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# Effect of substrate temperatures on evaporated $In_2S_3$ thin film buffer layers for $Cu(In,Ga)Se_2$ solar cells

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ABSTRACT

For the realization of vacuum in-line process in the fabrication of $Cu(In,Ga)Se_2$ (CIGS) solar cells, $In_2S_3$ thin film buffer layers for CIGS have been deposited on glasses and CIGS layers with a thickness of about 650 Å by thermal evaporation process. During the thermal evaporation, the temperature of the substrate was varied from room temperature to 500 °C by heating and the grown $In_2S_3$ films were investigated and analyzed in terms of the optimized buffer layer for CIGS solar cells. From the results of scanning electron microscope and X-ray diffraction, the $In_2S_3$ thin film deposited at a higher substrate temperature showed the larger grain size and the films have amorphous structural characteristics. Although the structural characteristics such as the atomic ratio of In to S and transmittance of the $In_2S_3$ thin films were not proportional to temperature, it was possible to obtain the large optical band gap of $In_2S_3$ films of about 3.8–3.9 eV enough to be used as the buffer layer of CIGS.

## 1. Introduction

Recently, $Cu(In,Ga)Se_2$ (CIGS) thin-film solar cells have a higher efficiency of about 20% [1]. These photovoltaic devices have been typically fabricated using a high-resistive cadmium sulfide (CdS) buffer layer deposited by chemical bath deposition (CBD) in order to avoid the formation of undesirable shunt paths between aluminum doped zinc oxide/intrinsic zinc oxide n-type window layers and p-type CIGS absorber layers [2–4]. In spite of the high efficiency of a CIGS solar cell and the low cost process by using CBD CdS buffer layers, it is required to use a Cd-free buffer layer because cadmium is toxic material and the Cd-containing devices is able to be legally prohibited [5]. Furthermore, because of its relatively low optical band gap of about 3.3 eV, the efficiency of CIGS solar cells can drop at a lower wavelength due to optical absorption loss from the CdS buffer layer [6]. In fabrication of CIGS solar cells, the CBD wet process is not suitable for the application of the in-line vacuum deposition system for mass production. Therefore, it is indispensable to use a buffer layer deposited in the vacuum equipment instead of the CBD process for the deposition of CdS buffer layer [7]. Indium sulfide ($In_2S_3$), as a III–VI compound semiconductor, is one of the most potential materials as the alternative buffer layer because it is environment friendly and is deposited in a vacuum equipment [8,9]. To date, a lot of researches were carried out for the application of $In_2S_3$ films to the buffer layers of CIGS solar cells. In addition to chemical bath deposition, atomic layer deposition, physical vapor deposition such as e-beam or thermal evaporation, and sputtering method were used for the characterization of $In_2S_3$ films [10–13].

For the realization of a sequential vacuum in-line process, it is most suitable to use sputtering or evaporation as a deposition method of the $In_2S_3$ film because the buffer layer is deposited on the CIGS absorber. To avoid the sputtering damage on the CIGS film after sputtering, we used evaporation method for the optimization of $In_2S_3$ films as a buffer layer in CIGS solar cell.

For the formation of $In_2S_3$ films during the evaporation, temperature is considered as the most important factor to determine the compositions and the structural characteristics of $In_2S_3$ films. Therefore, the temperature of the substrate was varied from room temperature to 500 °C by heating and the physical and optical characteristics of the grown $In_2S_3$ films were studied for the optimized buffer layer in CIGS solar cells.

## 2. Experimental details

Fig. 1 shows the configuration of the thermal evaporation deposition system used for the formation of $In_2S_3$ thin films. As a substrate, a soda-lime glass with a size of $50 \times 50$ $mm^2$ was prepared. The glass substrate was degreased in an ultrasonic cleaner, dried by $N_2$ gas flow, and subsequently annealed at 120 °C for 20 min in the atmosphere before the deposition. After the glass substrate was loaded in the thermal evaporator, $In_2S_3$ bulk of 0.1 g was loaded on a tungsten boat in the thermal evaporator as shown in Fig. 1. The substrate was rotated during the process and the voltage and the current was fixed at 0.45 V and 45 A, respectively. The evaporation was carried out for 8–10 min after the base vacuum was reached to $4.67 \times 10^{-4}$ Pa.

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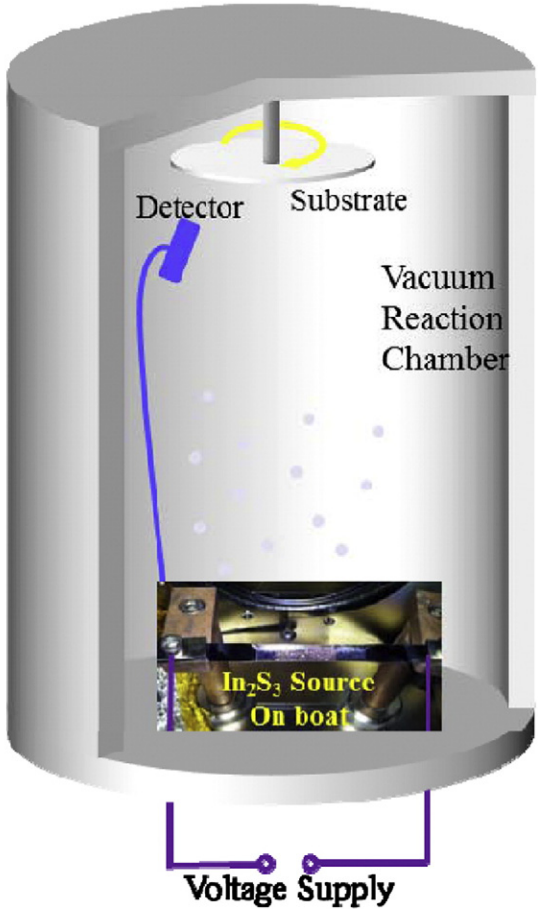

**Fig. 1.** Schematic diagram of thermal evaporator for $In_2S_3$ deposition.

$In_2S_3$ films were formed at different substrate temperatures from room temperature (RT) to 500 °C.

After the formation of $In_2S_3$ films, the thickness and the transmittance were measured by using a super surface profiler (KLA TENCOR, alpha-step 500) and an ultraviolet–visible light (UV–vis) spectrometer (Cary 100 Cone), respectively. The surface morphologies were observed by a scanning electron microscope at the operating voltage of 15 kV(SEM, Hitachi S-4700) and the composition ratio of In and S were obtained by energy dispersive X-ray spectroscopy (EDX). The Horiba EMAX EDS system was interfaced at the Hitachi S-4700 SEM system and the accelerating voltage of incident electron beam was kept at 20 kV to measure the chemical compositions. Furthermore, the optical band gap ($E_g$) of of the film was calculated according to the equation related with the absorption coefficient obtained from the transmittance data.

The crystallinity of the grown $In_2S_3$ films was measured by an X-ray diffractometer (XRD). Rigaku D/MAX-2200 XRD system was used to analyze the phase of thin films using 2θ method. Typical wide-angle 2θ scans 20° to 80° at step of 0.02° and the incident angle ω was usually kept at 3 to 8°. The Cu-$k_\alpha$ radiation was generated from a sealed Cu tube at the voltage and current of 40 kV and 20 mA. The measurement was performed at RT. The measured XRD spectrums were analyzed using the MDI Jade 5 software by taking the Joint Committee on Power Diffraction Standards (JCPDS) cards as references.

## 3. Results and discussion

The thicknesses of the $In_2S_3$ films were maintained at about 645–680 Å irrespective of the substrate temperature. For the confirmation of the uniform and coherent thin film, the adherences of the $In_2S_3$ films on glass substrates were tested by pasting the Kapton tapes onto the films and then taking them off to investigate whether the films can be dropped out with the tapes. From the results of the test, only the tapes were dropped out and it was possible to conclude that the films are deposited on glass substrate uniformly and coherently. From the SEM images in Fig. 2, it is apparent that the grain size of $In_2S_3$ was increased at a higher substrate temperature. Generally, the grain sizes of thin film increase at a higher temperature due to the higher ad-atom mobility that induces the nucleation and coalescence of the deposited $In_2S_3$ molecules [7].

Fig. 3 shows EDX data that indicate the atomic ratio of In to S in $In_2S_3$ films at different substrate temperatures. The data were also summarized in Table 1. We could see that the atomic ratio of In to S increased with the increasing substrate temperature and had a peak value of 0.82 at 300 °C. The atomic ratio was also decreased at a substrate temperature higher than 300 °C. These results show that the deposition temperature has a significant influence on the stoichiometry of the formed $In_2S_3$ layer. A slight deviation of the stoichiometry at room temperature might be due to the slight decomposition of the starting material during the evaporation or due to the differences in the vapor pressures of indium and sulfur elements in the $In_2S_3$ compound. From the EDX results, a large deficit of sulfur content in the film was noticed as the substrate temperature increases to about 300 °C. This could be due to the re-evaporation of sulfur from the evaporated film prior to the formation of $In_2S_3$. In other chalcogenide films the re-evaporation could also be observed as this type of behavior [8] and it was reported that the constituent elements might be dissociated into its individual component due to the large differences in the dissociation energy and the heat of vaporization that subsequently condense on the substrate leading to the formation of the required film similar to the films formed by two source elemental evaporation and condensation [9]. The dissociated In and S molecules can have different velocities and sticking coefficients as a result of their different vapor pressures. Hence, the vapor molecules reach the substrate with different kinetic energies. In such cases, the number of condensing atoms and that of re-evaporating atoms are determined by the substrate temperature. Due to the higher vapor pressure of sulfur than indium, an excess of sulfur might remains so that every condensing In atom forms $In_2S_3$ and the newly arriving In atoms are adsorbed on to $In_2S_3$. The In-rich films at a higher substrate temperature might be due the higher sticking coefficient of In. It was also reported that the sticking coefficient of metal to the substrate is varied at a change of substrate temperature [10,11]. At a substrate temperature higher than 300 °C, the sulfur atoms are also expected to be vaporized and form the $In_2S_3$ films and the atomic ratio of In to S are decreased. Therefore, the analysis reveals that temperature of the source can be a critical factor to form the stoichiometric films.

Fig. 4(a) shows the transmittances of the $In_2S_3$ films at a range of 200–1100 nm. From the results, the transmittance of the $In_2S_3$ films on glass was maintained at about 50%. As the substrate temperature was increased to 380 °C, the transmittance of the $In_2S_3$ film was slightly decreased. At a substrate temperature higher than 380 °C, the transmittance was increased as shown in Fig. 4(b).

For the optimization of the grown $In_2S_3$ film as a buffer layer of CIGS solar cell, it is necessary to obtain the optical band gap of the film. From the transmittance data of Fig. 4(a), it was possible to calculate the absorption coefficient as follows:

$$T = e^{-\alpha d} \qquad (1)$$

where $d$ is the thickness of the $In_2S_3$ film.

Then, the absorption coefficient $\alpha$ is used to obtain the following expression for near-edge optical absorption of semiconductors:

$$\alpha h\nu = k\left(h\nu - E_g\right)^{\frac{n}{2}} \qquad (2)$$