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Microstructure characterization of the soda-lime-glass/copper–indium–gallium–selenium interface in Cu-poor $Cu(In,Ga)Se_2$ thin films

Jian Wang, Yi Qiao, Jie Zhu *

State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China

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A B S T R A C T

The microstructure characteristics of the soda-lime-glass/$Cu(In,Ga)Se_2$ (SLG/CIGS) interface in Cu-poor CIGS films are investigated by transmission electron microscopy and selected area electronic diffraction (SAED). The SAED patterns show very sharp and strong spots, indicating the main structure of CIGS chalcopyrite. Small dispersed crystals with size distribution from 2 to 5 nm seem to be embedded in amorphous matrix, and additional spots indicate the presence of an ordered vacancy compound (OVC). This observation is consistent with the Raman results, and the OVC phase with the nanoclusters exists in the CIGS matrix, instead of layer structure. Lattice distortion results in local changes in contrast. Some pseudo-disordered structure is observed, however, the structure is actually the chalcopyrite CIGS structure. 180° rotation twins are also observed at the SLG/CIGS interface. Lattice distortion is widely observed at the interface of the Cu-poor CIGS films, and the extra spots could be caused by different lattice orientations.

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1. Introduction

Chalcopyrite $Cu(In,Ga)Se_2$ (CIGS) is an attractive material candidate for high-efficiency thin-film solar cells. Among all thin-film type solar cells, the record conversion efficiency of CIGS has reached at highest value of 20.8% by co-evaporation [1,2]. Up to now, most of the CIGS thin films used for high-performance solar cells are grown by either the co-evaporation or the post-selenization processes. Despite the great progress made on optimizing the preparation processes and photovoltaic performance of CIGS devices, the full potential of the CIGS absorber material has yet to be realized [2,3]. It is well known that the microstructure, optical and electronic properties of CIGS thin films strongly depend on the Ga/(In + Ga) and Cu/(In + Ga) compositional ratios, which plays a crucial role in achieving high conversion efficiency [4]. Generally, the CIGS absorbers of the high-efficiency solar cells are deliberately Cu deficient. For Cu-poor CIGS material, the formation of an ordered vacancy compound (OVC) on the surface is feasibility. This Cu-poor OVC phase, like $Cu(In,Ga)_3Se_5$ or $Cu(In,Ga)_2Se_{3.5}$, which is indicated to be *n* type, creates a buried heterojunction to replace the *p*-*n* junction between *p*-type CIGS chalcopyrite and *n*-type CdS [5].

Raman scattering measurements have shown that the presence of the OVC phase not only at the surface, but also next to the back contact in Cu-poor $CuInSe_2$ films [6]. Yan et al. reported on convergent-beam electron diffraction and energy-dispersive X-ray spectroscopy (EDS) study of the microstructure and composition of the surface region in Cu-poor CIGS thin films, and no OVC structure was detected in their samples [3]. Additionally, Zhang et al. found the surface and the bulk of the Cu-poor CIGS material exhibit a similar crystal structure, and OVC phases have been not observed by transmission electron microscopy (TEM) [7]. Understanding the proper physics and growth mechanism for the OVC phase formation in CIGS material is critical for further improvements of the devices performance. A Cu-deficiency parameter, Z, defined as (1-Cu/Ga) was used to study the phase transition in $CuGaSe_2$ material, and a series of OVC phase formations were observed with an increasing Z-value [8]. Raman spectra intensity of the chalcopyrite $Cu(In,Ga)Se_2$ band progressively increases with higher Cu content ($Cu/(In + Ga) \geq 0.60$), and the contribution from the OVC bands becomes negligible with higher $Cu/(In + Ga) > 0.80$ [9]. Therefore, the reason for the absence of OVC phases in TEM investigations may be the higher Cu/(In + Ga)-value.

In our previous studies, we have found that the OVC phases are located not only at the surface region, but also inside and next to the back interface in the Cu-poor CIGS layers [10,11]. Some groups have reported the microstructure and chemical composition of the surface layer and the bulk region in CIGS thin films by TEM [3,7,12,13]. However, so far, direct structural proof of the back interface is still missing. This work reports the results of our investigations on the microstructure and chemical compositions of the back interface regions in the Cu-poor CIGS thin films.

* Corresponding author. Tel.: +86 010 62334333; fax: +86 010 62333447.
E-mail addresses: wangjustb@gmail.com (J. Wang), jiezhu@ustb.edu.cn (J. Zhu).

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2. Experimental details

The CIGS films used in this study were grown by the post-selenization process, as described in Ref. [11]. For CIGS-based solar cells, the absorber films should be deposited on Mo back contact layer. To measure the optical properties of $Cu(In,Ga)Se_2$ films, however, we prepared the CIGS layers on bare soda-lime-glass (SLG) without Mo contact. The crystal phases and structures of the CIGS films were characterized with grazing incidence X-ray diffraction by X-ray diffractometer (XRD, Rigaku D/max2550HB +/PC, Cu $K\alpha$ and $\lambda = 1.5418$ Å). The step-scan covered the angular range 10–90° in steps of 0.02°, and the incidence angle was 1.0°. The results revealed that the films grown by the post-selenization process are of the chalcopyrite phase (not shown here). XRD result indicates no OVC phase detected in the CIGS films, and it is possible that the OVC phase may exist in a much thinner layer in the thin films than XRD can actually detect [3,7] and/or the peaks overlapping of the OVC and CIGS phases [11]. To further investigate the structural properties of CIGS thin films, depth-resolved Raman spectra measurements were performed at room-temperature, using a multichannel modular triple Raman system (JY-HR800) with a solid-state diode laser excitation source ($\lambda = 532$ nm) in backscattering configuration. The depth-resolved measurements were achieved by acquiring sequentially a series of Raman spectra after sputtering the samples with the laser beam. The typical spectrum acquisition time was 200 s, leading to a total measurement time per line of 5000 s [11]. In order to determine the microstructure of the SLG/CIGS interface region, TEM investigations were performed on a Tecnai G2 F30 S-TWIN microscopy operating at 300 kV. The sample for TEM measurements was prepared by a dual-beam focused ion beam (FIB, Zeiss Auriga) operating over a range of 5–30 keV with a milling current of 50 pA (Ga^+ ions), having a unique 2.5 nm resolution. By using Gatan DigitalMicrograph (DM, Gatan Inc.) 3.7.0 software, a fast Fourier transform (FFT) and/or an inverse fast Fourier transform (IFFT) of high resolution TEM (HRTEM) images can be conducted in a small assigned area.

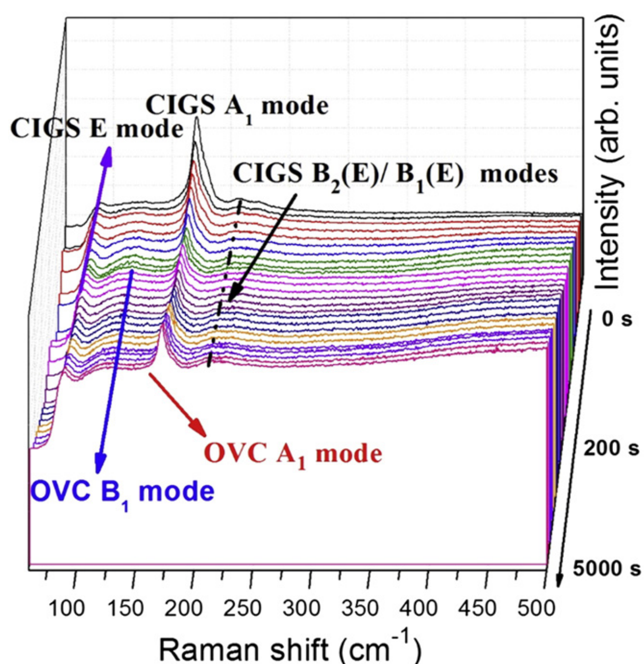

Fig. 1. Depth-resolved Raman spectra measured after sputtering the CIGS thin film down to various depths. The wavelength of the solid-state diode laser excitation source is 532 nm, and the step size is 200 s. The spectra are normalized to the intensity of the $Cu(In,Ga)Se_2$ A_1 mode.

3. Results and discussion

Fig. 1 shows the depth-resolved Raman spectra measured after sputtering the surface of the CIGS material at different depths. Details of the depth-resolved Raman analysis were described in Ref. [11]. The result indicated that the detected Cu-poor OVC phase was located not only at the surface region but inside and next to the SLG/CIGS interface in the Cu-deficient CIGS layer, which is similar to the finding in Cu-poor $CuInSe_2$ films [6,11].

The atomic percentage of Cu, In, Ga, and Se of the CIGS material by EDS measurement was 19.89%, 21.86%, 4.31%, and 53.94%, respectively. The Cu/(In + Ga) and Ga/(In + Ga) ratios calculated from EDS results were 0.76 and 0.16, respectively, indicating a Cu-deficient CIGS material with a low Ga content [11]. To get a better understanding of inner structure, the microstructure of the SLG/CIGS interface region was analyzed in the Cu-poor CIGS layer. Fig. 2(a) shows a cross-sectional bright field TEM image with four contrasts, denoted as P1, P2, P3, and P4, respectively. The substrate is on the left-hand side (not shown here). Similar to the findings at the Mo/CIGS [2,9,14,15] and/or GaAs/CIGS [16] interfaces by other research groups, voids are observed at the SLG/CIGS interface, which may be harmful to the device performance [10]. To examine the local chemical composition, TEM-EDS data, as shown in Fig. 2(b), were taken from the four regions P1, P2, P3, and P4, respectively. It can be seen that the P1 (Cu:Pt = 96.68 at.%:3.32 at.%) region contains only two elements Cu and Pt, originating from the copper TEM holder and the ion assisted Pt protection during the FIB process, respectively. In the P2 (Cu:Si:O = 77.05 at.%:3.87 at.%:19.08 at.%) region, Si and O are detected, which may be from the thermal-excitation loss of the SLG substrate during the selenization process. TEM-EDS data taken from the P3 (Cu:In:Ga:Se = 87.59 at.%:2.48 at.%:4.05 at.%:5.88 at.%) and P4 (Cu:In:Ga:Se = 68.52 at.%:5.69 at.%:3.23 at.%:22.56 at.%) regions show the coexistence of four elements Cu, In, Ga, and Se, however, the chemical composition in the two regions varies, indicating the presence of different quaternary compound phases. Fig. 2(c) shows a selected area electron diffraction (SAED) pattern along the [110] zone axis, which is taken from the designated area within the square box in Fig. 2(a). The SAED pattern indicates the coexistence of phases, including a chalcopyrite CIGS phase and an fcc Cu phase. Fig. 2(d) exhibits an HRTEM image of the P3 region, where small dispersed crystals with size distribution from 2 to 5 nm seem to be embedded in amorphous matrix (marked by red ovals). Fig. 2(e) depicts an HRTEM image of the selected area marked by the white circle in the P4 region (shown in Fig. 2(a)). The SAED pattern shows very sharp and strong spots (see inset of Fig. 2(e)), which can be indexed by chalcopyrite structure. The spacing of the lattice fringes was measured to be 0.3378 nm, which corresponds to the (112) lattice plane of the chalcopyrite CIGS structure. Fig. 2(f) is the IFFT image of Fig. 2(e) (marked by red square), and it reveals local changes in contrast (marked by red ovals), which may be caused by the lattice distortion in CIGS films.

To get a better understanding of the crystal structure, the microstructure of the regions P3 and P4 interface in the as-prepared CIGS film was analyzed. Fig. 3(a) exhibits an HRTEM image taken from the interface between the P3 and P4 regions, and the corresponding FFT image given in the inset verifies the chalcopyrite CIGS structure. The lattice structure of the CIGS is clearly visible in the P4 region, whereas there are occasional crystals showing lattice fringe contrast in the P3 region. Interestingly, some pseudo-disordered structure is observed in P4 (marked by red square in Fig. 3(a)). However, the IFFT and FFT images reveal that the structure is actually the chalcopyrite CIGS structure, as shown in Fig. 3(b). Fig. 3(c) shows the IFFT and FFT images of the selected oval area in Fig. 3(a). The bright main diffraction spots indicated by the white arrows are indexed to be ($2\bar{2}0$), ($1\bar{1}2$), and (004), demonstrating almost the same as the structure of chalcopyrite seen in Figs. 2(e) and 3(a). However, additional spots at ($00\bar{2}$), ($\bar{1}10$), and ($\bar{2}22$) are seen as indicated by the blue arrows in the inset of

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