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Microstructural characterization of CIGS formation using different selenization processes

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ABSTRACT

$Cu(In_{1-x},Ga_x)Se_2$ (CIGS) thin films were prepared by the sputtering of CuInGa precursors followed by chalcogenization via an isothermal (one-zone) selenization and a two-zone selenization. The effects of two selenization processes on the microstructural characteristics of CIGS films were also studied. In addition, we varied the selenization temperature for the two processes between 450 °C and 580 °C to investigate this effect on the microstructural characteristics and compositions of the CIGS films. The results indicated that the CIGS thin films formed using isothermal selenization had dense grain structure whose grains increased in size after an increase in the selenized temperature. However, the Se/(Cu + In + Ga) ratios of the films indicated that Se was distributed non-uniformly in the films, with Se-saturated CIGS present on the front side of the films and incompletely formed CIGS on the back side. In addition, it was noticed that Ga accumulated in large amounts in the films, depending on the chemical affinity between In and Se. Comparatively, the films prepared using two-zone selenization showed Ga accumulation that was only slightly greater than that in the films fabricated by the isothermal selenization. It is likely that the slow selenization of the CIG precursors reduced the extent of Ga accumulation because of the presence of Se in insufficient amounts. However, the presence of Se in insufficient amounts may also format the CIGS thin films with a porous microstructure.

1. Introduction

$Cu(In_{1-x},Ga_x)Se_2$ (CIGS)-based solar cells have been shown to have efficiencies as high as 20% during laboratory tests and 16.7% when used in solar cell modules in the field [1,2]. Two-stage methods are the most promising processes for fabricating these solar cells in a low-cost manner on an industrial scale [3]. In general, two-stage methods can be divided into the following two categories: (1) isothermal (one-zone) selenization [4–7] and (2) two-zone selenization [8–11]. Fig. 1a and b illustrates a schematic of the two selenization processes. In the isothermal selenization process, the selenization of the CuInGa precursors is carried out using Se vapors at around 550 °C in a vacuum chamber while ensuring that the vacuum is not broken. The temperature of the CuInGa precursors is increased steadily and rapidly along with the evaporation of Se, from room temperature to 550 °C and maintained at this temperature. The evaporation of Se is stopped once all the Se available has been exhausted. The films are annealed further to ensure the complete selenization and homogenization of the absorbers. In the two-zone selenization process as shown in Fig. 1(b), the distance between Se source and CIG precursor could adjust, depending on the viewpoints of seleinization design. During two-zone selenization, the precursors are annealed in a two-temperature-zone quartz, using which the temperatures of the Se source and the reaction zone can be detected and controlled independently. The Se source is heated to 350 °C and the resulting Se vapors transported using a carrier gas at a suitable flow rate to the reaction zone where the precursors, which are kept at 550 °C, are converted into CIGS films. During this selenization process, the vapors from the Se source and the flux of the carrier gas must be controlled precisely to induce the incorporation of Se into the metallic precursors while the carrier gas is being delivered.

Previous studies [9,12] have highlighted the importance of achieving sufficient homogenization of the CIGS films during the two-zone selenization process. A seemingly insurmountable disadvantage of this process is that the resultant absorber films are heterogeneous in nature. Because of the difference in the chemical affinity between Se and In and that between Se and Ga [13,14], the bulk of the material contains discrete $CuInSe_2$ and $CuGaSe_2$ phases, which are formed during the selenization (on-site or subsequent) process [15]. Meanwhile, the accumulation of Ga at the back contact, which is noticed in all the films, can inhibit the realization of the improvements in open circuit voltage (VOC) expected as a result of the increase in the band gap owing to the Ga alloying

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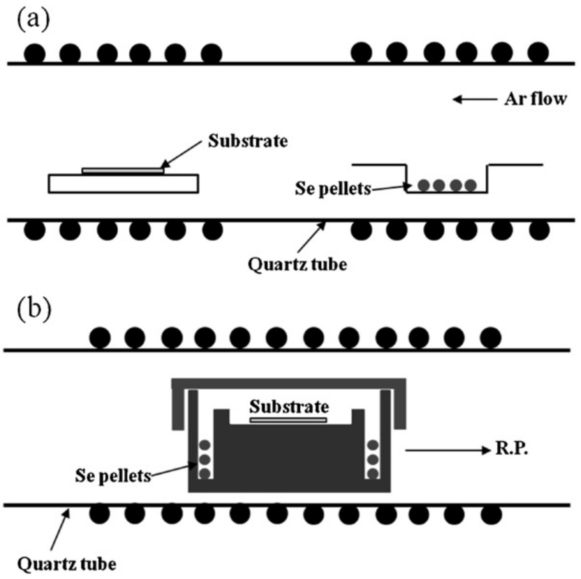

Fig. 1. The sketch of (a) isothermal selenization and (b) two-zone selenization.

[16]. In this sense, chalcogenization processes such as selenization and sulfurization should allow the control of the properties of the CIGS thin films used in I–III–VI$_2$-based solar cells. However, the standardization of the selenization process is important from the viewpoint of the mass production of solar cells. A detailed study of the effects of the two selenization processes on the microstructure of the prepared CIGS thin films is still lacking. In this study, we synthesized CIGS thin films via both isothermal (one-zone) selenization and two-zone selenization. The effects of the choice of the selenization process on the microstructural characteristics of the CIGS films were studied in detail. Additionally, in an attempt to study the chemical affinities between the various elements (Se–In and Se–Ga) and the extent of selenization, we varied the selenization temperature from 450 °C to 580 °C during the two selenization processes. This was also done to investigate its influence on the microstructural characteristics of and composition variations in the CIGS films in order to develop thin films with suitable properties.

2. Experimental detail

CIGS thin films were prepared by a two-stage process. During the first stage, an unbalanced magnetron (UBM) sputtering system was used to deposit CuGa/In/CuGa/In periodic precursors with total thickness of about 800 nm. The UBM system was equipped with a DC power supply (Advanced Energy, Pinnacle Plus +). Deposition was carried out in a vacuum chamber with a base pressure of 2×10^{-5} Torr. Prior to sputtering, the soda-lime glass (SLG) substrates were successively cleaned with acetone, isopropyl alcohol, alcohol, and deionized water, and finally dried under flowing N$_2$. The working pressure was maintained at 5×10^{-3} Torr during deposition to fabricate CIG precursors. During sputtering, the sputtered power density of CuGa and In were fixed at 1.25 W/cm^2 and 0.75 W/cm^2, respectively.

During the second stage of the process, solid Se pellets were used as a selenium source instead of highly toxic H$_2$Se. Metallic precursors were selenized by two different processes: (1) isothermal (one-zone) selenization; (2) two-zone selenization. The heating profile of the selenization methods was composed of four annealing steps: precursors homogenization (1st step), copper selenide and indium selenide compounds formation (2nd step), chalcogenization (3rd step), and recrystallization and grain growth (4th step). More details of this selenization process can be found elsewhere [17]. In this paper, we specially adjusted the 4th step from 450 °C to 580 °C to accomplish the CIGS thin films and further observed the microstructural characteristics of films.

In order to investigate composition variations between the front side and the back side of CIGS films, sections of reacted CIGS films were delaminated from the SLG substrates by bonding the film surface to a SLG glass then prying apart. The weakest interface was between the reacted film and SLG glass, so that the back side of the reacted CIGS films was exposed [18].

The morphologies and phase identification of CIGS thin films were determined by field-emission scanning electron microscopy (FESEM, JEOL operating at 5 kV, JSM-6500F, Japan) and by X-ray diffraction (XRD, MAC Science M03-XHF with a Cu Kα radiation, Japan), respectively. An electron probe X-ray microanalyzer (EPMA, JEOL, JXA-8200SX, Japan) was used for the elemental composition analysis.

3. Results and discussion

3.1. Microstructure analysis of the CIGS thin films

SEM images of the microstructures of the CIGS thin films synthesized at varied temperature between 450 °C and 580 °C using the isothermal (one-zone) selenization process are shown in Fig. 2a–c. The CIGS thin films selenized at 450 °C have a densely packed, small-grained structure and large grain boundaries. After an increase in the selenization temperature to 500 °C, the CIGS thin films produced show a dense surface with their structure being made of larger grains. In the latter case, a temperature as high as 500 °C is necessary to facilitate recrystallization and grain growth in the CIGS thin films. After an increase in the selenization temperature to 580 °C, the CIGS thin films formed showed good crystallinity, with their grains being well faceted (Fig. 2c). Interestingly, the grains of CIGS thin films formed by isothermal selenization at 580 °C became polyhedral in shape. In general, polyhedral-shaped grains are indicative of the CIGS chalcopyrite phase [12]. We noticed that temperatures greater than 550 °C have a much greater influence on the microstructure of the CIGS thin films, and infer that this could significantly affect the electrical properties of the thin films.

The CIGS thin films prepared at varied temperature between 450 °C and 580 °C by two-zone selenization are shown in Fig. 3a–c. The CIGS thin films formed by selenization at 450 °C have a porous (particle-like) morphology and intergranular voids. When the selenization temperature was increased to 500 °C, the CIGS thin films thus formed showed lower porosity while continuing to exhibit a porous (sheet-like) morphology. Lastly, the CIGS thin films formed by selenization at 580 °C comprised a polyhedral-shaped chalcopyrite phase, while exhibiting very few voids. The films were analyzed using an electron probe microanalyzer (EPMA), and the results of the analyses showed that the surface morphologies of the CIGS thin films depended on their compositional ratios. This indicates that the CIGS thin films with the polyhedral-shaped grains (Figs. 2 and 3c) have a Cu-rich chalcopyrite phase. However, a near-stoichiometric chalcopyrite phase is observed in the films with a relatively smooth surface morphology (Fig. 2a and b). This observation was also reported previously [12].

Fig. 4 a and b shows the back side morphologies of CIGS thin films selenized at 450 °C using two selenization processes. Meanwhile, the two figures are as representatives because of the similarity of back side morphologies in the different selenized temperature. The back sides of the CIGS thin films present rough surface with particle-like microstructure. Interestingly, there are distinct difference in the microstructure between the front side and back side on CIGS thin films. We could infer that the selenization condition has a much influence on the microstructure of entire CIGS thin films, which