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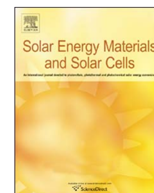

Influence of Cu on Ga diffusion during post-selenizing the electrodeposited Cu/In/Ga metallic precursor process

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ABSTRACT

Gallium accumulation, caused by faster reaction of indium with Se than gallium with Se, is a critical issue for post-selenization process, which limits the optimization of surface energy bandgap and open circuit voltage of CIGSe thin film solar cell. In this study, large-grained and compact CIGSe thin film was successful fabricated by electrodeposition and a three-step vapor Se/N_2/vapor Se reaction process. The influence of the Cu content on gallium diffusion and grain growth of CIGSe thin film was studied. The compositions, element distributions, and morphologies of CIGSe thin films were studied. The results revealed that the gallium diffused homogenizely through the film with Cu/(In + Ga) < 0.9, while accumulated at the back contact region with Cu/(In + Ga) > 0.9. Single phase and large-grained CIGSe thin films were obtained with Cu/(In + Ga) ratios between 0.78 and 0.9. $Cu(In,Ga)Se_2$ solar cells made with the CIGSe thin films presented highest efficiency of 11.22%. The solar cell based on the single phase and large-grained CIGSe absorber with Cu/(In + Ga) = 0.85 presents highest conversion efficiency of 11.22%, fill factor of 63.83% and V_{OC} of 514 mV.

1. Introduction

$Cu(In,Ga)Se_2$ (CIGSe) based thin film solar cells have presented high efficiency of up to 22.6% [1]. Up-to-date, the best CIGSe absorbers have been obtained by coevaporation [1–3], which requires an evacuated confined space and is not conducive to the cost-effective deposition of uniform films over large-area substrates. The process of electrodepositing Cu/In/Ga precursors followed by post-selenization treatment has been demonstrated a promising alternative method for scaled-up productions with low cost. The highest efficiency for CIGSe solar cell prepared by electrodeposition method is 17.4% [4], which is far below the certified efficiency of 22.6% [1]. One of the factors responsible for this underperformance is gallium accumulation, which leads to the formation of fine-grained $CuGaSe_2$ phase near the back contact region [5–7]. This fine-grained $CuGaSe_2$ layer increases the defects and grain boundaries, inducing the increase of recombination loss. Besides, the accumulation of gallium induces a formation of bi-layered structure with $CuInSe_2$ layer (Eg = 1.0 eV) on the top surface and $CuGaSe_2$ layer (Eg = 1.68 eV) at the bottom of the film. The absence of gallium near the p-n junction leads the film surface energy bandgap lower than the ideal bandgap of 1.3–1.5 eV, which will result in a low open circuit voltage and an increased operating current. Thus, gallium homogenization during post-selenization process is key to fabricate high quality CIGSe thin films and solar cells.

Studies have demonstrated that the preferential or faster reactions of indium with Se than gallium with Se yielded the accumulation of gallium [8–10]. Marudachalam et al. [11] reported that the indium and gallium could be homogenized with higher annealing temperatures (> 600 °C) and/or longer selenization times (> 60 min). Single phase CIGSe films could be obtained by annealing bi-layered CIGSe films in argon atmosphere with lower temperatures (500–600 °C), which was benefited from Se vacancies created by Se loss from the film. Hanket and Kim et al. [9,10,12] reported a three-step $H_2Se/Ar/H_2Se$ or H_2S reaction to enhance gallium diffusion successfully, and gallium homogenization was obtained during the Ar annealing step. Other studies have shown that the issue of gallium accumulation could also be overcame by controlling the reaction process [13,14]. Schroeder et al. [15] demonstrated that the film composition was an important factor in controlling Ga diffusion in $CuInSe_2$. Actually, in the CIGSe chalcopyrite crystals, there are two types of cation site, one site is occupied by Cu

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(group I) atoms, the other site is occupied by gallium and indium (group III) atoms [8,11]. The sites available for the gallium atoms near the surface are very limited with most of the group III sites being occupied by the indium atoms forming $CuInSe_2$ phase on the film surface. As a result, gallium is driven to the Mo back contact interface and form $CuGaSe_2$ phase. However, if the cation site of group I is available, gallium atoms may diffuse through the film by these sites. In Cu-poor films, Cu vacancy (V_{Cu}) will form to account partially for the deviation from stoichiometry, and a gallium atom may occupy this cation site to form Ga_{Cu} defects, which will help to improve the gallium diffusion. Additionally, Cu can produce copper-selenide phase during selenization step, which helps to form large-grained CIGSe thin film and high quality device [16,17]. Therefore, it is meaningful to study the correlation between Cu content and gallium diffusion during post-selenization process.

In this work, we studied the influence of Cu content on gallium diffusion of CIGSe thin film fabricated by electrodeposition and post-selenization process. A three-step vapor Se/N_2/vapor Se reaction process was employed to prepare CIGSe thin films. The compositions, elemental distributions, and morphologies of CIGSe thin films are characterized. Single phase and large-grained CIGSe thin film with homogenized gallium distribution was prepared when the ration of Cu/(In + Ga) was in the range of 0.78 and 0.9.

2. Experimental

Mo layer (1 µm), as substrate and cathode, was deposited on soda-lime glass (SLG) by direct current magnetron sputtering. Prior to depositing Cu/In/Ga precursors, all the Mo/SLG substrates were ultrasonically cleaned in ethanol for 30 min followed by being ultrasonically cleaned in HCl solution ([HCl]: [H_2O] = 1:2) for 5 min, then were rinsed with deionized (DI) water. Cu, In, and Ga layers were prepared sequentially on clean Mo/SLG substrates by pulse current electrodeposition method. The pulse current density used for Cu, In, and Ga deposition were 62.50, 125, and 125 mA cm^{-2}, respectively. The pulse frequency were 100,000, 100,000, and 5 Hz, respectively. The duty cycle were all 25%. The unit quantity of electricity used for Cu, In, and Ga deposition were 0.5 C cm^{-2}, 0.75 C cm^{-2}, and 2 C cm^{-2}, respectively. The solution composition of Cu, In, and Ga were reported elsewhere [18]. All the chemicals are analytically pure reagent (AR). When the based pressure in vacuum chamber is below 3×10^{-4} Pa, the electrodeposited Cu/In/Ga metal precursors were annealed with three-step vapor Se/N_2/vapor Se reaction process to prepare CIGSe absorbers [18–20]. The reaction process: In the first step, the substrate temperature was set at 400 °C, the samples were annealed in a Se-containing atmosphere for 8 min with a Se temperature of 240 °C; In the second step, the samples were annealed at 580 °C for 30 min in an environment of pure N_2 at a pressure of 1000 Pa; In the third step, the samples were further selenized at 580 °C for 15 min in a Se-containing atmosphere with a Se temperature of 240 °C. There were two sets of CIGSe absorbers: one set was with the Cu/(In + Ga) ratio in the range of 0.3 and 1.1, it was intend to confirm the proper range of Cu content that would favour Ga diffusion and grain growth; the other set was with Cu/(In + Ga) ratio between 0.78 and 0.92, aiming to fabricate high quality and large-grained CIGSe absorbers; Ga/(In + Ga) ratios of two sets were both 0.3. CIGSe solar cells with the structure of SLG/Mo/CIGSe/CdS/i-ZnO/ZnO:Al/Ni-Al were fabricated, as shown in ref. [19]. The active areas of CIGSe solar cells were 0.34 cm^2.

The composition of CIGSe thin films were determined by a MagixPW2403 X-ray fluorescent spectrometer with an Rh-anode calibrated using inductively coupled plasma spectroscopy to ensure its accuracy. The structure of CIGSe films were analyzed by a Philips X-pert pro X-ray diffractometer with Cu Kα as the radiation source and a Raman spectrometer (Renishaw + Nanonics) with an excitation wavelength of 514 nm. A scanning electron microscope (SEM, Hitachi S-4800) coupled with an energy-dispersive spectrometer (EDX) was used to characterize the morphology and elements content of the precursors and the selenized films. The J-V characteristics of the CIGSe solar cells were measured by a solar simulator under the standard AM1.5 spectrum with illumination intensity of 1000 W m^{-2} at room temperature. The light intensity of the solar simulator was calibrated with a standard monocrystalline Si reference solar cell. External quantum efficiency (EQE) measurements were performed by measuring the short-circuit current with spectrally resolved monochromatic light.

Table 1
Atomic concentration (at%) of the CIGSe thin films with different Cu/(In + Ga) ratio measured by XRF, noted as B-1, B-2, B-3, B-4, and B-5, respectively.

No.	Cu, at%	In, at%	Ga, at%	Se, at%	Cu/(In + Ga)	Ga/(In + Ga)
B-1	9.79	22.58	9.83	57.80	0.302	0.303
B-2	14.73	20.76	8.69	55.83	0.500	0.295
B-3	19.24	18.98	8.32	53.46	0.705	0.305
B-4	23.44	18.22	7.87	50.37	0.898	0.301
B-5	26.21	16.76	7.02	50.02	1.102	0.295

3. Results and discussion

Table 1 lists the compositions of CIGSe thin films with different Cu/(In + Ga) ratio measured by XRF, named B-1, B-2, B-3, B-4, and B-5. The Cu/(In + Ga) ratios of B-1, B-2, B-3, B-4, and B-5 samples are about 0.3, 0.5, 0.7, 0.9, and 1.1, respectively. As listed in Table 1, the Se atomic concentrations of sample B-1, B-2, and B-3 are all above 50%, which may due to the formation of ordered vacancy compounds (OVC) such as $CuIn_3Se_5$ or $CuGa_3Se_5$ on the top surface or $MoSe_2$ phase at the Mo/CIGSe interface.

Fig. 1 shows XRD patterns of B-1, B-2, B-3, B-4, and B-5 samples, the inset is CIGSe(112) peaks. In Fig. 1, the XRD patterns of B-1, B-2, and B-3 samples show single phase, while B-4 and B-5 samples show two separated phases. Combined with the selenium amount listed in Table 1, the single phase of B-1, B-2, and B-3 samples may be composed of CIGSe phase and OVC, which is due to the XRD pattern of CIGSe similar with that of OVC. The formation of CIGSe single phase indicates that the gallium has been incorporated into $CuInSe_2$ lattice to form $Cu(In,Ga)Se_2$ compound. In the inset, the two separated peaks in B-4 sample at the

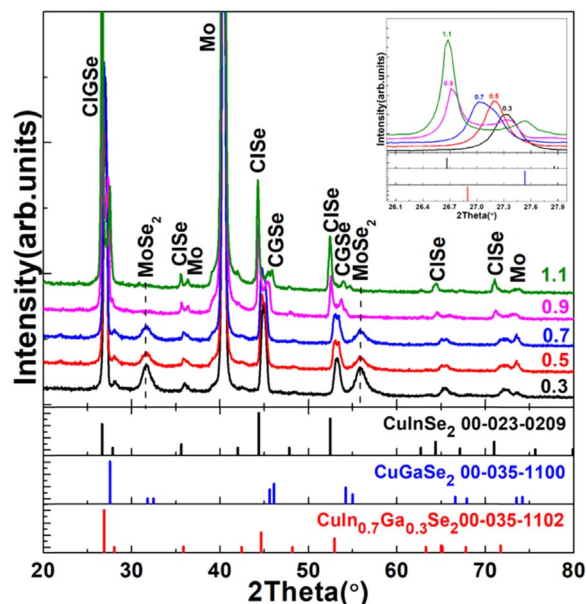

Fig. 1. XRD patterns of CIGSe thin films with Cu/(In + Ga) = 0.3, 0.5, 0.7, 0.9, and 1.1, noted as B-1, B-2, B-3, B-4, and B-5, respectively, and the XRD stick patterns of $CuInSe_2$ (PDF 00-023-0209), $CuGaSe_2$ (PDF 00-035-1100), $CuIn_{0.7}Ga_{0.3}Se_2$ (PDF 00-035-1102) located at the bottom, inset of Fig. 1 showing details of CIGSe (112) peaks.

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