Influence of growth temperature and thickness on the orientation of $Cu(In,Ga)Se_2$ film*

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$Cu(In,Ga)Se_2$ (CIGS) films are deposited on the Na-free glass substrate using three-stage co-evaporation process, and the effects of thickness and growth temperature on the orientation of CIGS film are investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). When the growth of CIGS film does not experience the Cu-rich process, the increase of the growth temperature at the second stage (T_{s_2}) promotes the (112) orientation of CIGS film, and weakens the (220) orientation. Nevertheless, when the growth of CIGS film experiences Cu-rich process, the increase of T_{s_2} significantly promotes the (220) orientation. In addition, with the thickness of CIGS film decreasing, the extent of $(In,Ga)_2Se_3$ (IGS) precursor orientation does not change except for the intensity of Bragg peak, yet the (220) orientation of following CIGS film is hindered, which suggests that (112) plane preferentially grows at the initial growth of CIGS film.

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To date, $Cu(In,Ga)Se_2$ (CIGS) solar cell is one of the most promising thin film solar cells because its efficiency nearly reaches the record of multi-crystalline Si solar cell[1]. For the orientation of polycrystalline CIGS thin films, it is usually with (112) or (220) preferred orientation. Some studies[2,3] reveal that different preferred orientations of CIGS films can bring different effects to the grain boundary activities. Chaisitsak et al[4] reported that with the increase of (220) orientation of CIGS film, the efficiency of CIGS solar cell increases at first and then declines, suggesting that the preferred orientation of CIGS film has significant effect on the device performance. In order to control and optimize the electro-optical properties of CIGS solar cell, some studies focus on investigating the preferred orientation of the films[4,5]. Contreras and Yamada[6,7] reported that the orientation of CIGS films is strongly dependent on the structural properties of the Mo layer. Some researchers[8,9] have suggested that the Se to metal flux ratio (SMR) during the co-evaporation process greatly affects preferred orientation of CIGS films, and with increasing the SMR, (220) orientation is promoted. Besides, Na-doped CIGS film can reduce the surfaces energy of (112) plane, which promotes the (112) orientation of CIGS film[10-13]. The results in our previous work[14] suggested that Fe-doped CIGS film increases the surface energy of (112) plane, thus hindering (112) orientation of CIGS film. In addition, another two factors of the growth temperature at the second stage (T_{s2}) and the film's thickness might have some effects on the orientation of CIGS film, which are not investigated in our previous work. In this paper, in order to exclude the Na or Fe doping effect on the orientation of CIGS film, Na-free glass substrates are used to investigate the influence of T_{s2} and thickness on the orientation of CIGS film.

CIGS films were deposited on the Na-free glass substrate using three-stage co-evaporation process. At first, the growth temperature at the first stage was kept at 350 °C, while CIGS films experiencing Cu-rich process and not experiencing Cu-rich process were deposited at 450 °C and 550 °C, respectively. The impacts of T_{s2} on CIGS film were investigated. In addition, in order to explore the relationship between the thickness and the orientation of CIGS films, CIGS films with the thicknesses of 0.8 μm, 1.5 μm and 2 μm were deposited through adjusting the deposition time.

The film thickness was measured by an AMBIOS XP-2 stylus profiler. The chemical composition of the films was measured by XRF-800 X-ray fluorescent spectrometer (XRF)

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with an Rh-anode, which was calibrated by inductivity coupled plasma spectroscopy (ICP) to ensure its accuracy. The structure and morphology of the CIGS films were measured by a Philips X pert Pro diffractometer with CuK_α radiation and JEOL JSM-6700 scanning electron microscopy (SEM), respectively.

Fig.1(a) and (b) show the X-ray diffraction (XRD) pattern and SEM image of $(In,Ga)_2Se_3$ (IGS) film. From Fig.1 (a), it can be seen that IGS exhibits strong (300) orientation, and no (006) peak is observed. Besides, the surface of IGS precursor is compact and smooth, as shown in Fig.1(b). Thus, the effect of roughness on the orientation of following CIGS film is not considered[15].

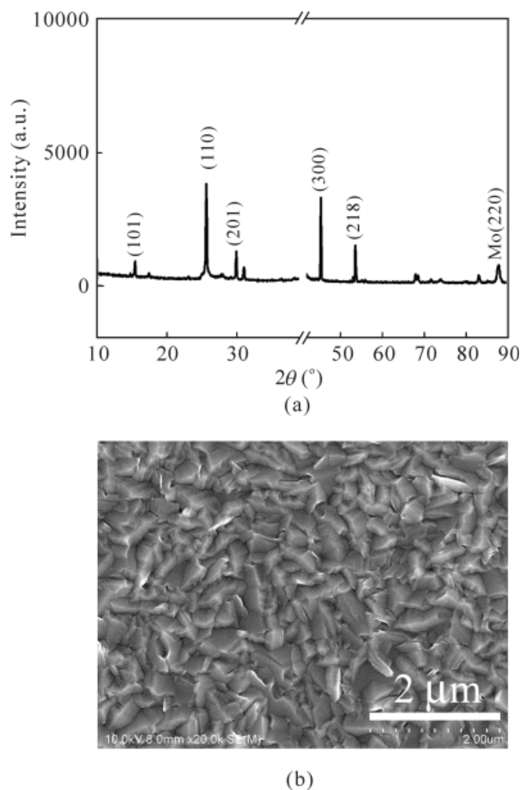

Fig.1(a) XRD pattern and (b) SEM image of IGS film

Fig.2(a) and (b) show XRD patterns of CIGS film not experiencing Cu-rich process and deposited at 450°C and 550°C, respectively. The composition ratios are Cu/(In + Ga)≈ 0.6 and Ga/(In+Ga)≈ 0.3, respectively. Here, we define F as the intensity ratio of (220) peak relative to (112) peak. The Cu-poor phase $CuIn_3Se_5$ is observed[16] due to the low Cu/(In+Ga). It can be seen from Fig.2(a) that when T_{s_2}=450 °C, F equals 7.3. However, with T_{s_2} increasing, F decreases from 7.3 into 3.9 as shown in Fig.2(b), suggesting that the (220) orientation of CIGS film becomes weaker with the increase of T_{s_2}. This phenomenon might be related to the fact that the increase of T_{s_2} accelerates the reconstruction from unstable (220) to stable (112) plane when CIGS is in considerably Cu-poor condition.

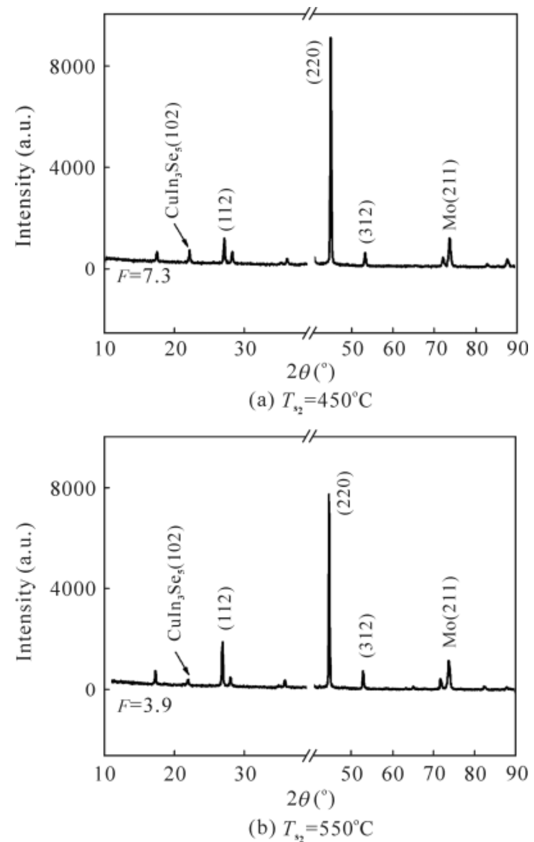

Fig.2 XRD patterns of CIGS films not experiencing Cu-rich process deposited at different temperatures

Fig.3(a) and (b) show XRD patterns of CIGS film experiencing Cu-rich process and deposited at 450°C and 550 °C, respectively. The composition ratios are Cu/(In+Ga)≈ 0.9 and Ga/(In+Ga)≈0.3, respectively. From Fig.3(a), it can be seen that when T_{s_2}=450°C, F equals 12.2. However, it is unexpected that when T_{s_2} is elevated into 550°C, F climbs up from 12.2 to 19.8, suggesting that the increase of T_{s_2} promotes the growth of (220) plane, and weakens the orientation of (112) plane. This result is different from Fig.2. Therefore, it is inferred that the impact of T_{s_2} on CIGS film depends on whether the CIGS film experiences Cu-rich process. In addition, the result from comparing Fig.3(a) with Fig.2(a) suggests that F rises from 7.3 to 12.2 at 450°C when CIGS film experiences Cu-rich process. However, for 550°C, F increases more evidently from 3.9 to 19.8.

At the initial stage of CIGS film growth, Cu content in the whole film is rather low, thus lower Cu content in grain boundaries (GBs). Similar to the surface of CIGS film, the interface near GBs reconstructs from unstable (220) to stable (112) plane. When T_{s_2} increasing, the accelerated reconstruc-

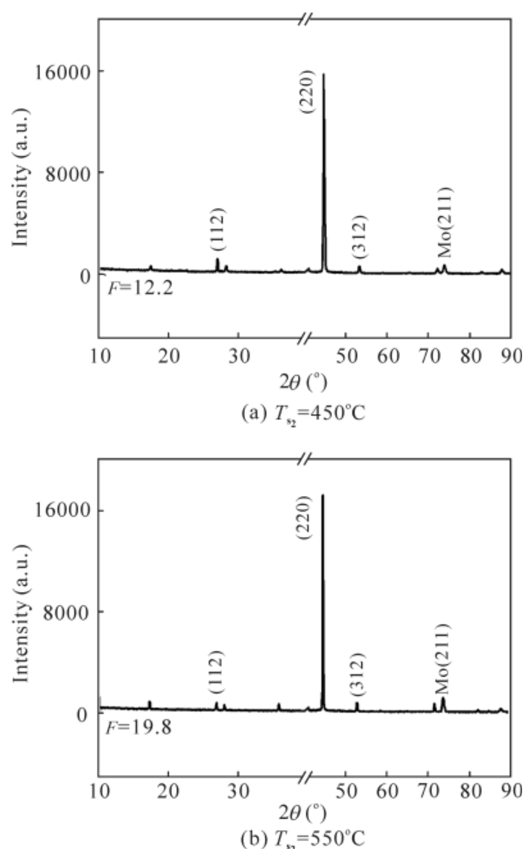

Fig.3 XRD patterns of CIGS films experiencing Cu-rich process deposited at different temperatures

tion may occur, and thus (220) orientation of CIGS film decreases. However, with the Cu content increasing in the CIGS film, Cu-Se compound appears at GBs, and covers the surface of grain. When the whole CIGS film is Cu-rich, the surface of CIGS film is also covered by Cu-Se compound. In this condition, the surface energy of (220) plane is lower than that of (112) plane[17]. In addition, in this condition, the surface and interface of CIGS film are not reconstructed. Therefore, high Cu content can promote the preferential growth of (220) plane. Moreover, the more evident increase of (220) orientation at 550 °C is attributed to the liquid Cu-Se when the temperature is higher than 523 °C[18]. Liquid Cu-Se compound can cover the surface and interface better, reducing the reconstruction probability.

Fig.4 shows XRD patterns of CIGS films with different thicknesses of 0.8 μm, 1.5 μm and 2 μm, respectively. The composition ratios are Cu/(In+Ga)≈0.9 and Ga/(In+Ga)≈0.3, respectively. It can be seen that the preferred orientation changes from (220) for CIGS film with 2 μm into (112) for that with 0.8 μm. It is reported that the orientation of CIGS film is very dependent on the orientation of its IGS precursor, where (006)-oriented IGS precursor promotes (112) orientation of CIGS film while (300)-oriented IGS precursor promotes the preferential growth of (220) plane[7]. Therefore, the orientation of IGS film is investigated when the thickness of IGS film decreases.

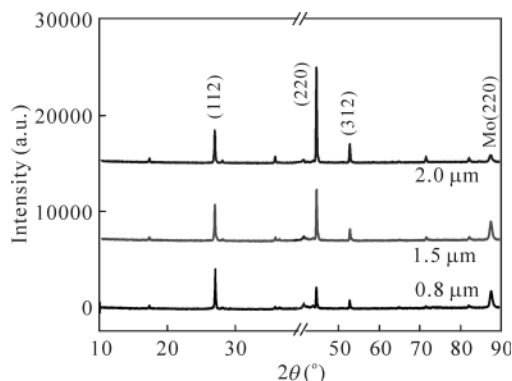

Fig.4 XRD patterns of CIGS with the thicknesses of 0.8 μm, 1.5 μm and 2 μm, respectively

Fig.5 shows XRD patterns of IGS films with the thicknesses of 0.7 μm and 1.5 μm, respectively. It is found that the (110) and (300) planes of IGS film with the thickness of 1.5 μm preferentially grow, and almost no (006) peak is observed. When the thickness of IGS film decreases, the intensity of (300) Bragg peak decreases, and (006) peak is still not observed yet. Therefore, we think that the decrease of the IGS film thickness leads to the reduced intensity of (300) peak, and does not promote the (006) peak. Besides, in Fig.4, it is also found that the intensity of (220) plane decreases evidently with the reduction of the CIGS film thickness, while that of (112) plane is nearly invariable. As we know, the structure of film is dependent on the surface energy and strain energy, and the surface energy plays the dominant role. Based on the above theory, the plane with the low surface energy could grow preferentially. As far as Cu-poor CIGS film, it is reported that the polar (112) surface is more stable than the non-polar (220) surface[19,20]. When Cu-Se compound reacts with the IGS precursor at the early stage, the CIGS film is in Cu-poor condition, and the (220) plane is easier to be recon-

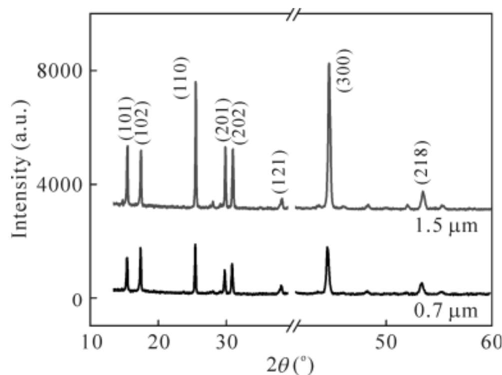

Fig.5 XRD patterns of IGS films with the thicknesses of 0.7 μm and 1.5 μm, respectively

structed into the (112) plane. Therefore, it is inferred that (112) plane of CIGS film could preferentially grow at the initial stage of film growth.

In conclusion, in this paper CIGS films are deposited on the Na-free glass substrate using three-stage co-evaporation process, and the impacts of thickness of films and growth temperature on the orientation of CIGS film are investigated by XRD and SEM. From the results, we find that the influence of the growth temperature T_{s_2} on the orientation of CIGS film is related to whether CIGS film experiences Cu-rich growth process. When the growth of CIGS film does not experience the Cu-rich process, the increase of T_{s_2} promotes the (112) orientation of CIGS film, and weakens the (220) orientation. Nevertheless, when the growth of CIGS film experiences Cu-rich process, the increase of T_{s_2} significantly promotes the (220) orientation of CIGS film. Therefore, it is inferred that Cu-Se compound can hinder the (112) orientation, and promote the growth of (220) orientation. In addition, the results suggest that with the thickness of CIGS film decreasing, the extent of IGS precursor orientation does not change except for the intensity of Bragg peak, yet the (220) orientation of following CIGS film is hindered, which suggests that (112) plane of CIGS film preferentially grows at the initial stage of film growth.

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