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Characterization and performance of $Cu(In,Ga)Se_2$ thin films incorporating low-temperature pre-annealing process

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ABSTRACT

This paper focuses on the characterization and performance evaluation of the $Cu(In,Ga)Se_2$ (CIGS) thin films fabricated using the low-temperature pre-annealing process, followed by the plasma-enhanced Se vapor selenization coupled with etching (PESVSE) and thermal-assisted Se vapor selenization (TASVS). The XPS data reveals that the increase of pre-annealing temperature can facilitate the diffusion of Ga towards the surface of CIGS thin film by stabilizing more Ga distribution on the surface of the annealed precursor. The PESVSE process can effectively increase Ga content on the film surface with the help of low-temperature pre-annealing process. Results also indicate that the PESVSE combined with a low-temperature pre-annealing process can significantly weaken and even eliminate the adverse phase separation to yield a single-phase CIGS thin film with a moderate Ga content. The PESVSE process helps to improve and even achieve a homogeneous depth distribution of Ga in the whole CIGS thin film in comparison with the TASVS process. The PESVSE process achieves a higher open circuit voltage and also higher conversion efficiency of CIGS solar cell treated by the low-temperature pre-annealing process. The feasibility of using this low-temperature pre-annealing method to make high-quality CIGS thin films for photovoltaic applications has been successfully validated in this work.

1. Introduction

$Cu(In, Ga)Se_2$ (CIGS) solar cells have been recognized as the most promising thin film solar cells due to their high absorption coefficients, excellent stability and high conversion efficiency. The highest conversion efficiency of 22.6% has been achieved for the CIGS thin film solar cell based on the co-evaporation process [1]. Nevertheless, fabricating CIGS thin film solar cells by this method requires expensive vacuum-based apparatus with a high production cost, which limits the mass production and commercialization of the CIGS solar cell. In this regard, post-selenization of metallic precursors is proposed to be a low-cost alternative for producing the CIGS thin films. On the one hand, it can be achieved by the use of the nontoxic Se vapor instead of the highly toxic H_2Se gas [2]. On the other hand, Se vapor can diffuse into the thin film to react with the Mo back contact to form a $MoSe_2$ layer [3], which is beneficial to the formation of an ohmic contact at the CIGS/Mo interface [3,4]. Furthermore, many advantages such as low production cost, high throughout and good uniformity for large-area modules have been revealed. Based on this technique, the conversion efficiency of up to 17.3% has been achieved for the device [5].

A pre-annealing process is usually proposed to facilitate the diffusion of elements in the metallic precursors before the post-selenization process [6–10], which can affect the grain growth of the CIGS thin films. Conventionally, a high pre-annealing temperature is preferred to achieve the sufficient diffusion of elements in the metallic precursors so that the high-quality selenized thin films can be obtained. Our previous work showed that a high pre-annealing temperature as much as 400 °C was necessary to significantly improve the depth distribution of Ga in the selenized thin film and enhance the crystallinity of CIGS thin film [7]. Some other researches also revealed that a high temperature pre-annealing process (i.e. 330 °C) helped stabilize Ga distribution on the surface of CIGS thin film [6,10], leading to the increase in the performance of corresponding solar cells. However, a high temperature pre-annealing process could consume more energy during the production process and would inevitably increase the fabrication cost to some degree. Therefore, it is essential to develop a low-

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temperature pre-annealing method to fabricate the post-selenized CIGS thin films. However, in view of the open literature, we find that there is barely report involving the low-temperature pre-annealing process to fabricate the high-quality CIGS thin films. This motivates us to investigate the grain growth of the CIGS thin films based on the low-temperature pre-annealing process.

With this background, the feasibility of using a low-temperature pre-annealing method to fabricate the post-selenized CIGS thin films is explored in this study. The electrodeposited Cu/In/Ga precursors are pre-annealed at a relatively lower temperature of 150 and 250 °C, respectively, and selenized using plasma-enhanced Se vapor selenization coupled with etching (PESVSE) process to make the CIGS thin films. The samples based on the conventional thermal-assisted Se vapor selenization (TASVS) process are also prepared for comparison. The compositional, structural and morphological details of the CIGS thin films based on the PESVSE and TASVS processes coupled with the low-temperature pre-annealing process are provided. A series of new features not reported in the previous study are reported in this work. The photovoltaic performances of the newly-developed CIGS solar cells are also demonstrated. It is believed that this study illuminates more useful information about the fabrication process of post-selenized CIGS-based solar energy materials.

2. Experimental

2.1. Fabrication process

The Cu/In/Ga precursors were successively electrodeposited from aqueous bath solutions at room temperature on the Mo-coated soda-lime glass (SLG) substrates. The detailed electrodeposition parameters for the Cu, In and Ga layers can be found in our previous study [9]. Then the Cu/In/Ga precursors were pre-annealed at a lower temperature of 150 and 250 °C, respectively for 30 min in a vacuum chamber under an initial back pressure of ~5×10^{-4} Pa to facilitate the diffusion of elements in the precursors. Next, the pre-annealed Cu/In/Ga precursors were selenized at 550 °C for 30 min using the TASVS (samples A and B) process and PESVSE process (samples C and D) to form the CIGS thin films, respectively. The schematic design and process condition of the PESVSE process is shown in Fig. 1. The Ar gas was adjusted by a mass flow controller to flow into the chamber to be the discharge gas. The capacitive coupled plasma (CCP) was generated by two electrodes, i.e. the stainless-steel shower head and the sample, at a radio-frequent (RF) power of 50 W. The distance between two electrodes, e.g. 60 mm, has been accurately adjusted to obtain the desirable etching effect. The Se pellets in the tank were heated up to ~240 °C to provide the Se vapors that flowed through the shower head into the plasma region to be transformed into the Se radicals with the enhanced reaction activity [10]. Then the chamber was filled with the Se radicals which reacted with the sample. At the same time, the Ar-plasma etched the sample during the PESVSE process, which could help to preferentially remove the excessive metallic-indium in the sample [11,12]. Finally, the corresponding CIGS solar cells were completed with a CdS buffer layer, a window layer composed of i-ZnO and ZnO:Al and a Ni/Al grid contact.

2.2. Characterization

The crystal structure of the thin films was characterized by X-ray diffraction (XRD, Bruker, D8 ADVANCE) using a Cu Kα 1 (λ = 1.5418 nm) source. The surface and cross-sectional morphologies of the thin films were characterized using a field emission scanning electron microscopy (FESEM, Zeiss Merlin). The surface composition and bulk composition of the thin films were measured by X-ray photoelectron spectrometer (XPS, Kratos) and X-ray fluorescence spectrometer (XRF, Panalytical), respectively. Raman spectrometer (LabRAM Aramis, H.J.Y) was used to test the CIGS thin films. The depth profiles of elements in the CIGS thin film were acquired by a secondary ion mass spectrometer (SIMS, CAMECA, IMS-4F, France), using O_2^+ primary ions (15 kV, 200 nA). The current density-voltage (J-V) measurements of the solar cells were conducted under the standard AM1.5 conditions (1000 W/m^2).

3. Results and discussion

3.1. Pre-annealed precursors

Before the selenization process, the electrodeposited Cu/In/Ga precursors were pre-annealed at a low temperature of 150 and

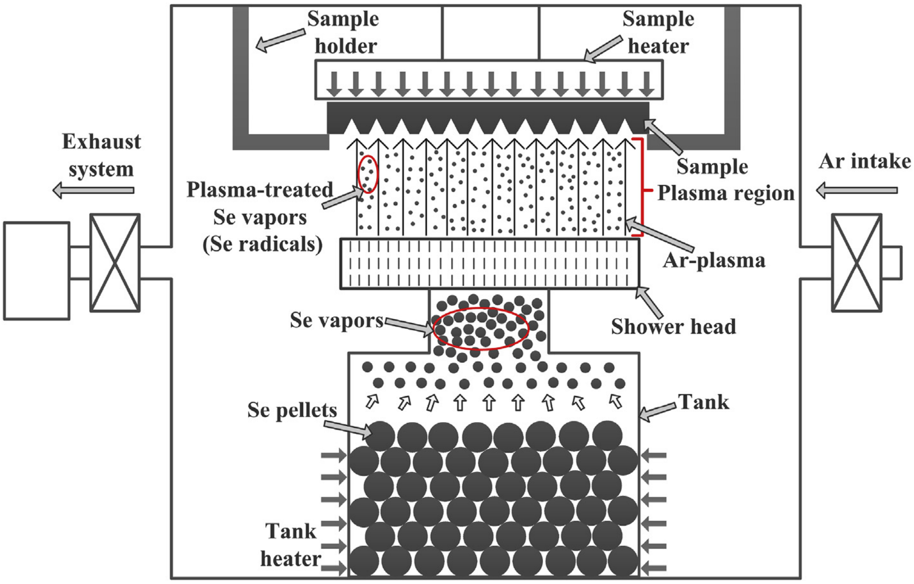

Fig. 1. The schematic design and process condition of the PESVSE process.