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Pulsed-DC magnetron sputtering of intrinsic ZnO film and its application to CIS solar cell

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ABSTRACT

To create an intermediate layer in $CuInSe_2$(CIS)-based solar cells, an intrinsic zinc oxide(i-ZnO) thin film was deposited on a glass substrate and a cadmium sulfide(CdS) buffer layer using an in-line pulsed-DC sputtering. In comparison with i-ZnO films sputtered using RF power, i-ZnO films sputtered using pulsed-DC power showed much higher deposition rates and similar structural characteristics, without causing any damage to the CdS buffer layer. During pulsed-DC sputtering, the O_2/Ar gas ratio, reverse time, and pulse frequency were changed to optimize the process parameters. From the transmittance and scanning electron microscope(SEM) images, the optimized i-ZnO film was obtained at an O_2/Ar gas ratio of 1%, a pulsed frequency of 200 kHz, and a reverse time of 1.3 μs. For showing the feasibility, it was applied to the fabrication of a CIS solar cell which was processed using the two step method by the rapid thermal processing (RTP) annealing of Cu–In stacked layers. It showed a possibility of the pulsed-DC sputtered ZnO as an intermediate layer of a CIS solar cell even though a cell efficiency was shown with a low value of 2.2% due to an early stage of our study in the two step CIS process.

1. Introduction

The chalcopyrite $CuIn_{1-x}Ga_xSe_2$ (CIGS) thin film solar cell has come to the forefront because of its high-efficiency and low manufacturing cost. Fig. 1 shows the aligned energy band structure of CIGS and the window layer is composed of undoped intrinsic zinc oxide (ZnO) and aluminum-doped zinc oxide (AZO). Intrinsic zinc oxide (i-ZnO) film has traditionally been used as an intermediate layer between the AZO and the cadmium-sulfide (CdS) buffer layer because its high resistivity can reduce current leakage through the CIGS solar cell [1–4]. Because the chemical bath deposition (CBD) process is used as a deposition method of CdS, it is easy to investigate the CIGS absorber layer uncovered by CdS after CBD process. As a result of the incomplete CBD process, an electrical path may be caused between the Mo back contact and the AZO window layer instead of the *p-n* diode characteristics of the solar cells after the deposition of n-type AZO layer. The shunting leakage current can reduce the cell efficiency via the reduction of both the open-circuit voltage of the solar cell, V_{oc}, and the fill factor, FF. When i-ZnO is formed between CdS layer and AZO layer, a shunting path across the *p-n* junction between the *p*-type CIGS absorption layer and the *n*-type AZO window layer can be prevented and the *p-i-n* diode characteristics may be formed in the structure of the CIGS/CdS/i-ZnO/AZO layers. The i-ZnO can also act as a protective layer for the CdS buffer layer, reducing sputtering damage caused by the high power AZO sputtering. The transmittance and the energy bandgap of the 50-nm i-ZnO are expected to be above 80% and 3.3 eV, respectively.

Several techniques can be used for the fabrication of the i-ZnO film, i.e., direct current (DC) or radio frequency (RF) sputtering from a metallic or an alloy target, pulsed laser deposition, and sol–gel deposition [5–9]. Owing to its high reproducibility, flexibility in the control of composition, and high scalability, magnetron sputtering is the most commonly used technique. It is reported that the crystallinity of RF sputtered i-ZnO films is higher than that of DC sputtered films [10]. However, because of the low deposition rate of RF sputtering, it is necessary to increase the sputtering power to achieve a higher deposition rate for the i-ZnO films in the manufacturing of CIGS solar cells. However, CdS layers may be damaged (or removed) as a result of sputtering at higher powers. In our previous results, i-ZnO films were deposited at different powers from 0.4 kW to 1.0 kW using both pulsed-DC sputtering and RF sputtering. The pulsed-DC sputtered i-ZnO films showed a higher deposition rate than those using RF sputtering without causing any

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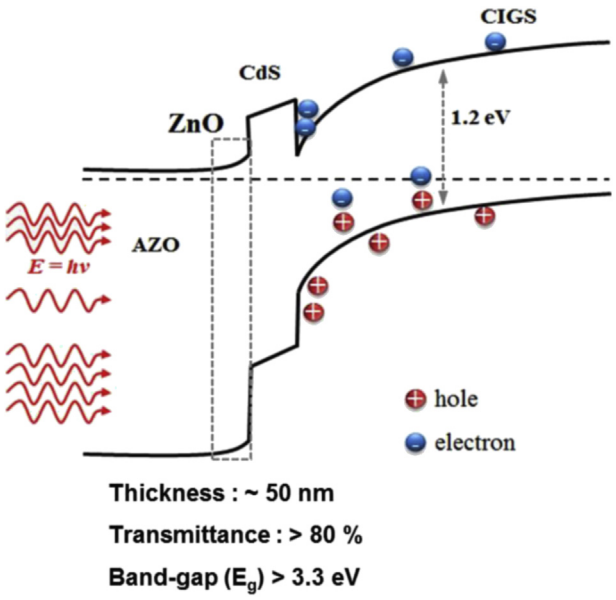

Fig. 1. The well-aligned energy band structure of a CIGS solar cell.

damage to the CdS layer and any degradation of transmittance [11].

For the operation of CIGS solar cell with the intermediate i-ZnO film sputtered with pulsed-DC power, i-ZnO films were deposited using pulsed-DC magnetron sputtering and optimized. First, i-ZnO films were deposited at different O_2/Ar gas ratios for both pulsed-DC power and RF power. The deposition rates and the structural characteristics of pulsed-DC sputtered i-ZnO films were compared to those of RF sputtered i-ZnO films. Then, i-ZnO films were deposited at different duty ratios of the pulsed-DC power by changing parameters such as pulse frequency and reverse pulse time. Through the analysis of the pulsed-DC sputtered i-ZnO films, we expect to obtain the optimized pulsed-DC sputtering for the intermediate layer in CIGS solar cells. The feasibility of the optimized i-ZnO was tested by the application of the i-ZnO to the fabrication of CIS solar cell instead of CIGS solar cell.

2. Experimental procedures

ZnO thin films were deposited on a 370 × 470 mm^2 soda-lime glass (SLG) using a vertical in-line sputtering system with a 520(L) × 160(W) × 6(T) mm^3 ZnO target. The SLG substrate was fixed on the carrier and could be moved into the main process chamber after the loading chamber was pumped to 3.0×10^{-3} torr. Then, the process chamber was pumped down to 5.0×10^{-6} torr using a turbo molecular pump (TMP). Next, argon (Ar, 99.999%) gas was injected into the process chamber at a flow rate of 50 sccm, controlled using a mass flow controller (MFC). Plasma was generated using a pulsed-DC power supply and an RF power supply, respectively. Fig. 2 shows an applied voltage pattern of several pulsed-DC cycles. At first, the frequency and reverse time of the pulsed-DC voltage were set to 200 kHz and 1.5 μs, respectively. The applied powers for the pulsed-DC voltage and RF voltage were 1.0 kW and 900 W, respectively. Sputtering was carried out at room temperature with a pressure of 5 mtorr. During the sputtering process, oxygen (O_2, 99.999%) gas was injected at various flow rates from 0.5 sccm to 3.0 sccm. In order to acquire the film homogeneity, the glass substrate was moved back and forth in front of the ZnO target during RF sputtering. The distance between the substrate and the ZnO target was maintained at about 100 mm. In the case of RF sputtering, the carrier with the SLG substrate was moved

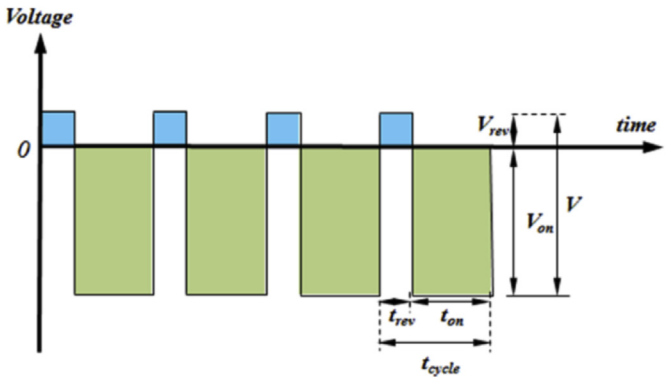

Fig. 2. Pulse waveform of sputtering output voltage in pulsed-DC mode.

through in front of the deposition area with 9 cycles of back-and-forth scans due to its much low deposition rate of the RF plasma. The speed of the carrier was maintained at 30 cm/min during sputtering. Secondly, the properties of the i-ZnO films were investigated using various duty ratios of pulsed-DC power. The pulse frequency was changed from 100 kHz to 300 kHz at a fixed reverse time; the reverse time was then varied from 0.4 μs to 2.2 μs at a fixed pulse frequency.

The thickness and optical transmittance of the i-ZnO film were measured using a surface profiler (KLA Tencor, Alpha-Step 500) and a UV–VIS spectrophotometer (Agilent Technologies, Cary 100). The surface morphologies of the film were observed using a scanning electron microscope (SEM, Hitachi, S-4700).

3. Results and discussion

Fig. 3 (a) shows the thicknesses of the i-ZnO films sputtered using pulsed-DC power and RF power at different O_2/Ar gas ratios. As the O_2/Ar gas ratio increased, the thicknesses of the i-ZnO decreased for both pulsed-DC and RF sputtering. Although the i-ZnO films were deposited during in-line movement of the substrate in front of the ZnO target over 1 cycle in the case of pulsed-DC sputtering, they were much thicker than those deposited over 9 cycles using RF sputtering, except for the case of an O_2/Ar gas ratio of 1%. Despite a slight difference in the power for pulsed-DC sputtering (1 kW) and RF sputtering (0.9 kW), the deposition rates for i-ZnO films sputtered using pulsed-DC power were much higher than those using RF power. For the i-ZnO films of Fig. 3 (a), the average transmittances in the wavelength range from 400 to 800 nm and the transmittance at a wavelength of 550 nm are shown in Fig. 3 (b), in which all values were obtained including the glass substrate. For all i-ZnO films, the transmittance was greater than 80%, which is quite a good as an intermediate layer in the CIGS solar cell if we take the transmission of the glass substrate itself into consideration. The transmittance was also improved by increasing the O_2/Ar gas ratio. For a given thickness of the i-ZnO film in Fig. 3 (a), the RF-sputtered films showed a slightly higher transmittance than pulsed-DC films. This is due to the increased crystallinity owing to much slower deposition in the case of RF sputtering in comparison with that of pulsed-DC sputtering.

For the calculation of the optical band gap (E_g) of the i-ZnO film, the absorption coefficient (α) was obtained using the measured transmittance via the following equation:

$$\alpha = (1/d)\ln(1/T) \quad (1)$$

where d is the thickness of the film, and T is the transmittance. The i-ZnO film has a direct energy band gap, as obtained using the