recombination centers for photo-generated charge carriers and deteriorate the solar cell performance. Therefore, it is highly desirable to obtain large grains so as to minimize such recombination effects[6].

Doping is a commonly used strategy to improve the performance of CIGS[7,8]. The incorporation of Sb has been reported to increase the grain size of CIGS thin films, so as to enhance the device performance[9-12]. However, a majority of investigation on the Sb doping of CIGS thin films is based on the hydrazine-based approach, co-evaporation, and sputtering, which is quite different from electrodeposition.

In this study, we prepared Sb-doped CIGS thin films by selenizing stacked Cu/Sb/In/Ga layers prepared by sequential electrodeposition. The phase separation phenomenon and the recrystallization process have been discussed. A modified two-step selenization process is adopted as the optimized selenization strategy. At last, the current-voltage (*J-V*) characterizations are measured to analyze the effect of Sb doping on the performance of CIGS solar cells.

The Mo (1-μm-thick) layer was sputtered on the cleaned soda-lime glass as the back contact by direct current (DC) magnetron sputtering. The Cu/Sb/In/Ga metallic stacks were sequentially electrodeposited on the Mo substrate by electrodeposition from acidic aqueous solutions. The thickness of the metal precursor was approximately 0.8 μm, and the ratios of Cu/(In+Ga)≈0.80 and Ga/(In+Ga)≈0.25 were obtained by X-ray diffraction (XRD) analysis. The content of Sb was estimated to be 1 mol% based on the total charge used for Sb deposition. Solid Se pellets were used in selenization process. A laboratory-made furnace was used to carry out the selenization and the vacuum chamber provided a vacuum environment of 10^{-4} Pa. The

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CIGS solar cells were then completed by the chemical bath deposition of CdS buffer layers, sputtering i-ZnO/Al-ZnO for window layers, and evaporating Ni/Al for front contacts.

The film compositions were measured by XRD analysis using a Philips Magix PW2424 spectrometer. Structure properties were characterized using a PANalytical X'Pert pro XRD with Cu Kα radiation (λ=1.541 6 Å). The morphologies of the films were characterized by a scanning electron microscope (SEM, Hitachi S-4800). The *J-V* measurements were performed under the standard AM1.5 spectrum for 100 mW/cm^2 at 25 °C.

A conventional two-step selenization consists of a low-temperature pre-heating treatment and subsequent annealing (see Fig.1)[13]. The pre-heating treatment in Step I was used to heat the stacked Cu/In/Ga layers in vacuum to alloy the metal precursor. Additionally, the annealing (Step II) was performed by supplying an Se vapor on the pre-heated precursor that was heated to 550 °C in succession for the formation of CIGS phase. The duration of two-step selenization procedure is 20 min for pre-heating (Step I) and 60 min for annealing (Step II), respectively.

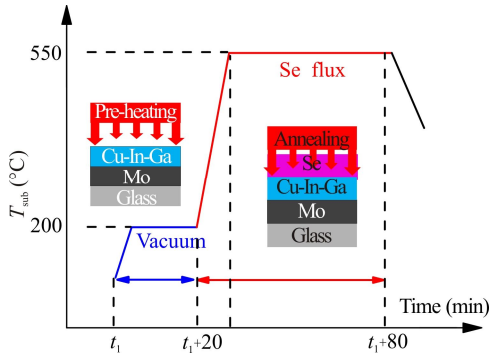

Fig.1 Schematic of the two-step selenization process

Fig.2 displays the surface morphologies of CIGS films with and without Sb layer incorporation fabricated by the conventional two-step selenization method. The grains in the plane of undoped CIGS films are significantly smaller. This contrast indicates that Sb doping is beneficial for the grain growth in CIGS thin films.

Fig.3(a) shows XRD patterns of CIGS films with and without Sb layer incorporation fabricated by the conventional two-step selenization method. The occurrence of diffraction peaks along (112), (220/204) and (116/312) planes matched well with the standard chalcopyrite structure. Enlarged (112) diffraction peaks are shown in Fig.3(b). The distinct phase separation of $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) can be clearly observed in both samples. It is thought that the phase separation of CIS and CGS is an inevitable outcome in the post-selenization process, because the growth of Ga selenides is slow[14]. However, the sample with Sb doping shows worse Ga incorporation than that without Sb doping.

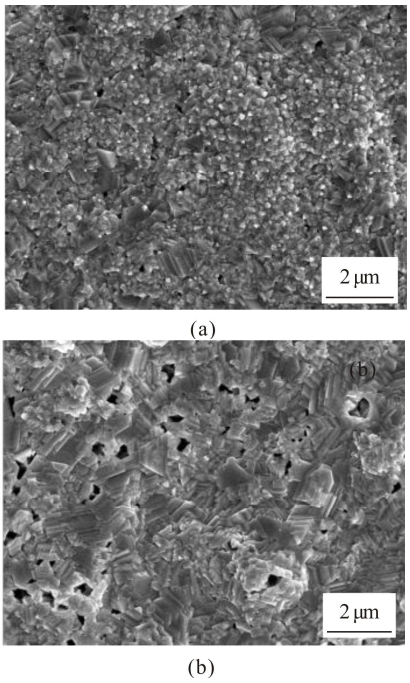

Fig.2 Surface morphologies of (a) pure CIGS films and (b) Sb-doped CIGS film fabricated by conventional two-step selenization method

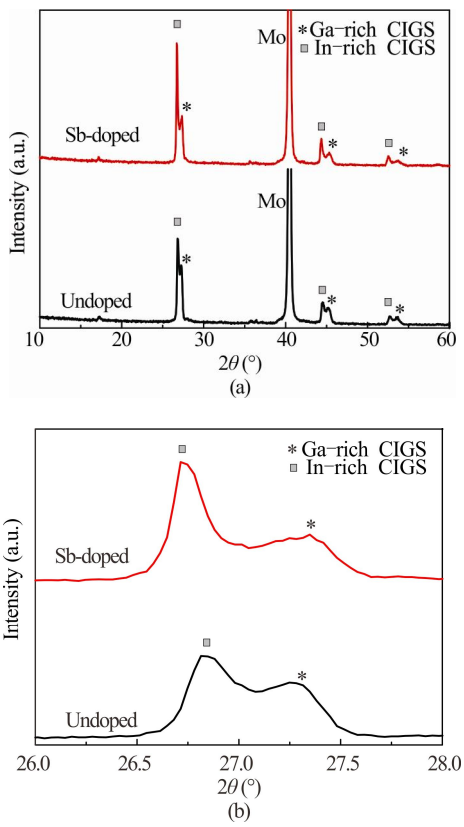

Fig.3 (a) XRD patterns of CIGS films with and without Sb doping fabricated by conventional two-step selenization method; (b) Enlarged XRD peaks of CIGS films from 26° to 28°

We thus carried out the selenization at low temperature (400 °C) to investigate the phase separation mechanisms. As can be seen from the expanded XRD patterns in Fig.4, the phase separation is more significant at 400 °C than that at 550 °C. Moreover, the Sb-doped sample shows a smaller full width at half maxima (*FWHM*), which means that the Sb-doped sample exhibits better crystal quality predicted by the Scherrer's formula[15], and Sb promotes the growth of CIS at a lower temperature.

The compact CIS obstructs the path through which Se further diffuses into the film as substrate temperature increases[16]. Even temperature reaches the reaction threshold between Ga and Se, Ga could not effectively substitute In into the chalcopyrite structure to form CIGS. And Ga-related binary selenides have been buried by a fast grain growth CIS in the initial stage of selenization process, finally inducing an uneven distribution of Ga[17].

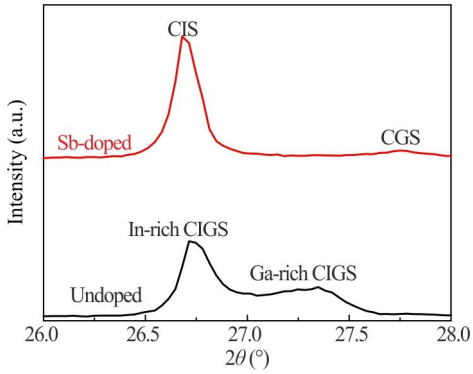

Fig.4 The (112) peaks of CIGS films with and without Sb doping selenized at 400 °C

The existence of the phase separation of CIS and CGS (or In-rich CIGS and Ga-rich CIGS) in CIGS alloys results in the inhomogeneous distribution of elemental Ga[18]. The inhomogeneity causes band gap fluctuations which have a detrimental effect on the conversion efficiency of solar cells[19,20].

To reduce the phase separation between CIS and CGS phase in Sb-doped films, we modified the process by annealing the precursors in Se vapor in Step I to incorporate Se into the precursors before Step II. Fig.5 shows XRD patterns of CIGS films with and without Sb layer incorporation fabricated by the modified two-step selenization method. As expected, the Sb-doped sample selenized by the modified method shows improved Ga incorporation to chalcopyrite structure as compared to that selenized by the conventional method (Fig.3).

The V_{oc} of the Sb-doped samples is ~50 mV higher than that of the pure CIGS samples, indicating a higher absorber quality and less recombination for the Sb-doped films. We repeated this experiment and the Sb-doped samples still showed better performance.

Fig.6 shows SEM images of pure CIGS and Sb-doped CIGS samples prepared by the modified selenization process. As can be clearly discerned, the Sb-doped CIGS films show significant improvement in grain sizes. The reported mechanisms or explanations about how Sb promotes the grain growth are divergent. One possible mechanism of the grain growth improvement is the migration of Sb, which facilitated the mass transport in CIGS thin films[21].

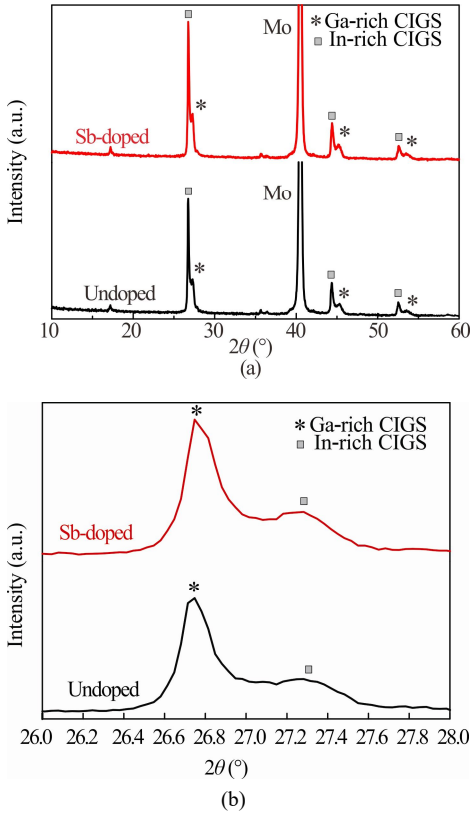

Fig.5 (a) XRD patterns of CIGS films with and without Sb doping fabricated by modified two-step selenization method; (b) Enlarged XRD peaks of CIGS films from 26° to 28°

To explore the impact of Sb doping on the device performance, we fabricated two cells using the modified selenization process. When thicker Sb layers were used (1 mol%), we have encountered peel-off problems in the CdS deposition step, while the films deposited with a thinner Sb layer (0.1 mol%) showed good adhesion. The reason might be that the Sb has not been consumed during the CIGS growth, leading to detachment of the CIGS layer from the Mo back contact in the chemical bath deposition (CBD)-CdS bath. Tab.1 lists the device parameters of CIGS solar cells with and without Sb doping, where V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, *FF* is the filling factor, and R_s is the square resistance. The Sb-doped cell shows superior device characteristics. Power conversion efficiency was improved from 6.13% to 7.15% with Sb doping.

The effects of Sb doping on the properties of CIGS thin films and solar cells prepared by electrodeposition have been demonstrated. Stacked Cu/Sb/In/Ga layers

Tab.1 Performance parameters of CIGS solar cells with and without Sb doping

Samples	V_{oc} (mV)	J_{sc} (mA/cm^2)	*FF* (%)	R_s (Ω/cm^2)	Efficiency (%)
Pure CIGS	402	24.94	61.3	2.92	6.13
Sb doped CIGS	448	24.72	64.5	2.99	7.15

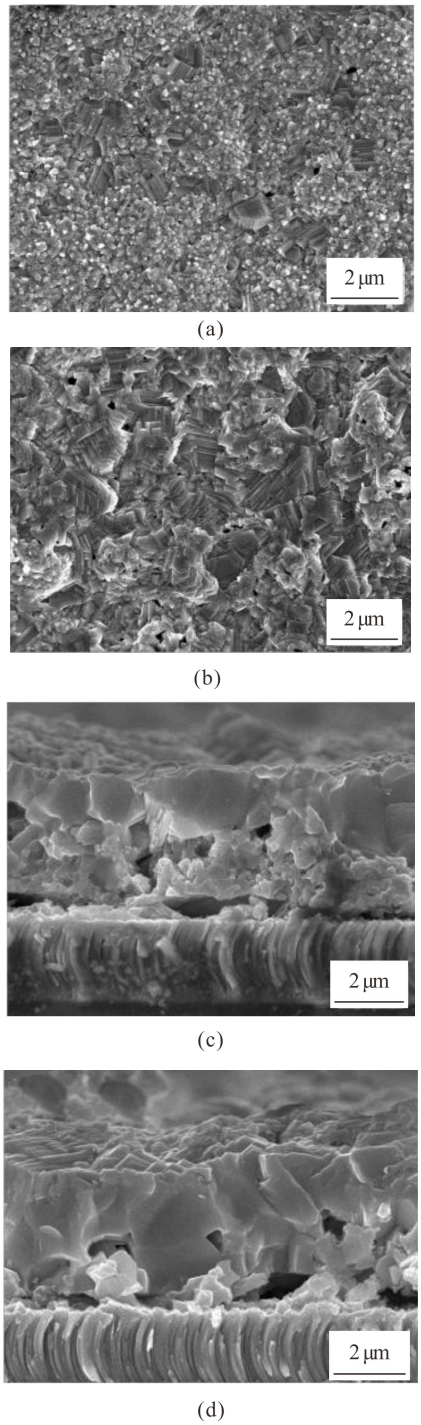

Fig.6 SEM topographic and cross-sectional images of (a, c) pure CIGS film and (b, d) Sb-doped CIGS film prepared by modified selenization process

were deposited in order to dope Sb into CIGS. Both doped and undoped films were annealed in Se vapors and the effect of Sb doping on the structural properties of CIGS thin films was investigated. A distinct phase separation of CIS and CGS occurred in Sb doped CIGS thin films and the mechanism is analyzed. A modified selenization is presented to reduce the phase separation. Consequently, the conversion efficiency of the completed device is improved from 6.13% to 7.15% by Sb doping, probably related to the significant improvement in grain structure of the Sb doped CIGS thin films.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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