Journal of Alloys and Compounds 708 (2017) 562–567

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of the deposition process of window layers on the performance of CIGS solar cells

Jung-Hwa Cha, Soo-Min Kwon, Jin A. Bae, So Hyun Yang, Chan-Wook Jeon*

School of Chemical Engineering, Yeungnam University, 280Daehak-ro, Gyeongsan 38541, Republic of Korea

ARTICLE INFO

Article history:
Received 17 November 2016
Received in revised form
28 February 2017
Accepted 4 March 2017
Available online 6 March 2017

Keywords:
Transparent conducting oxide
Sputtering
MOCVD
CIGS
Reflectance

ABSTRACT

The effects of the formation process of transparent conducting electrodes on the performance of $Cu(In,Ga)Se_2$ thin film solar cells were examined. B:ZnO and (Ga,Al):ZnO thin films deposited using metalorganic chemical vapor deposition (MOCVD) and magnetron sputtering, respectively, were compared in terms of the unit thin films and solar cell device performance. Both unit films formed under optimized process conditions showed similar electrical resistance, whereas the optical reflectance of B:ZnO by MOCVD was superior to that of the sputtered film. In the case of the B:ZnO film deposited on the absorber layer, the surface roughness became greater than the unit film on the test glass. The short-circuit current of the solar cell fabricated with B:ZnO was 3% higher than that with (Ga,Al):ZnO due to the enhanced light scattering. The junction quality and defect chemistry were identical in both devices, which suggests that there was no plasma damage due to sputtering.

1. Introduction

Transparent conductive oxides (TCOs) are applied widely in optoelectronic devices, such as thin film solar cells, flat-panel displays (FPDs), and light-emitting diodes (LED) [1–10]. In general, TCO, particularly for solar cells, requires high light transmissivity and low resistivity for reducing the series resistance [6–9,11–13].

Indium tin oxide (ITO) and zinc oxide (ZnO) doped with Group III elements, such as B, Al, and Ga, are well known transparent electrode materials [9,10,14,15]. In particular, ZnO with a wide band gap of 3.3 eV is used widely as a substitute for ITO in many research groups owing to its easy control of the optical and electronic properties through doping [15–19]. Sputtering and metal-organic chemical vapor deposition (MOCVD) are representative commercial methods for transparent electrode deposition but atomic layer deposition (ALD), ion layer gas reaction (ILGAR), and electrodeposition methods are also used for research purposes [19–26].

Sputtering, which is the best known deposition method for oxide thin films, facilitates the deposition of various kinds of materials, low temperature process, and scale-up as well as high quality smooth surfaces [14,34–36]. Generally, a TCO is fabricated by double layer deposition to prevent current leakage in a solar cell; a thin ZnO layer without doping is deposited first, followed by the deposition of a heavily doped ZnO layer [27–34]. On the other hand, interfacial defects may be induced by plasma damage during deposition of the undoped ZnO [37–40], which was reported by the Nakada group [40]. To minimize damage during oxide deposition, extensive studies aimed at developing a low damage process, including MOCVD and ALD, are ongoing [18,41–43].

The ZnO thin layers fabricated with MOCVD, facilitate a reduction of optical loss with a spontaneously textured rough surface and result in enhanced device efficiency with increased light utilization, which differentiates them from the sputter deposited thin layers with a smooth surface [44–47]. MOCVD and sputtering take the spotlight in the industrial fields, which prefer a high deposition rate and low deposition temperature, even with large scales [46,48].

In this study, solar cells and unit thin film were fabricated by sputtering and MOCVD, which are representative deposition processes for transparent conducting electrodes, and analyzed them in the points of device performance, physical properties, and surface morphology of the unit thin film, to explore the correlation of the thin film properties and the performance of the $Cu(In,Ga)Se_2$ (CIGS) solar cell device.

2. Experimental details

The CIGS solar cells with two different window layers with a Ag/Ni/window/CdS/CIGSe/Mo/glass structure were fabricated using a chemical bath deposited CdS buffer layer (50 nm), either sputtered i-

* Corresponding author.
E-mail address: cwjeon@ynu.ac.kr (C.-W. Jeon).

http://dx.doi.org/10.1016/j.jallcom.2017.03.021
0925-8388/

ZnO/(Ga,Al):ZnO (GAZO) layers (80 nm/500 nm) or i-ZnO/B:ZnO (BZO) layers (80 nm/500 nm) by MOCVD, and electron beam evaporated Ni (50 nm)/Ag (1.7 μm) grids. The CIGS absorber thin films used in this study were grown thermally at the maximum substrate temperature of 530 °C using a 3 stage co-evaporation process.

RF/DC magnetron sputtering was used for i-ZnO/GAZO deposition (hereafter SP GAZO), respectively, on both a test glass and device structure. The sputter system was pumped down to a base pressure of approximately 10^{-7} Torr and the targets were pre-cleaned for 10 min i-ZnO deposition was carried out at RF power of 75 W, Ar flow rate of 40 sccm, and a working pressure of 8×10^{-3} Torr. The GAZO film was deposited in sequence at DC 200 W, 20 sccm Ar, and 1×10^{-3} Torr. The distance between the substrate and target was 16 cm and the substrates were not intentionally heated.

Another window of i-ZnO/BZO bi-layer films was formed by MOCVD (hereafter, MO BZO). Diethylzinc (DEZn) (8.66 sccm) and H_2O vapor (12.6 sccm) were supplied as the Zn and O source, respectively, using N_2 carrier gas. B_2H_6 was used as a doping gas to adjust the electrical performance of the BZO film. BZO deposition was carried out for 5 min at 240 °C. To prevent residue condensation, the shower head and delivery pipes were maintained at the same temperature (55 °C). The deposition conditions described above correspond to the optimized conditions for the best performance of each TCO layer, and the electrical properties of those are summarized in Table 2.

The performance of the solar cell devices fabricated with SP GAZO or MO BZO were evaluated in terms of their current density-voltage (I-V) characteristics and external quantum efficiency (EQE). The carrier concentration and depletion width were obtained from the capacitance-voltage (C-V, 4200-SCS, Keithley) curves measured with a 30 kHz modulation frequency of 30 mV DC bias over the range of −1.0 V to +1.0 V at room temperature under dark. Admittance measurements were taken using Keithley 4200-SCS over the frequency range from 1 kHz to 1 MHz at zero bias. The ac signal amplitude was 30 mV. The samples were mounted on a sample stage cooled by liquid nitrogen inside a vacuum chamber allowing to vary the temperature between 100 and 350 K. The performance was correlated with the optical and electrical properties of the unit films deposited on a test glass. The surface morphology was observed by field emission scanning electron microscopy (FE-SEM, HITACHI, S-4800). The transmittance and reflectance of GAZO or BZO films grown on the CIGS or test glass were analyzed by UV–Vis–NIR spectrophotometry (Agilent, Cary5000). The electrical properties were measured using a Hall Effect measurements system (Ecopia, HMS-5000).

3. Results and discussion

Fig. 1a shows the J-V curves for the devices fabricated with MO BZO and SP GAZO as the window materials, and performance parameters extracted from the curves are summarized in Table 1. Both devices showed a similar conversion efficiency; however, the solar cells with MO BZO (hereafter, MO device) yielded a 29 mV lower open-circuit voltage (Voc) but a 0.9 mA/cm^2 higher short-circuit current density (Jsc) compared to that with SP GAZO (hereafter, SP device). This observation is inconsistent with T. Kobayashi et al. [49] who compared MOCVD and sputtering to produce a TCO layer for Zn(O,S) buffered CIGS solar cells, where the MO device showed higher Voc and Jsc. They attributed the increased Voc to the lack of plasma damage, which is not the case in this study and suggests that SP GAZO does not leave any damage on the CdS/CIGS underlayers. Evidence for plasma damage will be presented below. The increased Jsc in MO device was attributed to the reduced surface reflection, which is consistent with this study. Hagiwara et al. [16] compared Al-doped ZnO and B-doped ZnO, both deposited using sputtering process, and obtained similar results to this study, where a lower Voc and higher Jsc due to a decrease in free-carrier absorption of the B-doped ZnO window layer. Although they did not explain the origin of the Voc improvement and relevance with the window property, BZO was superior in terms of optical transmittance over the long wavelength range. The higher Voc from the MO device may have originated from different electrical properties of the i-ZnO layers. H_2O vapor is normally used as the oxygen source in MOCVD and the electron concentration in i-ZnO deposited by MOCVD is expected to be far lower than that by sputtering. Although it was not possible to directly evaluate the carrier concentration of the i-ZnO layers through Hall Effect measurement due to their high resistance, it would be possible to indirectly compare the electron concentration of i-ZnO from the C-V measurement results of each device. Fig. 1b shows doping profiles obtained from the two devices. Despite using the same absorbers, a much lower hole concentration was obtained in the MO device. Considering the fact that the electron concentration of MO BZO is about twice as high as that of SP GAZO (see Table 2), the hole concentration value of about 5 times lower suggests that the electron concentration of MOCVD grown i-ZnO layer existing between n^+ TCO and p-type absorber is much lower than that of sputtered -iZnO. The low

Table 1
Performance parameters of the solar cell with different TCO layers.

Parameter	MOCVD	Sputter
V_{OC} (V)	0.620	0.649
J_{SC} (mA/cm^2)	33.19	32.3
FF (%)	73.40	73.54
Efficiency (%)	15.11	15.42
R_{Sh} (Ωcm^2)	13837	4891
R_S (Ωcm^2)	0.57	0.50
J_O (mA/cm^2)	8.0×10^{-8}	6.3×10^{-8}
Diode factor	1.23	1.28

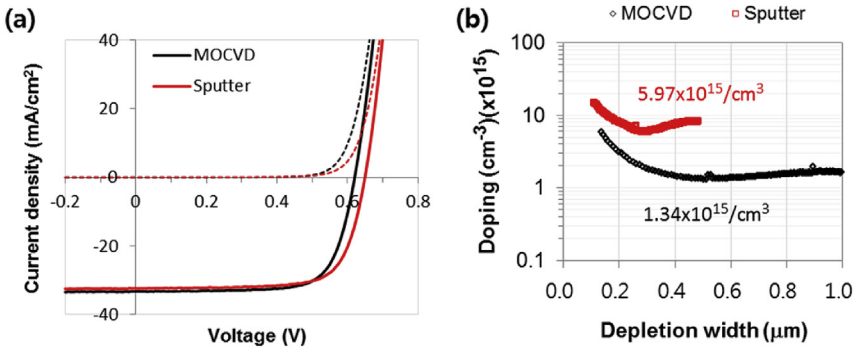

Fig. 1. (a) current density-voltage characteristics and (b) doping profiles of solar cells with different TCO layers.