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Metal precursor with bi-layer indium for Cu(In,Ga)Se_2 thin film preparation

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ABSTRACT

A novel process was developed to prepare a sequentially stacked CuGa/In precursor using DC magnetron sputtering to make absorber for Cu(In,Ga)Se_2 (CIGS) solar cell. Compared with precursor made of normally used single-layer In, CuGa/In film with bi-layer In was found to be with smoother surface and better coverage of the CuGa film by In islands. CIGS absorber prepared by selenizing the precursor with bi-layer In film showed a surface with less roughness, which indicated strong influence of the surface texture of the precursor on the morphology of the absorber. Furthermore, the thickness inhomogeneity of the In islands on the CuGa layer in the precursor was found to induce different degree of mixing for Ga and In, resulting in a lateral composition fluctuation among CIGS grains in addition to the normally observed vertical Ga grading in each grain. By using a precursor with bi-layer In film, an improvement of cell efficiency is always obtained resulting from the increased open circuit voltage (V_{oc}) and larger fill factor (*FF*).

1. Introduction

Cu(In,Ga)Se_2 (CIGS) thin film solar cell with a world-record efficiency of 21.7% [1] has shown great potential for commercial applications. The CIGS absorber layer of high efficiency cell is usually fabricated by a "3-stage" co-evaporation technique [2,3]. However, the disadvantages such as complicated processes and high cost make it difficult to scale up. While a "two-step" method to fabricate the CIGS absorber layer [4] which consists of a sputtering deposition of a precursor layer followed by a subsequent selenization is considered to be one of the most promising pathways to mass production [5]. Based on this technique, a sulfurization after selenization (SAS) process has been developed to manufacture a 30 $\times$30 cm^2 sub-module with efficiency of 17.8% [6].

For the "two-step" method, the precursor layer deposition is of the same importance as the selenization process. It is studied by several research groups with different technologies, including the stack sequence of deposited metal layers [7–9], the multi-target co-sputtering method [10,11] and the single target sputtering method [12,13]. A typical precursor structure has been reported with CuGa layer and indium (In) is deposited sequentially on a molybdenum (Mo) coated glass [14]. As the CuGa film usually shows a smooth surface morphology, the In metal layer brings significant influence on the roughness of the precursor [7] due to the clustering of In grains resulting from its low-melting point. The morphology of the precursor has been found to determine that of the CIGS absorber layer [13,15,16], and thus affect the performance of cells [17].

In this work, we report a novel technique to prepare the indium (In) film with a bi-layer structure for the CuGa/In precursor with much improved surface morphology. The In film was designed to have a bi-layer structure which consists of a bottom layer deposited under low argon pressure with high sputtering power and a thin top layer under high argon pressure with low sputtering power. Compared with the commonly used CuGa/In precursor with single In layer, the precursor with bi-layer In shows smoother surface and better coverage of CuGa layer, which consequently leads to a smoother and more compact CIGS absorber film. Furthermore, different lateral composition uniformity of CIGS, especially for Ga distribution is observed in samples using different indium deposition processes. We believe that the control of surface morphology and lateral Ga distribution by using a bi-layer In film precursor will provide new insights for the "sputtering-selenization" process. An improvement of cell performance is obtained resulting from the increase of open circuit voltage (V_{oc}) and fill factor (*FF*) in CIGS solar cells. Since the additional top layer in the precursor is very thin, the newly developed processing will show

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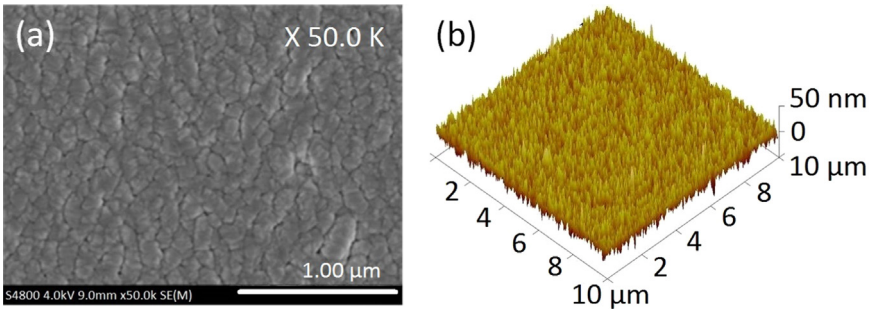

Fig. 1. SEM plan view (a) and 3D AFM image (b) of CuGa film.

advantage in improving device performance without sacrificing throughput of the production.

2. Experiments

2.1. Sample preparation

To make the CIGS device, Mo film is firstly coated on a soda lime glass (SLG, 10 cm × 10 cm × 2 mm) as the back contact. CuGa/In precursor is deposited on the Mo film by DC magnetron sputtering system which is equipped with quartz monitor crystals to control the thickness of deposited film. CuGa film with thickness of 250 nm is obtained by sputtering a CuGa alloy target (Ga: 25 at%) with the argon pressure of 0.25 Pa and sputtering power density of 3 W/cm^2. In film is subsequently deposited on the CuGa layer to make a precursor with the Cu:In:Ga atomic ratio around 0.85:0.72:0.28. The Cu/Ga ratio in the precursor is slightly deviated from that in the target due to the different ablation rates between Cu and Ga atoms during the sputtering process. Se film with thickness about 1 µm is deposited on the CuGa/In precursor by thermal evaporation to serve as Se source.

CIGS absorber is prepared by annealing the Se coated CuGa/In precursor in a rapid thermal processing (RTP) system equipped with quartz halogen lamps. The temperature profile is similar to that reported previously [18]. Firstly, the precursor is kept at 100 °C as a preheating stage. Then the temperature is raised quickly and held at 350 °C for 2 min. Afterwards, with a rate of 4 °C/s, the temperature is ramped up and held at 560 °C/s for 10 min. During the annealing process, additional Se is supplied using Se vapor carried by N_2 gas flow in order to maintain a high Se vapor pressure at temperatures above 350 °C.

After the selenization process, a 50 nm thick CdS film is deposited on the CIGS absorber layer by chemical bath deposition (CBD). The device is finished by depositing a 50 nm thick high resistivity ZnO (i-ZnO) and 600 nm thick transparent conducting ZnO:Al_2O_3 (AZO) using RF-sputtering. The rectangular targets used for Mo, CuGa, In, i-ZnO and AZO films deposition are with the same dimension of 25.4 cm × 10 cm. During each sputtering processes, the substrate sitting 7 cm above the target moves back and forth to get a homogeneous film with desired thickness.

2.2. Materials characterization

The microscopic structure of the film is studied by field emission scanning electron microscopy (FE-SEM: Hitachi, S-4800). Atomic force microscope (AFM: Veeco, Dimension 3100) is used to measure the surface roughness of the films. The composition of the films is analyzed by both energy-dispersive X-ray (EDX) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). To get the depth profile of the composition in the CIGS absorbers, glow discharge optical emission spectrometry (GDOES, Spectruma Analytik GmbH, GDA750HP) equipped with pulsed radio frequency generator is employed [19–21]. Samples are sputtered with a 2.5 mm diameter glow discharge source. Two standard samples of $CuInSe_2$/Mo/SLG and $CuGaSe_2$/Mo/SLG are used for atomic concentration quantification of Cu, In, Ga, Se and Mo. The crystalline structure is characterized by X-ray diffraction (XRD) with a Cu-Kα radiation using a θ–2θ scan along the surface normal. The performance of the cells is measured with illumination from a solar simulator under standard condition (1000 W/m^2, AM1.5 Global spectrum at 25 °C) by a Keithley 2400 current–voltage source meter. External quantum efficiency (EQE) is determined at room temperature using a grating monochromator-based dual-beam setup under chopped light from a xenon lamp.

3. Results and discussion

3.1. Properties of CuGa/in precursor layer

Fig. 1(a) and (b) presents the morphology of a 250 nm thick CuGa film deposited on Mo coated glass using SEM and AFM, respectively. The surface of the CuGa layer is found to be very smooth and the root mean square roughness (R_{rms}) of the film is around 8.7 nm. To study the morphology evolution of the precursor after In coverage, we have firstly prepared very thin (~80 nm) In layer with different sputtering parameters on the CuGa layer. Fig. 2(a) shows the SEM revealed surface morphology of the In film on CuGa layer (named as Pre-1) deposited under high sputtering power density (1 W/cm^2) and low working pressure (0.25 Pa). The morphology of Pre-2, for which In is deposited under low sputtering power density (0.5 W/cm^2) and high working pressure (0.5 Pa) is shown in Fig. 2(b). The detailed sputtering parameters for the In layers are listed in Table 1. One can easily find that Pre-1 shows high density of large grains with size around 950 nm, while Pre-2 shows a bi-modal grain size distribution which consists of high density of small islands around 260 nm and scattered low density of larger In droplets (~ 700 nm). It clearly indicates high sputtering power density (1 W/cm^2) and low working pressure (0.25 Pa) help to get In film with large islands, while low sputtering power density (0.5 W/cm^2) and high working pressure (0.5 Pa) facilitate the nucleation of high density of small In grains. AFM measurement revealed that the height of the islands in Pre-1 is very close to the thickness of the In film, which indicates that the area between the neighboring big islands is the exposed Ga surface. For Pre-2, we find that the Ga surface is more uniformly covered by small In grains.

The drastic change of surface morphology mainly results from the different kinetic energy of In atoms under different deposition conditions. When using high power density (1 W/cm^2) and low working pressure (0.25 Pa), the sputtered In atoms are with higher kinetic energy and higher mobility which would help the growth of larger islands. When In atoms are with small kinetic energy as