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Wide-bandgap $CuGaSe_2$ thin film solar cell fabrication using ITO back contacts

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ABSTRACT

In the tandem $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin film solar cell fabrication, Indium tin oxide thin film (ITO) is a promising material as back contacts of the top cell. ITO thin films were deposited by radio frequency (rf) magnetron sputtering in pure argon atmosphere at a working pressure of 9×10^{-4} Torr with substrate temperature (T_{sub}) of 300 °C. The sheet resistance of as-deposited 200 nm-thick ITO thin films was about 1.3×10^{-4} Ω cm. The ITO thin films were subsequently annealed by rapid thermal annealing (RTA) at a temperature range between 400 and 550 °C for application of the high-temperature $CuGaSe_2$ (CGS) deposition process. After the annealing processes of ITO thin films, we have examined the optical and electrical properties as transparent conducting oxide (TCO) back contacts. CGS thin films were prepared for the top cell in a tandem solar cell structure with wide bandgap of above 1.6 eV as high open circuit voltage photovoltaic devices. The optical and electrical properties of CGS thin film solar cells with ITO back contacts were investigated as compared with that of metallic Mo back contacts. Also, the CGS thin film solar cells were fabricated using ITO and MO back contacts with a conversion efficiency of 5 and 8.2%, respectively.

1. Introduction

The chalcopyrite semiconductor $Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin film is the most promising absorber material for high efficiency solar cells using low-cost processing techniques. Many research groups around the world have reported the high-efficiency CIGS thin film solar cells about 20% using various deposition processes [1,2]. Recently, Jackson et al. reported a new world record 20.8% energy conversion efficiency for CIGS thin film solar cells using intentional potassium doping [3]. The band-gap energy of CIGS thin films can be controlled between 1.04 eV for $CuInSe_2$ (CIS) and 1.68 eV for $CuGaSe_2$ (CGS) by varying the Ga content [Ga]/([In] + [Ga]). In case of single junction solar cells, the ideal band-gap energy for AM 1.5 is estimated to be about 1.4 eV [4]. However, the best conversion efficiency of CIGS solar cells has been recorded in the band-gap energy of about 1.15 eV, which is the [Ga]/([In] + [Ga]) ratio of about 0.3. Thus, the wide band-gap CIGS is required by theoretical calculations for achieving high efficiency solar cell. CGS thin film has an effect on developing wide band-gap as the high open circuit voltage (V_{oc}) photovoltaic cells. CGS thin film is very useful for a top cell of a tandem stacking solar cell structure [5–7]. Currently, Ishizuka et al. achieved a CGS solar cell efficiencies exceeding 10% fabricated on Mo-coated soda-lime glass (SLG) substrates [8]. However, Mo back contacts can't apply to the top cell of tandem devices because it is impossible for light to pass through the metal electrode layer. To solve the problem, transparent conducting oxide (TCO) back contacts are the necessary materials with excellent optical and electrical properties for application of top cell [9,10]. TCO films deposited on glass substrates such as ITO, SnO_2:F, sputtered ZnO:Al, or LPCVD ZnO:B can be used as back contact for thin-film solar cells fabrication [11–13]. Among these TCO materials, ITO films are the promising materials because of good electrical conductivity, high optical transparency in the visible region, wide optical bandgap and high IR reflectivity properties. In order to achieve high quality ITO films, various

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deposition techniques have been studied, such as magnetron sputtering [14,15], pulsed laser deposition [16], chemical vapor deposition [17], electron beam evaporation [18] and reactive thermal evaporation [19].

In this work, ITO thin films were prepared on SLG substrates by rf magnetron sputtering, and the films were annealed by RTA system under vacuum. The effect of annealing temperature on the optical and electrical properties of ITO films was investigated for application of CGS thin film deposition processes.

2. Experimental

ITO thin films were grown on SLG substrates by RF magnetron sputtering systems at the substrate temperature (T_{sub}) of 300 °C using ITO (10 wt.% SnO_2) target which was located at a distance of 100 mm from the substrate. To remove contaminants on the surfaces, the glass substrates were ultrasonically cleaned using acetone, isopropyl alcohol (IPA) and de-ionized water (DIW). The working pressure was controlled by the flux of pure argon (99.999%) using a throttle valve positioned in front of the pumping system and was kept in the range 9×10^{-4} Torr. The deposition conditions for the ITO thin films are summarized in Table 1. Based on the growth of ITO thin films, the highest optical transmission and lowest electrical resistivity have the working pressure of 0.9 mTorr. ITO thin films were not formed below 0.9 mTorr. Also, the optical transmission became lower and the electrical resistivity grew higher above 0.9 mTorr. After the film deposition process, the as-deposited films were cooled to room temperature. The ITO-coated glass substrates were subjected to rapid thermal annealing (RTA) under a base pressure of 7×10^{-3} Torr in the range of temperatures between 400 and 550 °C for 30 min. CGS thin films were prepared using three-stage co-evaporation process of Cu, Ga, and Se element sources at the pressure of about 2×10^{-6} Torr. In the first stage, a Ga_2Se_3 precursor was prepared by elemental Ga and Se fluxes at T_{sub} of 350 °C. The elemental Cu and Se fluxes were supplied during the second stage at T_{sub} of 550 °C. Finally, the Cu-poor ([Cu]/[Ga] < 1) thin films were formed by supply of elemental Ga and Se fluxes during the third stage at T_{sub} of 550 °C. The composition ratios measured by EDS analysis for as-deposited CGS thin films are shown in Table 2. The film compositions were Cu/Ga = 0.9 and Se/(Cu + Ga) = 1.1 for CGS thin films.

Solar cell devices were fabricated by a 60 nm-thick CdS buffer layer using chemical bath deposition (CBD) method, followed by the deposition of 50 nm-thick intrinsic (i-ZnO) and 400 nm-thick aluminum-doped zinc oxide (ZnO:Al) using rf magnetron sputtering. Surface grid-electrodes were formed by thermal evaporation technique using Al sources. As shown in Fig. 1, the device structure can be described as Al/ZnO:Al/i-ZnO/CdS/CGS/ITO/SLG.

The electrical resistivity of ITO thin films was measured using a four-point probe (MCP-T610, Mitsubishi Chemical, Japan) and Hall mobility and carrier concentration were examined by the Hall measurement (HMS-7000, ECOPIA, Korea) using the Van der-Pauw method. The optical transmission values of the deposited thin films were measured using a UV spectrophotometer (UV–vis, Shimadzu Japan, UV–VIS–NIR 3101). Cs-corrected scanning transmission electron microscopy (Cs-corrected STEM, JEM-ARM200F, JEOL, Japan) was used to investigate the interface properties of CGS/ITO and CGS/MO bilayers. Morphologies and compositions of the CGS thin films were examined using field emission scanning electron microscopy (FESEM, Hitachi S4700, Japan at 10 kV), and energy dispersive spectroscopy (EDS, EDAX Genesis apex, acceleration voltage: 30 kV, collection time: 100 s with standardless method), respectively. The external quantum efficiency (EQE) and the conversion efficiency for the CGS solar cells were characterized using an IPCE (incident photon conversion efficiency) measurement unit (PV Measurements, Inc., USA) and a solar simulator (94082A, Newport, USA) at 25 °C under 100 mW cm^{-2} (AM 1.5 G) illumination, respectively.

Table 1
Deposition conditions for ITO thin films.

Parameter	Value
Target	4 inch – In_2O_3:SnO_2 (10 wt.%)
Target-substrate distance (mm)	100
Base pressure (Torr)	$<5 \times 10^{-7}$
Working pressure (mTorr)	0.9
Plasma power density (W/cm^2)	0.85
Sputtering gas and flow rate (sccm)	Ar, 30
Substrate temperature (°C)	300

Table 2
Composition ratios measured by EDS analysis for as-deposited CGS thin films.

Element	Cu	Ga	Se	Cu/III
Composition (%)	22.54	25.06	52.40	0.90

3. Results and discussion

Fig. 2 shows the optical transmission and average transmission of ITO thin films as a function of annealing temperature in the wavelength range from 300 to 1200 nm. In Fig. 2(a), the transmission spectra have a slight decrease in the visible wavelength region by increasing the annealing temperature. It is clearly observed that these spectra show a distinct difference at wavelengths longer than 900 nm. As a result of spectral transmission curve, the as-deposited ITO thin film shows an average transmission of 83.1% as can be seen in Fig. 2(b). For the film annealed at 450 °C, an average transmission has a minimum value of 80.9%, which decreases about 2.2% compared with that of as-deposited ITO film. However, these measures increase above 450 °C and are 81.3 and 82% at annealing temperature of 500 and 550 °C, respectively. The optical transmission of CGS thin film increases in the wavelength of 740 nm and shows high transparency above this wavelength range [20]. Therefore, this result indicates that the optical properties of ITO back contact can be applied to CGS thin film solar cells for the top cell of CIGS-based tandem solar cell structure.

The influence of annealing temperature on the electrical properties of ITO thin films was examined using a four-point probe and hall measurement. As shown in Fig. 3, the resistivity, carrier concentration and hall mobility of as-deposited ITO film are approximately 1.3×10^{-4} Ω cm, 3.1×10^{20} cm^{-3} and 56 cm^2/V s, respectively. The resistivity of ITO films decreases by 1.0×10^{-4} Ω cm at the annealing temperature of 450 °C and then increases by 1.4×10^{-4} Ω cm at the annealing temperature of 550 °C. As the annealing temperature increased from 400 to 550 °C, the resistivities of ITO films have excellent thermal stability with a slight variation. The lowest resistivity of ITO film annealed at 450 °C is caused by a maximum carrier concentration of 1.4×10^{21} cm^{-3} and a minimum hall mobility of 47.5 cm^2/V s. For the film annealed at 550 °C, the carrier concentration and hall mobility are 7.1×10^{20} cm^{-3} and 50 cm^2/V s, respectively. The carrier concentration increased to reduce the resistivity has an effect on reduction of TCO film transmission in the near infrared (NIR) region as a result of absorption by free carriers or by metal-like reflection [21]. Therefore, as presented in Fig. 2(a), the optical transmission spectra of ITO thin films at the annealing temperature of 450 °C reduce in the NIR region.