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The effect of composition on structural and electronic properties in polycrystalline $CuGaSe_2$ thin film*

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Polycrystalline $CuGaSe_2$ thin films on Mo-coated soda-lime glass substrates have been synthesized by co-evaporation process from Cu, Ga and Se sources. Structural and electrical properties of the as-grown $CuGaSe_2$ films strongly depend on the film composition. Stoichiometric $CuGaSe_2$ is fabricated, as indicated by x-ray diffraction spectroscope (XRD) and x-ray fluorescence (XRF). A two-phase region is composed of $CuGaSe_2$ and $Cu_{2-x}Se$ phases for Cu-rich films, and $CuGaSe_2$ and $CuGa_3Se_5$ phases for Ga-rich films, respectively. Morphological properties are detected by scanning electron microscope (SEM) for various compositional films, the grain sizes of the $CuGaSe_2$films decrease with the extent of deviation from stoichiometric composition. Raman spectroscopy of Cu-rich samples shows that there exist large Cu-Se particles on the film surface. The results from Hall effect measurements for typical samples indicate that $CuGaSe_2$ films are always of p-type semiconductor from Cu-rich to Ga-rich. Stoichiometric $CuGaSe_2$ films exhibit relatively large mobility than any other compositional films. Finally, polycrystalline $CuGaSe_2$ thin film solar cell with a best conversion efficiency of 6.02% has been achieved under the standard air mass (AM)1.5 spectrum for 100 mW/cm^2 at room temperature (aperture area, 0.24 cm^2). The open circuit voltage of the $CuGaSe_2$ solar cells is close to770 mV.

Keywords: $CuGaSe_2$ thin films, $CuGa_3Se_5$, $Cu_{2-x}Se$
PACC: 8360J, 7280E, 7360F

1. Introduction

The advantages of developing wide band gap $CuGaSe_2$ (CGS) thin film solar cells are as follows: i) as a high open circuit voltage device, they offer the prospects of reducing serial resistance losses in a module and of lower temperature sensitivity; ii) CGS can be used as a high band gap partner for the top cell in a tandem stacking solar cell structure.[1,2] Currently, considerable efforts have been made to optimize the device performance of CGS films. Unfortunately, the CGS thin film solar cells cannot reach the conversion efficiency of $Cu(In_{1-x}Ga_x)Se_2$ devices due to their basic differences in doping behaviour, recombination mechanism and interface formation.[3] So far the surface-modified CGS/CdS/ZnO solar cells based on CGS polycrystalline thin films have demonstrated a record efficiency of 10.2%.[2] The cell performance was limited by the quality of CGS absorber including the structural and electrical properties of the as-deposited films. As is known, the properties of I–III–VI chalpyrite semiconductor films strongly depend on the compositional ratios of Cu/III and Se/metal.[4−8] Therefore the study of composition-dependent structural and electrical properties is necessary for improving the performances of CGS thin film solar cells.

In our previous studies, we have fabricated CGS thin films on Mo-coated soda-lime glass substrates by using the physical vapour deposition (PVD) technique.[9] In order to better understand the relations between compositional ratios and structural properties, electrical properties and CGS solar cells, in this paper, we systematically investigate CGS thin films by using XRD, Raman spectra, SEM, Hall effect measurement, and we also report on an efficient CGS thin film solar cell.

2. Experimental details

Polycrystalline CGS thin films were deposited by using a three-stage co-evaporation process from Cu,

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Ga and Se sources. The substrate temperature during the first stage and second stage were kept at 350°C and 550°C, respectively. In the first stage, the 90% Ga and Se elements were co-evaporated to form a Ga_2Se_3 precursor. In the second stage, Cu and Se were evaporated onto the precursor to grow Cu-rich CGS thin films. The end of the second stage was determined by sensing the drop of the substrate temperature. In the third-stage, the remaining 10% Ga and Se were evaporated to finish the deposition of the $CuGaSe_2$ thin films. Various compositional CGS thin films with a thickness range of 1.5–2.5 μm were obtained by changing depositions conditions. The chemical compositions of the CGS films were determined by x-ray fluorescence spectroscope (XRF). Structural and morphological properties were determined by XRD, and SEM and Raman, respectively. Electrical characterizations of the films were carried out by Hall effect measurement. The completion of CGS thin film solar cells on Mo-coated soda-lime substrate followed the standard process as described elsewhere.[2] The current density–voltage (J–V) measurements were performed under the standard AM1.5 spectrum for 100 mW/cm^2 at room temperature.

3. Results and discussion

3.1. Structural properties of $CuGaSe_2$ films with different compositions

3.1.1. XRD analysis

X-ray diffraction patterns of several $CuGaSe_2$ films from Cu-rich to Cu-poor compositions deposited on glass substrates are indicated in Fig.1. Figure 1(a) shows the XRD pattern of single phase $Cu_{2-x}Se$, which was deliberately synthesized for a comparison. For the Cu-rich thin films as shown in Fig.1(b), in addition to the typical diffraction planes of the tetragonal CGS phases, two peaks characteristic of the $Cu_{2-x}Se$ (111), (220) phase are present as compared with Fig.1(a). The existence of this binary phase is consistent with the phase diagram for such compositional CGS films.[10] When the composition ratio of Cu/Ga is about 1:1, no second phases have been detected, and single phase $CuGaSe_2$ films are formed in Fig.1(c). The splitting of the (220), (204) and (312), (116) and (400), (006) and (332), (413) peaks for the single phase CGS film is an indication of the ordering in the tetragonal phase of the material. In the Cu-poor films, a two-phase region is composed of $CuGaSe_2$ and $CuGa_3Se_5$ which are the Ga-rich compounds. The presence of the single $CuGa_3Se_5$phase is detected when the ratio of Cu/Ga/Se is about 11.1:33.2:55.7 (Fig.1(d)). When the Cu/Ga ratio is less than 0.34, Ga_2Se_3 and $GaSe_{1.08}$ phases are also present, which maybe depends on the amount of excess of gallium and selenium present.[11] Additionally, we find that the values of FWHM of (112) and (220) chalcopyrite structural diffraction peaks become broadened from Cu-rich to Cu-poor samples, which are related to the grain size and the crystallinity of CGS films.

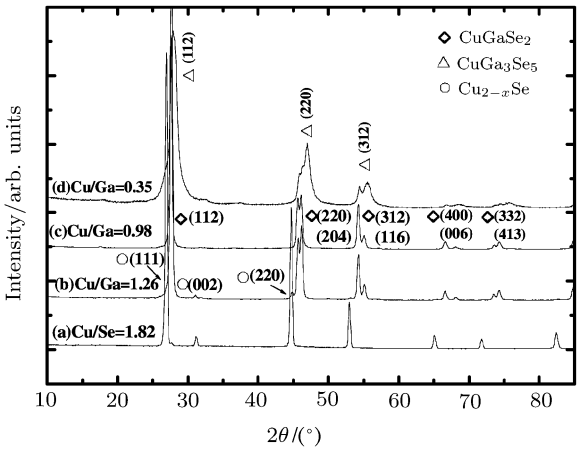


Fig.1. XRD spectra of CGS layers from Cu-rich to Cu-poor compositions: Cu/Se=1.82 (a), Cu/Ga=1.26 (b), Cu/Ga=0.98 (c) and Cu/Ga=0.35 (d).

3.1.2. SEM analysis

We can find that the morphologies of CGS thin films are strongly dependent on the composition from Figs.2(a)–2(d). Cu-rich samples in Fig.2(a) exhibit small and homogeneous grains and also present several large white dots on the film surface. Single phase CGS films show better crystalline quality than any other films whose compositions deviate from their corresponding stoichiometric ones (Fig.2(b)). And the average grain size of about 1–2 μm is observed for a single phase CGS film. The two-phase mixture of $CuGaSe_2$ and $CuGa_3Se_5$ show the morphologies similar to those of single phase CGS films (Fig.2(c)) except for the smaller grain size, which is because single phase CGS film experiences a liquid phase Cu_xSe enhanced grain growth during the second stage in the three-stage process.[2] SEM images of Fig.2(d) reveal triangular crystallites for single phase $CuGa_3Se_5$. Similar morphologies have already been observed in PVD-grown Ga-rich CGS films.[12] Dittrich *et al*[13] interpreted these crystallite shapes by analysing the theoretical growth rates in different lattice-directions.

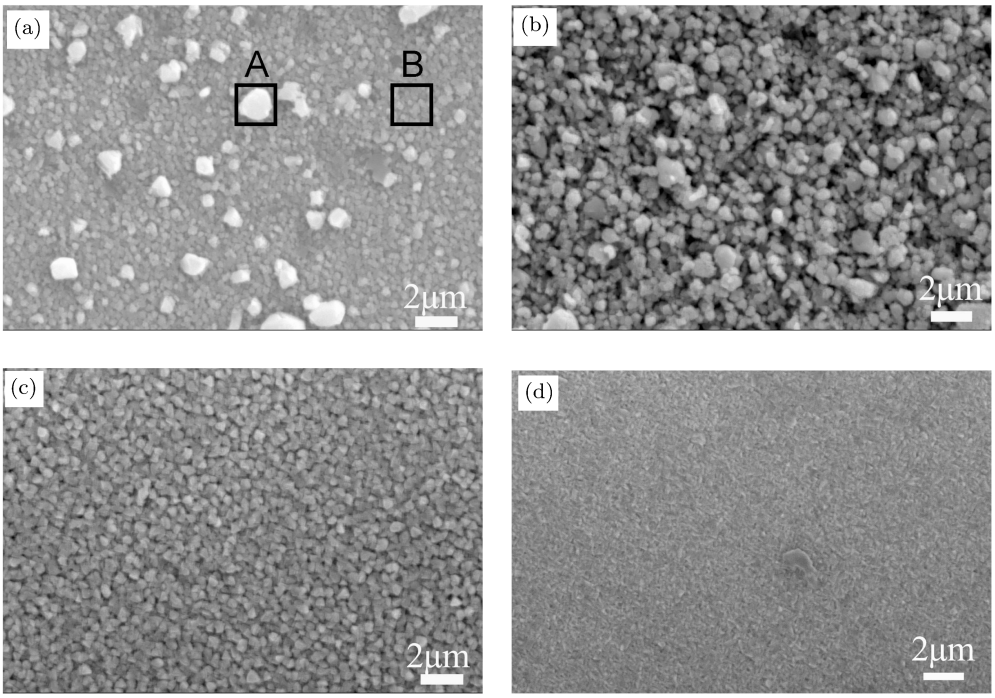


Fig.2. SEM images of Cu-rich CGS film with Cu/Ga=1.26 (a), single phase CGS film with Cu/Ga=0.98 (b), two-phase region of CGS and $CuGa_3Se_5$ with Cu/Ga=0.82 (c), and single phase $CuGa_3Se_5$ films with Cu/Ga=1:3 (d).

3.1.3. Raman spectra

CGS thin films used for record efficiency solar cells are grown via a Cu-rich phase, where Cu selenide is formed.[2] In order to obtain a larger grain size it is important to investigate the structure properties of Cu-rich CGS thin films. Figure 2(a) shows an SEM image of a Cu-rich CGS film. We can see that the relatively large white dots are formed on the film surface. Micro-Raman measurements were performed for the investigation of white dot A and other position B (without white dot) as shown in Figs.3(a)–3(c). The Raman spectra of $Cu_{1.8}Se$ show (Fig.3(a)) a distinct peak near 260 cm^{-1} (A1 mode),[14] indicates the presence of $Cu_{2-x}Se$ single phase consistent with XRD results. For dot A (Fig.3(c)) and the position B (Fig.3(b)), the Raman modes of CGS film appears at 181 cm^{-1} (A1 mode), 244 $cm^{-1}$and 270 cm^{-1} in addition to the Raman peaks $Cu_{2-x}Se$. The A1 mode of CGS has been ascribed to the motion of Se relative to Cu and Ga at rest (breathing mode).[15] In contrast to the CGS surface (position B), the increase in 260 cm^{-1} peak intensity of dot A is observed obviously. That should be attributed to the formation of Cu-rich Cu-Se compounds. Therefore, from the above analysis we can conclude that $Cu_{2-x}Se$ is formed if the film composition turns into Cu rich composition. These binary selenides of $Cu_{2-x}Se$ segregate mainly on the film surface and the white dots may be the large $Cu_{2-x}Se$ grains.

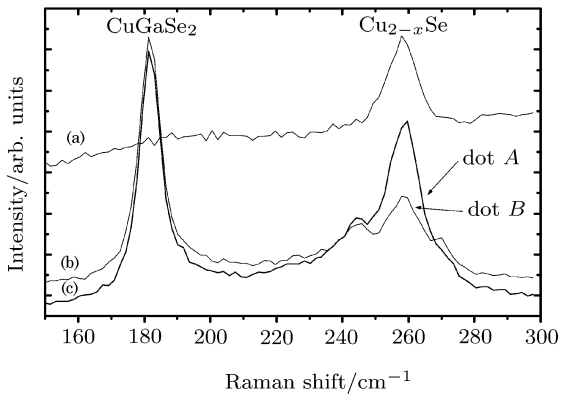


Fig.3. Micro-Raman spectra of a Cu-rich CGS film in which the $Cu_{2-x}Se$ is used as a reference (a), the CGS surface has no white dot B (b), and the CGS surface has white dot A (c).

3.2. Electrical properties of $CuGaSe_2$ films with different composition

3.2.1. Hall effect results

The conductivity (σ), the hall mobility and the carrier concentration were measured by using the van der Pauw technique. We have fused In balls on the surface as ohmic contact, thereby forming a slight contact resistance. The results from Hall effect measurements are shown in Table 1. $CuGaSe_2$ films are always of p-type semiconductor for all the compositions from Cu-rich to Ga-rich. Until now, only schöne *et al* have fabricated n-$CuGaSe_2$ single crystals by using the heavy co-doping Ge and Zn elements.[16] CGS films are shown to be always of p-type, which can be explained by using the doping pinning rule of CGS films.[17,18] The rule is that when the n-type dopants are introduced, the formation energy $\Delta H(V_{Cu})$ is lowered due to E_F moving towards the CBM. When the $\Delta H(V_{Cu})$ is close to zero, Cu atoms leave the lattice spontaneously. Since such Cu vacancies are acceptors which capture free electrons, the Fermi level can no longer rise towards the CBM. For Cu-rich CGS film, H1, the free carrier concentration and conductivity are higher than those other of samples, which is explained as resulting from the presence of metal-like $Cu_{2-x}Se$ secondary phase. The relatively low free carrier concentration for single phase CGS and Ca-rich films can be attributed to high degree self-compensation by intrinsic defects.[19] Hall effect measurements also reveal a dramatic increase of resistivity with Cu/Ga ratio of the films decreasing, and the values of mobility for all the samples increase with their compositions being close to their corresponding stoichiometric values. The mobility of 36.3 cm^2/Vs has been observed from H2 samples at room temperature for stoichiometric CGS films (Cu/Ga=0.98).

Table 1. Hall effect results from typical samples.

Sample number	Resistivity /Ω·cm	Mobility /(cm^2/V·S)	Carrier concentration /cm^{-3}	Consistent phases (XRD results)
H1	9.76	5.86	1.09×10^{17}	$Cu_{2-x}Se$, $CuGaSe_2$
H2	2.28×10^2	36.3	7.54×10^{14}	$CuGaSe_2$
H3	5.237×10^5	14.4	1.35×10^{12}	$CuGaSe_2$, $CuGa_3Se_5$

3.2.2. *J–V* analysis of $CuGaSe_2$/CdS solar cell

We have preliminarily made the CGS thin film solar cells with a structure of Al–Ni/i-ZnO/B:ZnO/CdS/CGS. The two different compositional films of Cu/Ga=0.82 (Fig.4(b)) and Cu/Ga=0.97 (Fig.4(a)) are used for device preparation. From the *J–V* curve in Fig.4(a), a conversion efficiency of 6.02% is obtained for our CGS solar cells, with the *J–V* parameters being as follows: short current density (J_{SC})=12.6 mA/cm^2, open circuit voltage (V_{OC})=767 mV and fill factor (FF)=61.2%. Such an efficient CGS solar cell, especially with a V_{OC} of 767 mV, should be related to the CGS absorber with large grain size, relatively high mobility and our optimized deposition process reported in the previous studies.[8] Compared with the solar cell of stoichiometric CGS film (Cu/Ga=0.97), the CGS solar cell with the Cu-poor composition (Cu/Ga=0.82) film shows a very lower efficiency of 2.15% (J_{SC}=9.05 mA/cm^2, V_{OC}=522 mV, FF=45.39% and active area S=0.24cm^2). The band gap of CGS film increases with the decrease of the ratio of Cu/Ga, and the band gap is around 1.83 eV when the Cu/Ga ratio is 0.35.[11] Thus, the CGS films with the Cu/Ga=0.82 should have a higher band gap which can elucidate the lower J_{SC} due to the light loss in a short wavelength region. However, we cannot achieve a higher V_{OC} as expected for widen band gap Cu-poor CGS films, which is attributed to the worse structural and electrical properties of CGS film with the composition deviating from the stoichiometric composition as shown by XRD, SEM and Hall effect measurements.

In contrast to the CGS thin film solar cell with a world record efficiency of 10.2%, however, the photovoltaic performance of our CGS solar cells is limited by their relatively low FF and V_{OC}. The lower FF results from a voltage dependence of the photocurrent as has been observed by Shafarman *et al*[7] for high Ga-content CIGS solar cells. The low V_{OC} compared with the band gap of CGS films can be explained from two aspects. Firstly, an inverted n-type interface is essential to the chalcopyrite based

solar cells because a p-type surface layer inverts an n-type layer which can cause a shallow buried p-n homojunction to avoid the dominance of interface recombination.[3] However, CGS films are always of p-type from our hall effect measurements in Table 1. That is reason why the world record CGS solar cells have been applied to a thin metal In layer for surface inversion.[2] Secondly, for the high efficiency Cu(In,Ga)Se_2(CIGS) solar cells, the conduction band offset between CIGS/CdS is positive while for $CuGaSe_2$ the band gap offset between CGS/CdS is negative. The negative offset of the conduction band will cause an interface-related and tunnelling-assisted recombination mechanisms, degrading V_{OC} finally.

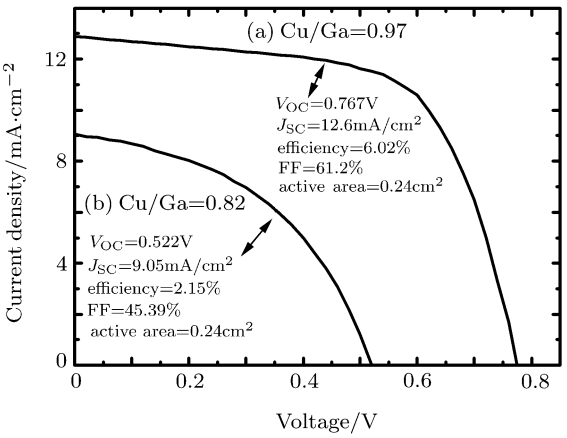


Fig.4. *J–V* curves of the CGS solar cell with different compositional ratios of Cu/Ga: 0.97 (a) and 0.82 (b).

4. Conclusions

Device-quality polycrystalline $CuGaSe_2$ thin films have been obtained on Mo-coated soda-lime glass substrates by using a three-stage deposition process. Structural and electrical characterizations of the as-grown $CuGaSe_2$ films strongly depend on the film composition. Stoichiometric CGS films are obtained with features expected for this kind of compound (p-type, single phase, relatively large grain size and mobility), showing the photovoltaic material quality. Cu-rich thin films exhibit the secondary $Cu_{2-x}Se$ phase which affects the various properties of the material. Ga-rich thin films are probably a mixture of phases: CGS and $CuGa_3Se_5$. The $CuGa_3Se_5$ phase is also grown and characterized; Ga-rich films show a high resistivity and a low mobility. Finally, polycrystalline CGS solar cells show a conversion efficiency of 6.02% without anti-reflection layer under AM1.5 illumination, and the loss mechanism of efficiency is analysed. Further improvement of the cell efficiency will depend on the careful treatment of the absorber surface to form the buried homojunction. More detailed research on widen band gap $CuGaSe_2$ thin film solar cells is in progress.

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