I O U R N A L O F

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Investigation on the interface of GZO/ITO double-layered transparent conducting oxide films for solar cells

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GZO/ITO double-layered films were deposited on non-alkali glass substrates by RF magnetron sputtering with various thicknesses at different deposition temperatures. The total thickness of the double layer was constant (~400 nm), and ITO thin films were prepared at various thicknesses (50, 150 and 250 nm) as function of the GZO film thickness (350, 250, 150 nm) at RT (or 200 $^{\circ}$ C). The resistivity of the double layer was found to be dependent on the thickness ratio between the two layers. The resistivity of the double-layered films decreased with increasing ITO film thickness according to the rules of parallel DC circuits of the two single layers. X-ray diffraction showed that the enhancement of the GZO (002) preferred orientation increased with increasing ITO thickness. The crystallinity of the GZO films was strongly affected by the microstructure of the buffer layer, which improved the Hall mobility and decreased the electrical resistivity. On the other hand, the crystallinity of the double layer decreased when the GZO films were deposited on the unstable buffer layer which was under post-annealed circumstances. In the case of the GZO (as-deposited at 200 $^{\circ}$ C)/ITO(RT) films, the diffusion of elements occurred between the upper and buffer layers, which caused microstructural changes in the films. This result was observed by scanning electron microscopy and energy dispersive X-ray spectroscopy. The transmittance of the double layer was > 85% in the visible region, which suggests that these films will be suitable for photovoltaic devices.

Key words: ITO, GZO, Double layer, Interface, Solar cells, Magnetron sputtering.

Introduction

Transparent conducting oxide (TCO) films are used widely for opto-electronic devices and are essential for solar cell applications. In particular, indium tin oxide (ITO) films are used extensively as transparent conducting electrodes in multiple fields, such as liquid crystal displays (LCDs), plasma display panels (PDPs) and organic light emitting diodes (OLEDs) [1, 2], on account of their high conductivity and transparency in the visible region [3]. On the other hand, when ITO films are exposed to an oxygen atmosphere at high temperatures, their electrical resistivity increases sharply due to the exhaustion of oxygen vacancies [4, 5]. Recently, ZnO-based TCO films have been widely used because they are abundant, nontoxic and inexpensive. In addition, their electrical properties can be improved by doping with impurity ions with a +3 valence, such as Al^{3+} or Ga^{3+} [6, 7]. For example, Ga-doped zinc oxide (GZO) films have high thermal stability [8] and transparency compared to ITO but they still have higher room temperature resistivity

than ITO films. TCO films are exposed to high temperatures during use as electrodes in solar panels. The electrical and optical properties of TCO films must be maintained under such environments. The properties of TCO need to be improved during heat treatment and interfacial reaction. Therefore, ITO films are used as buffer layers to compensate for the lower electrical conductivity of GZO films, GZO films are deposited on ITO films with various thicknesses to improve the low heat stability of ITO thin films. GZO/ITO double-layered films at various thickness ratios and deposition temperatures were deposited by RF magnetron sputtering using an ITO and GZO target. This study examined the effect of the thickness and deposition temperatures on the microstructural and electrical properties of the resulting GZO/ITO films. This paper discusses the phenomenon generated at the interface between GZO and ITO related to the deposition temperature and film thickness ratio.

Experimental details

GZO films and ITO films were deposited on nonalkali glass substrates (Corning 2000) by RF magnetron sputtering (multi-sputtering system-b, Daeki Hitech Co. Ltd.) using an ITO target (10 wt. % SnO₂) and GZO

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Conditions	GZO film	ITO film	
Target	GZO (Ga2O3 5.57wt. %)ITO (SnO ₂ 10 wt. %)	
T-S distance (mm)*	30	50	
RF power (W)	80	70	
Working pressure (Pa)	1	0.25	
Ar gas flow rate (sccm)	20	30	
Film thickness (nm)	150, 250, 350, 400	50, 150, 250, 400	
Substrate tempera- ture $\binom{0}{C}$	RT, 200	RT, 200	

Table 1. Deposition parameters for GZO/ITO film

*T-S distance : distance between target and substrate

Table 2. Deposition temperature for GZO(250 nm)/ ITO(150 nm) films

	Substrate temperature (°C)			
_	(a)	(b)	(c)	(d)
GZO(250 nm)	200	RT	RT	200
ITO(150 nm)	RT	RT	200	200

target (5.57wt. % Ga₂O₃). ITO film deposition was carried out in pure Ar gas (purity: 99.9999%) at a total gas pressure of 0.25 Pa. The substrate to target distance was 50 mm and the RF power was 70 W. The GZO film was deposited in a pure Ar gas atmosphere at 1.0 Pa. The substrate to target distance was 30 mm with a RF power of 80 W. The total thickness of the GZO/ITO double-layered films was constant at approximately 400 nm. The ITO thin films were prepared on nonalkali glasses at various thicknesses (50, 150 and 250 nm) and the GZO films were deposited on the ITO films at various thicknesses at room temperature and 200 °C. Each single layer GZO and ITO without a buffer layer with a thickness of 400 nm were made as a reference. Table 1, 2 lists the sputtering conditions. The film thickness was determined using a spectral reflectometer (ST2000-DLXn, K-Mac). The resistivity, carrier density and Hall mobility were measured by Hall Effect measurements (HMS-3000, Ecopia). The X-ray diffraction (XRD) patterns were measured using CuK α radiation (Bruker Gadds). The surface morphology was examined by atomic force microscopy (AFM, L-Trace II, Nano Navi). The optical transmittance was measured using a UV-Visible spectrophotometer (UV-1800, Shimadzu) over the wavelength range, 190 to 1100 nm. The diffusion at the interface of the double layer was investigated by scanning electron microscopy (SEM, S-4200, Hitachi Ltd.) and energy dispersive spectrometry (EDS, 7593-H, Horiba).

Results and discussion

Electrical properties

Fig. 1 shows the electrical properties of the GZO/ITO film as a function of the thickness ratio and deposition temperatures (RT, 200 °C). The double layer thickness was approximately 400 nm, and the GZO single layer and ITO single layer had the same thickness. The GZO single layer deposited at room temperature showed a resistivity of $2.19410^{-3} \Omega$ cm. The resistivity of the double layer decreased with increasing ITO thickness, indicating that the resistivity of a double layer depends on the thickness ratio of the two layers. This means that the electrical properties of GZO films are improved by introducing ITO films. The total resistivity of GZO/ ITO films is a result of the parallel combination of two single layers. The measured figures are not significantly different from the calculated figures [9, 10]. When the ITO thickness increased, the Hall mobility of GZO with the ITO film was improved significantly and was much higher than that of the GZO single layer. The difference of carrier concentration between the GZO single layer and ITO single layer was not much, which is in contrast to that of Hall mobility. Therefore, the resistivity of the double layer was affected more by the Hall mobility than the carrier concentration.

The resistivity of (b) GZO(RT)/ITO(RT) was higher than (c) GZO(RT)/ITO(200 °C). In addition, (d) GZO(200 °C)/



Fig. 1. Resistivity, carrier density and Hall mobility of GZO/ITO films deposited with various thicknesses at deposition temperatures.



Fig. 2. X-ray diffraction patterns of GZO(250 nm)/ITO(150 nm) films deposited at various temperatures.

ITO(200 °C) film showed good electrical conductivity. This was attributed to an increase in Hall mobility due to the improved film crystallinity, as confirmed by XRD (Fig. 2). On the other hand, the (a) GZO(200 °C)/ITO(RT) films had the lowest electrical conductivity of the films examined. Although heat treatment was performed, the (a)

films exhibited poor electrical properties. This will be discussed in detailed according to the film microstructure.

Structural properties

Fig. 2 shows XRD patterns of the GZO(250 nm)/ ITO(150 nm) films deposited at RT and 200 °C, respectively. The (002) peak intensity of the GZO layer increased with increasing crystallinity of the ITO films [11]. The XRD patterns of the (b), (c) and (d) films showed that the increase in the GZO (002) peak was attributed to the enhanced crystallinity of the ITO film with increasing deposition temperature. The ITO films had an amorphous structure deposited at room temperature [film (b)], which changed to a crystalline structure when deposited above crystallization temperature (approximately 170 °C [12]) [film (c)]. Therefore, GZO films grown on crystalline ITO films showed a high intensity (002) peak. The (d) films had the highest (002) peak intensity, as shown in the scale bar, which is in good agreement with the Hall mobility of the double layer. The GZO films showed a highly preferential growth along the c-axis orientation, as reported widely [13]. An improvement in crystallinity leads to an increase in Hall mobility, which results in a decrease in the electrical resistivity of the double layer. Therefore, the drastic increase in mobility is due to an improvement of crystallinity of the GZO film by employing an ITO buffer layer, which results in a decrease in the electrical resistivity of the double layer, as shown in Fig.1. The near epitaxial growth of the GZO films on the ITO films might be due to the small lattice mismatch between the neighboring oxygenoxygen (O-O) distances of In₂O₃ to that of ZnO on the close-packed [14]. On the other hand, the XRD pattern of (a) GZO(200 °C)/ITO(RT) film show ITO (222) peak and relatively weak peak for GZO (002) plan. The structure of ITO is believed to have changed from amorphous to crystalline. The crystal growth of ITO



Fig. 3. SEM images of GZO(250 nm)/ITO(150 nm) films as a function of deposition temperatures.







Fig. 5. AFM images and Ra values of GZO(250 nm)/ITO(150 nm) films as a function of deposition temperatures.

films was attributed to the annealing time when the substrate temperature was increased to 200 °C.

Microstructure

Fig. 3 shows SEM images of the double layer as a function of the deposition temperature. In the case of the (b) double layer, the GZO films were deposited on the amorphous ITO films, so the double layer on the substrate shows only a columnar structure. The image of film (c) showed the crystal structure of the ITO films and columnar structure of GZO films because the as-deposited ITO films at 200 °C were crystallized. The SEM image of the (d) film shows the grain growth of ITO and columnar structure of GZO films. This observation corresponds to the XRD patterns shown in Fig. 2. The improvement of crystallinity leads to an increase in Hall mobility and a decrease in the electrical resistivity. On the other hand, there is the exception of SEM image, which is unlike other films. In the case of the (a) films, the

SEM image showed a less columnar structure of GZO than the (b) images and the interface between GZO and ITO was unclear. This might be caused by the interruption of c-axis growth of the GZO film due to the introduction of a buffer layer which is an unstable structure because of heating and sputtering. ITO was deposited on non-alkali glass at room temperature and then post-annealed for 20~30 minutes while the substrate temperature was increased from room temperature to 200 °C. When the substrate temperature reached 200 °C, GZO was sputtered on the ITO film for 4 minutes (the film thickness was approximately 150 nm). On the other hand, the structure of the ITO films kept changing while GZO was deposited on the ITO film. Therefore, the GZO films were grown on an unstable buffer layer that interfered with the c-axis growth of GZO films. This can explain the decrease in the (002) peak intensity of the XRD patterns (Fig. 2) and the Hall mobility shown in Fig. 1. In addition, the electrical resistivity showed good agreement with the crystallinity of the double layer. The interface between the ITO and glass of the (a) and (d) films was not distinguished as clearly as the (b) and (d) images. The ITO film of the (a) and (d) film were affected by postannealing. Therefore, the elements of GZO and ITO films might have diffused to the interface during sputtering and heating time.

Fig. 4 shows the EDS mapping profile images with a cross-section of the double layer. The (a) and (d) images show that the elements of ITO had diffused more to the surface of the films than that of the (b) and (c) films which are GZO films deposited at room temperature. When the GZO films were sputtered on the ITO films deposited at 200 °C, indium was diffused to the upper layer and the GZO film grew on the less crystalline structure of the ITO film. Therefore, the columnar structure of the GZO was not depicted clearly in the SEM images (Fig. 3). This observation corresponds to the XRD patterns, which indicates that the (a) and (d) films show a relatively weak peak for the (002) plan.

Fig. 5 shows AFM images and R_a (average roughness) values of the GZO(250 nm)/ITO(150 nm) films as a function of the deposition temperature. The surface roughness of the films was quantified by the mean surface roughness (R_a). The R_a values of the double layer increased with increasing crystallinity of the ITO films. The uniformity of the (b), (c) and (d) films was improved by the introduction of an ITO buffer layer due to the preferential c-axis growth of the GZO films with increasing crystallinity in the ITO films. On the other hand, the R_a value of the (a) film was smaller than those of the other films. This might be due to the relative decrease in the crystallinity of GZO films caused by the interference of preferential c-axis growth due to the introduction of an unstable ITO film structure and the diffusion of elements to the interface. These results confirmed that the surface morphology of the double



Fig. 6. Transmittance of (A) GZO(250 nm)/ITO(150 nm), (B) GZO(400 nm) and (C) ITO(400 nm) films deposited at room temperatures.

layer is affected by the microstructure of the ITO films and the crystallinity of the GZO films.

Optical properties

Fig. 6 shows the optical transmittance for the GZO/ ITO films measured over the wavelength range, 190-1100 nm, as a function of the thickness and deposition temperatures. As shown in the figure, all the films had high transmittance > 85% in the visible light region. This suggests that the mean optical transmittance of the double-layer (90%) is slightly higher than that of the ITO single-layer (85%) in the visible region (550 nm), and there is no significant difference in the transmittance of the GZO single layer, which was estimated to be approximately 400 nm in thickness. Therefore, the double layer can be applied to the solar cells.

Conclusion

GZO/ITO double-layered films were deposited on non-alkali glass substrates by RF magnetron sputtering at various film thickness ratios and deposition temperatures (room temperature and 200 °C). The electrical properties showed good agreement with those of the ITO buffer layer. This confirmed that the electrical properties of the double layer were strongly affected by the thickness, microstructure and crystallinity of the ITO buffer layer. The electrical properties of the double layer were improved by introducing the ITO films according to the rules for parallel DC circuits of two single layers. The preferential c-axis growth of the GZO films was improved by increasing the crystallinity of the ITO films. This corresponds to the XRD patterns and an increase in the Hall mobility of the films. On the other hand, the unstable ITO buffer layer, which alters the structure due to post- annealing effect at 200 °C, interfered with the crystal growth of the GZO films. During heating and sputtering, elements of the GZO and ITO films could diffuse to the interface of the double layer, which was observed by SEM and EDS. The optical transmission data showed that GZO films with ITO a mean visible transmittance of 90%, which is slightly higher than that of an ITO single layer film. This suggests that the GZO/ITO double layers will be suitable for use in photovoltaic devices.

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