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Effects of selenization parameters on growth characteristics of the Cu(In,Ga)Se_2 films deposited by sputtering with a Cu-In-Ga, Cu-In-Ga_2Se_3, or Cu-Ga-In_2Se_3 target and a subsequent selenization procedure at 550–700 °C

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ABSTRACT

Cu(In,Ga)Se_2 (CIGSe) thin films were prepared by sputtering with a Cu-In-Ga, Cu-In-Ga_2Se_3, or Cu-Ga-Se_2Se_3 target and a subsequent selenization procedure at 550–700 °C. The utilization of In_2Se_3 is to avoid the pre-matured formation of $CuInSe_2$, which form easily during selenization when metallic In exists in an as-deposited film. CIGSe films prepared with a Cu-Ga-In_2Se_3 target had shown the composition uniformity. The variations of microstructure, structure, and electrical properties with selenization temperature for films deposited by a Cu-Ga-In_2Se_3 target were investigated under a one-step or two-step selenization procedure. Selenization mechanism was proposed and its problems were presented. The influence of crystallinity and thin film microstructure on performance of electrical properties were investigated. CIGSe films sputtered by a Cu-Ga-In_2Se_3 target after two-step selenization at 600 °C showed a good microstructure and high mobility of 106 $cm^2\,V^{-1}\,s^{-1}$, avoided a two-layer structure formation in the CIGSe film, and obtain a better crystallinity because of high solute solubility in the selenium solution during a selenization procedure.

1. Introduction

Cu(In,Ga)Se_2 (CIGSe) solar cells have reached the power conversion efficiency (η) above 20% after decades of efforts [1]. The preparation methods for the I-III-VI_2 solar cells have been involved co-evaporation [2–4], single-step or multiple-step sputtering [5–9], hybrid process of sputtering and thermal evaporation [10], electroplating [11,12], hydrazine-based solution coating [13,14], powder-ink printing [15–17] *etc.* These methods also can be divided into the vacuum and non-vacuum categories [18]. A post selenization/sulfurization procedure has been frequently used to improve quality of the I-III-VI_2 films.

High-temperature post-selenization has been difficult for CIGSe films to obtain large and dense-packing grains due to the constitutional loss [19,20]. Basically, CIGSe solar cells with good efficiency did show the good crystallization, high densification, right composition, and large grain size due to the formation of the passivated polycrystalline [21]. Vacuum-type co-evaporation and non-vacuum-type hydrazine solution coating are the two approaches to reach the good microstructure with processing temperatures below 550 °C [1,13,14]. The common feature of these two approaches is the *in situ* incorporation of Se. The post-selenization can provide a simplified procedure to obtain CIGSe films but the outcomes still do not reach the expectations. The post-selenization needs to be improved or understood in order to find a solution for the two-stage (sputtering + selenization) method.

Here we describe the preparation of CIGSe films by selenizing cermet films sputter deposited with a Cu-Ga-In_2Se_3 target and a subsequent selenization procedure. The CIGSe films deposited with single Cu-In-Ga and Cu-In-Ga_2Se_3 targets are also studied for a comparative purpose. Our research interest is in the effect of selenization temperature (T_{Se})on characteristics of the CIGSe absorption layer. Few reports have demonstrated the synthesis of CIGSe films above 600 °C. The utilization of Cu, Ga, and In_2Se_3 in a cermet target is to maximize the metal contents in the as-deposited films for the considerations of higher deposition rate and faster grain growth and to avoid the problem of non-uniform Ga distribution. As our process temperature extends from 550 °C to 700 °C, many challenges in the control of Se vapor, residual stress, interfacial reaction, composition stability, stoichiometry *etc.* are needed to be overcome.

2. Experimental

Cu(In,Ga)Se_2 thin films grown on Mo-free and Mo-coated soda-lime glass plates were prepared by the post-selenization of the precursor films deposited by dc-magnetron sputtering with different kinds of targets, which involved Cu-In-Ga, Cu-In-Ga_2Se_3,

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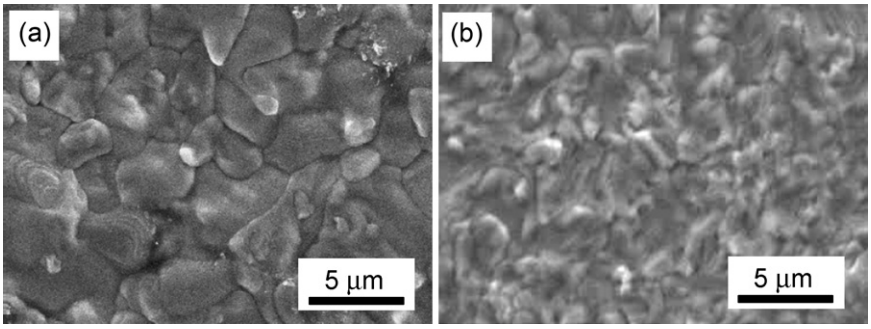

Fig. 1. Surface SEM images of CIGSe films deposited by selenizing the (a) Cu-In-Ga and (b) Cu-In-Ga_2Se_3 films at 600 °C for 1 h.

and Cu-Ga-In_2Se_3 targets. All the targets were formed by hot pressing the constituent powders into a 2-inch disc size. Cu-In-Ga target involved Cu, In, and Ga metal elements and Cu-In-Ga_2Se_3 contained Cu, In, and Ga_2Se_3, while Cu, Ga, and In_2Se_3 had been used for Cu-Ga-In_2Se_3 target. Different selenide powders were synthesized by reacting mixed constituent powders at their own adequate temperature. The contents of the constituent powders for different targets were focused to form the Cu-deficient CIGSe films with the composition of $Cu_{0.9}(In_{0.7}Ga_{0.3})Se_2$ after subsequent selenization. The double Mo back electrodes also were deposited on glass substrate by sputtering at 100 W. The as-grown films from Cu-In-Ga, Cu-In-Ga_2Se_3, and Cu-Ga-In_2Se_3 targets were deposited on un-heated substrates for 1 h. Our post-selenization was executed with one-step and two-step heating procedures in a tube furnace. For the one-step method, the film was heated to 550–700 °C with a holding time of 1 h. The two-step method was heated to 300 °C with a holding time of 0.5 h and followed by heating to 550–700 °C for 1 h. During selenization, the precursor films were loaded in a lid-covered ceramic crucible with a ($SnSe_2$ + Se) pellet together for atmospheric control.

Phase identification of CIGSe layer was analyzed by X-ray diffractometry (XRD, Rigaku D/Max-RC). A field-emission scanning electron microscope (SEM, JEOL JSM 6500F) equipped with energy dispersive spectroscopy (EDS) was used for composition analysis and microstructural characterization. A Hall measurement system (HMS 3000, ECOPIA, Korea) was used to measure the resistivity, mobility, and carrier concentration of the selenized film on Mo-free substrate.

3. Results and discussion

Fig. 1 shows SEM images of CIGSe films obtained by selenizing the (a) Cu-In-Ga and (b) Cu-In-Ga_2Se_3 films at 600 °C for 1 h. The metallic precursor film was selenized into a dense film with large grains of 3–5 μm. The cermet precursor led to non-uniform films with grains of different sizes and shapes. The selenized films obtained from the Cu-In-Ga target did show the good microstructure. However, both of these two selenized films showed Ga-free after the EDS composition analyses were conducted on film surface. The Ga disappearance is related to the easy formation of $CuInSe_2$ than $CuGaSe_2$. Cu and In elements favorably reacted with the absorbed Se vapor on the surface of precursor films to firstly form $CuInSe_2$, which covered over the Ga-containing species. Therefore, Ga was not detected on the film surface and was only detected beneath the surface. This type of Ga distribution might be good from the viewpoint of the energy-gap engineering, but it was a problem from the viewpoints of processing control and manipulation.

To solve the non-uniform problem of Ga distribution, the Cu and In metals cannot exist together under a selenization condition. To delay the $CuInSe_2$ formation, indium was replaced by In_2Se_3 to form precursor films with a Cu-Ga-In_2Se_3 target. This target containing metallic Cu and Ga and ceramic In_2Se_3 was a cermet target and the precursor film deposited from this target was a cermet precursor film. Fig. 2(a) displays surface SEM image of a cermet film deposited on an un-heated, Mo-coated substrate. The cermet film did not have good crystallinity. The inset in Fig. 2(a) was the XRD analysis of the CIGSe precursor film. The stronger diffraction peaks were contributed from Mo bottom electrode. To investigate the selenization of the cermet films, they were heated by one-step and two-step selenization procedures. Fig. 2(b) shows the heating profiles for the selenization of the CIGSe precursor films.

Fig. 3 displays compositional analyses of CIGSe films after selenization at 550–700 °C with (a) one-step and (b) two-step heating

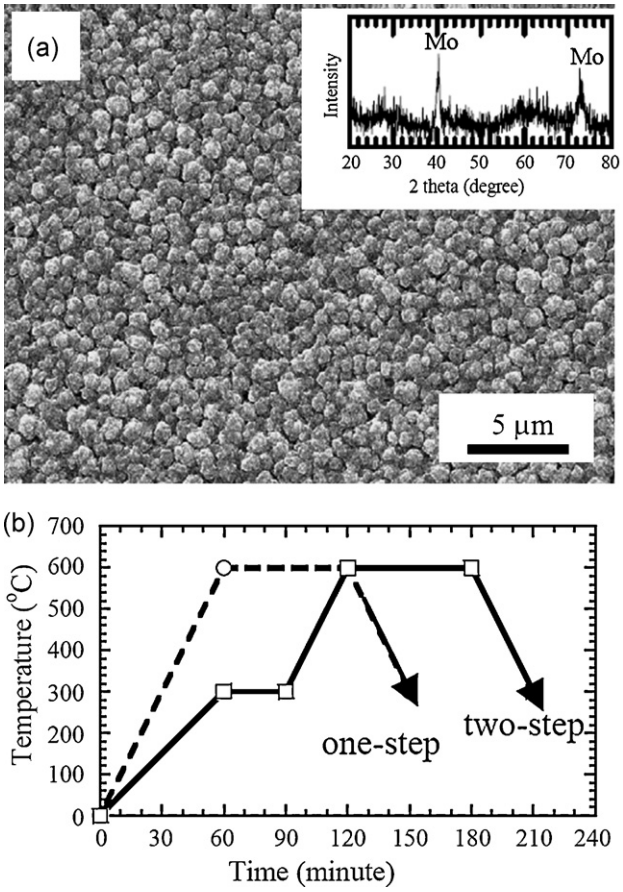

Fig. 2. (a) Surface SEM image of a cermet film deposited on un-heated, Mo-coated substrate by dc sputtering with a Cu-Ga-In_2Se_3 target. (b) The heating profiles for the selenization of the CIGSe precursor films. The inset in (a) was the XRD analysis of the CIGSe precursor film.