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Ceramics International 40 (2014) 1457–1460

CERAMICS INTERNATIONAL

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Improved electrical and optical properties of GZO films with a thin TiO_2 buffer layer deposited by RF magnetron sputtering

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Received 20 March 2013; received in revised form 3 July 2013; accepted 4 July 2013
Available online 21 July 2013

Abstract

Ga-doped ZnO (GZO) thin films were prepared by radio frequency magnetron sputtering without intentional substrate heating on bare glass and TiO_2-deposited glass substrates to investigate the effect of a thin TiO_2 buffer layer on the optical and electrical properties of the films. The thicknesses of the TiO_2 buffer layer and GZO films were kept constant at 5 and 100 nm, respectively.

As-deposited GZO/TiO_2 bi-layered films show a higher transmittance of 83.0% than that of the GZO films, and GZO/TiO_2 films show a lower resistivity (1.03×10^{-2} Ω cm) than that of the GZO single layer films. In addition, the work function of the GZO film was affected by the TiO_2 buffer layer, where the GZO/TiO_2 films had a higher work-function (4.86 eV) than that of the GZO single layer films. The experimental results indicate that a 5-nm-thick TiO_2 buffer layer in the GZO/TiO_2 films results in better electrical and optical performance than conventional GZO single layer films.

Keywords: GZO; TiO_2; Electrical properties; Optical properties; Grain size

1. Introduction

Recently, there has been considerable interest in the use of Ga-doped ZnO (GZO) films as a transparent and conducting oxide (TCO) for transparent electrodes in solar cells and display devices [1,2] due to the fact that they are less expensive than conventional Sn-doped In_2O_3 (ITO) films. However, conventional GZO films have some drawbacks such as a relatively higher resistivity than the ITO films and weakness to moisture, which may deteriorate the electrical and optical performances of devices. Thus, in order to overcome these problems, transparent diffusion barrier films have been researched to simultaneously optimize the optical and electrical properties of the GZO films. Recently, Nomoto reported the effects of a ZnO buffer layer on the characteristics of transparent conducting GZO films prepared by DC magnetron sputtering [3].

In this study, GZO thin films were deposited by radio frequency (RF) magnetron sputtering on glass substrates with and without a TiO_2 buffer layer, and then the effects of a TiO_2 buffer layer on the optical and electrical properties of the GZO films were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscope (SEM), Hall effect measurements, and UV-visible spectrometry. In addition, the influence of the TiO_2 buffer layer on the work function of GZO films was evaluated using UV photoelectron spectroscopy (UPS) to evaluate GZO/TiO_2 films as a transparent anode electrode for organic light emitting diode (OLED) applications.

2. Experimental

Both GZO and TiO_2 films were deposited on glass (corning 1737) substrates without intentional substrate heating using an RF (13.56 MHz) magnetron sputtering system equipped with two cathodes. The sintered ZnO (97%)–Ga (3%) and pure TiO_2 targets were both 3 in. in diameter and 0.25 in. thick. For all depositions, the distance between the target and substrate was constant at 6 cm, and the substrate rotation speed was set to 8 rpm. The GZO/TiO_2 bi-layered films were obtained by continuously depositing each film layer without exposure of the films to the atmosphere.

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http://dx.doi.org/10.1016/j.ceramint.2013.07.029

Substrate temperature was monitored using a K-type thermocouple in contact with the substrate, and the substrate temperature increased to 70 °C during deposition. Table 1 shows the main parameters used for deposition.

After deposition, high resolution XRD (X'pert Pro MRD, Philips) at the Korea Basic Science Institute (KBSI, Daegu center) was used to observe the thin film crystallinity. The grain size of the films was evaluated from the XRD pattern using the Scherrer formula [4].

Optical transmittance in the visible wavelength region was observed with a UV–vis spectrophotometer (Cary 100 Cone, Varian), and the glass substrates showed 92% optical transmittance in the visible wavelength range. The surface roughness investigation was performed by means of an AFM (XE-100, Park system) on $2 \times 2\ \mu m^2$ sample areas under ambient conditions. The thickness of the films was measured using a surface profilometer (Dektak 3D, Veeco), and the electrical properties, such as carrier concentration and mobility, were observed with Hall effect measurements employing the van der Pauw geometry (HMS-3000, Ecopia). The performance of GZO and GZO/TiO_2 films as a TCO electrode was compared using a figure of merit. In addition, to consider the influence of a TiO_2 buffer layer on the work function of GZO films, work functions of the films were evaluated using UPS analysis.

3. Results and discussion

Fig. 1 shows the XRD patterns of the GZO single layer and GZO/TiO_2 bi-layer films prepared without substrate heating. Although neither film showed a diffraction peak of ZnO (0 0 2), GZO/TiO_2 bi-layer films show a larger grain size of 10.21 nm than that (8.9 nm) of the GZO single layer films. In a previous study, Kim reported similar results, namely, that in ITO/Au bi-layered films, the crystallization of the upper ITO film is promoted by an Au buffer layer without intentional substrate heating [5].

Surface morphology of TCO films is an important factor in determining the optical and electrical properties [6]. Fig. 2 shows AFM images of GZO films prepared on bare glass substrates and TiO_2 deposited on glass substrates. The root mean square (RMS) roughness of the GZO film (2.2 nm) is higher than that of the GZO/TiO_2 film (1.1 nm). From the AFM images, one can conclude that TiO_2 buffer layers may enhance the flatness of the GZO/TiO_2 films. During buffer layer deposition, TiO_2 film grows preferably in a sunken region on the substrate. Thus, the GZO/TiO_2 film has the more

Table 1
Deposition conditions of GZO and TiO_2 thin films.

	GZO	TiO_2
Base pressure (Pa)	1.5×10^{-4}	1.3×10^{-4}
Deposition pressure (Pa)	1.8×10^{-2}	1.3×10^{-1}
Power density (W/cm^2)	RF, 3.5	RF, 4.0
Deposition rate (nm/min)	10	1
Ar/O_2 gas flow rate	5/0.03	20

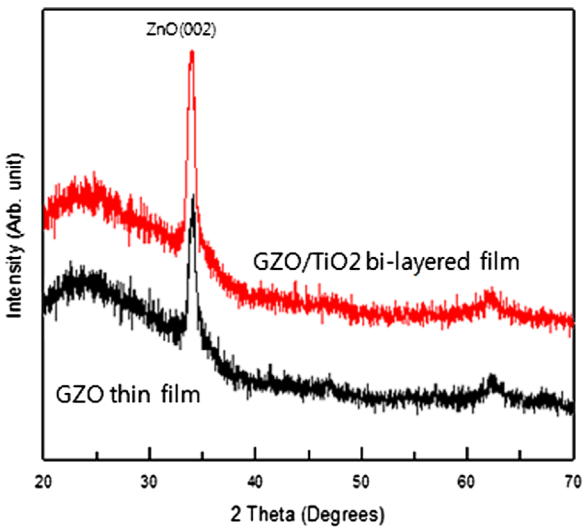

Fig. 1. The XRD patterns of the GZO and GZO/TiO_2 bi-layer films.

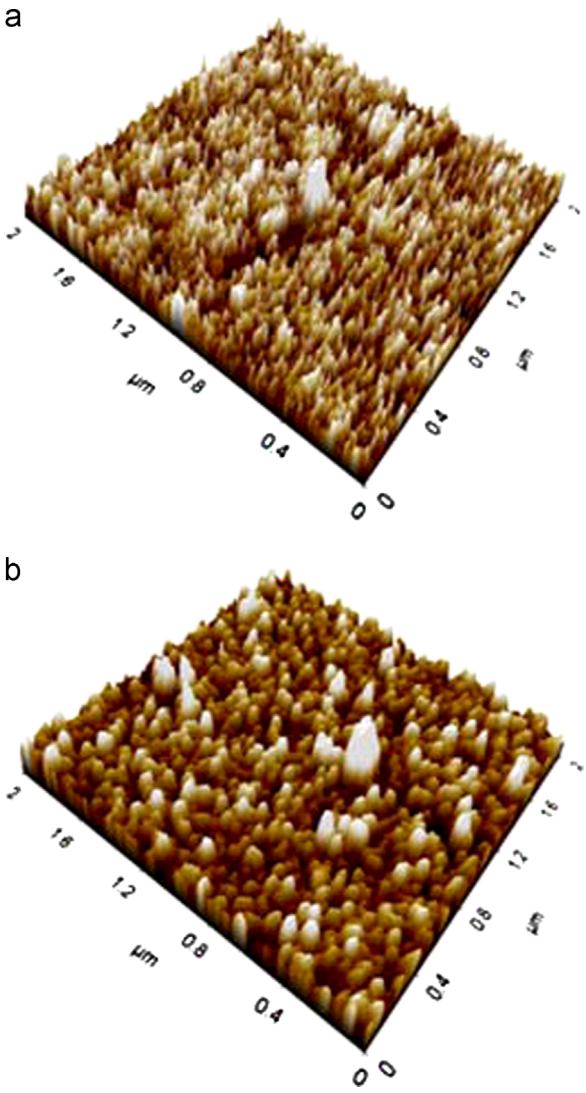

Fig. 2. The RMS roughness of the GZO and GZO/TiO_2 Bi-layer films. (a)GZO, 2.83 nm, (b) GZO/TiO_2, 1.53 nm.

flat surface than that of the GZO single layer films. Recently, J. Park reported that a Ni interlayer in ITO/Ni/ITO multilayer films also promotes the flatness of the upper ITO films [7].

Table 2 shows the influence of the TiO_2 buffer layer on the electrical properties of the films. The GZO/TiO_2 films have a lower resistivity of $1.03 \times 10^{-2}\,\Omega$ cm than that of the GZO single layer film due to increases in both carrier concentration and mobility.

Table 2
The comparison of electrical properties of the films.

Films	Concentration (10^{20}/cm^3)	Mobility (cm/S)	Resistivity (Ω cm)
GZO	4.4	7.2	1.9×10^{-2}
GZO/TiO_2	6.9	9.1	1.0×10^{-2}

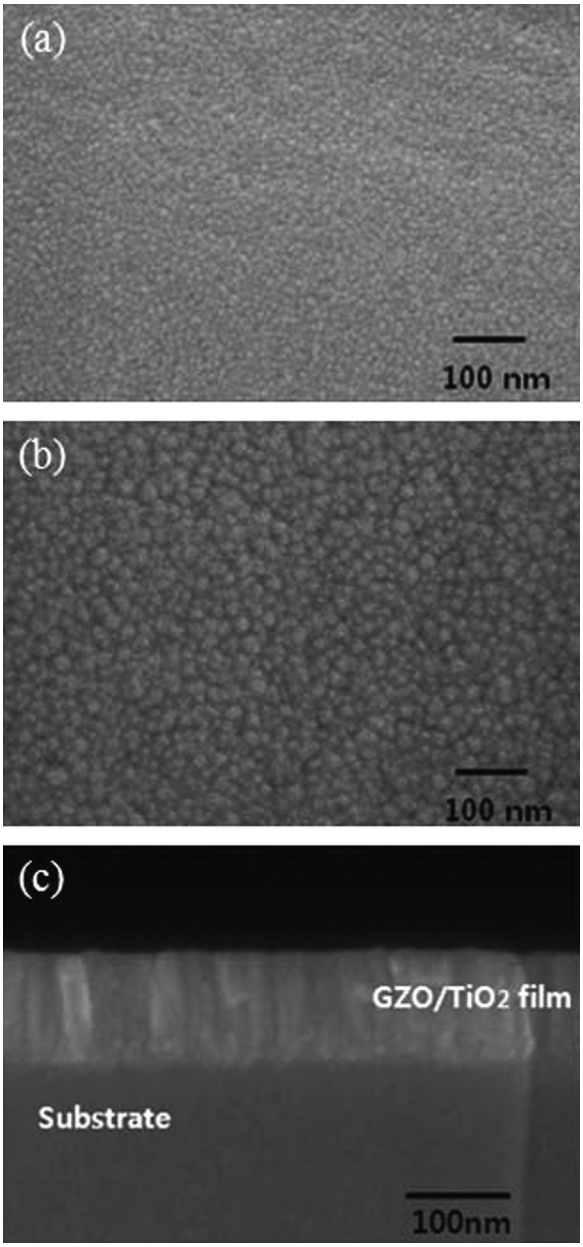

Fig. 3. SEM image of the GZO and GZO/TiO_2 bi-layer films. (a) GZO, (b) GZO/TiO_2 film, (c) cross-sectional image of GZO/TiO_2 film.

Fig. 3 shows the surface and cross-section images of as deposited GZO and GZO/TiO_2 films. The GZO/TiO_2 films show the lager grain size than that of GZO single layer films. Since increased crystallization of GZO/TiO_2 films results in a lower density of the grain boundary which acts as a trap for charge carrier, it can be concluded that the electrical resistivity of GZO/TiO_2 films is decreased with carrier concentration as shown Table 2.

Fig. 4 shows the optical transmittance for GZO and GZO/TiO_2 films. For the GZO film, the average transmittance in the visible range is about 82.5%, and the transmittance of ITO/TiO_2 films is about 83.0%. Table 3 provides a comparison of optical and electrical properties of the films. The GZO/TiO_2 films had a lower sheet resistance than that of the GZO single layer films.

The figure of merit (FOM) is an important index for evaluating the performance of transparent conducting oxide (TCO) films [8]. FOM is defined as $\mathrm{FOM} = T^{10}/R_s$, where T is the optical transmittance and R_s is the sheet resistance. The FOM reached a maximum of $1.4 \times 10^{-4}\,\Omega^{-1}$ for the GZO/TiO_2 films, which is higher than the $7.5 \times 10^{-5}\,\Omega^{-1}$ for the GZO single layer films prepared in this study. Since a higher FOM value indicates better quality TCO films, it is supposed that the GZO film with a 5-nm-thick TiO_2 buffer layer will likely perform better in TCO applications than GZO single layer films.

The high work function of TCO films, which is close to the value of the highest occupied molecular orbital (HOMO) of the organic layer, allows hole injection from TCO to the organic layer of OLED, which results in a decrease in the turn-on voltage of the OLED. However, the work function of conventional ITO films is lower than the HOMO of the organic layer of OLEDs. Thus, several techniques have been developed to increase the work function of ITO [9,10].

Fig. 5 shows the kinetic energy cut-off spectra obtained from the GZO/TiO_2 films. This allowed the determination of the work function values directly from the spectra by fitting straight lines into their kinetic energy cut-off and determining the intersection with the baseline of the spectra. Table 4 shows the compared work functions of conventional ITO, GZO and

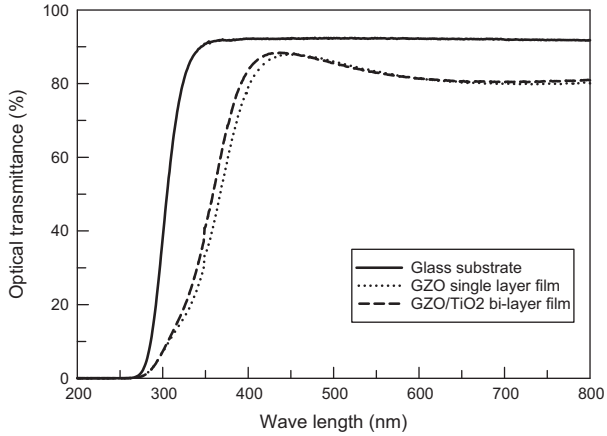

Fig. 4. The optical transmittance of the GZO and GZO/TiO_2 bi-layer films.

Table 3
The comparison of figure of merit (FOM, Ω^{-1}).

Films	Sheet resistance (Ω/□)	Transmittance (%)	FOM (Ω^{-1})
GZO	1930	82.5	7.5×10^{-5}
GZO/TiO_2	1037	83.0	1.4×10^{-4}

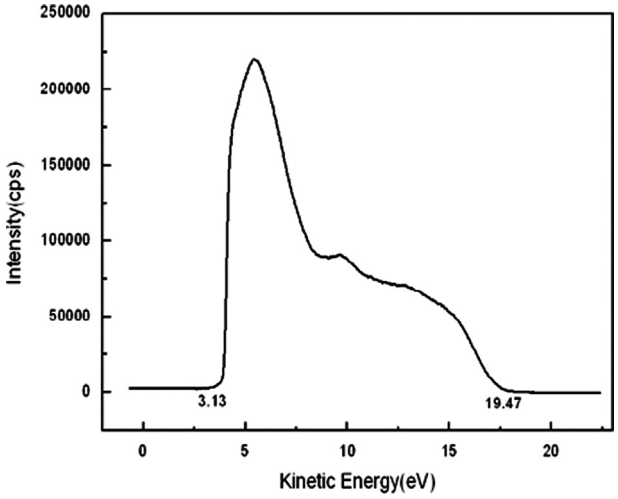

Fig. 5. The kinetic energy cut-off spectra obtained from the GZO/TiO_2 bi-layer films.

Table 4
Comparison of the work function of the ITO, GZO and GZO/TiO_2 films.

TCO films	Work function (eV)	Reference
ITO	4.43	[10]
GZO	4.47	This study
GZO/TiO_2	4.86	This study

GZO/TiO_2 films. The GZO/TiO_2 films show a higher work function of 4.86 eV. Thus, adding a TiO_2 buffer layer is one useful method to increase the work function of GZO films.

4. Conclusions

Both GZO single layer and GZO/TiO_2 bi-layered films were prepared by RF magnetron sputtering on glass substrates. The structural, optical and electrical properties of the GZO films were dependent on the TiO_2 buffer layer.

From AFM observations, it is apparent that TiO_2 buffer films enhance the flatness of the GZO/TiO_2 films. The figure of merit for the GZO/TiO_2 bi-layered films reached a maximum value of $1.47 \times 10^{-4}\ \Omega^{-1}$, which was greater than that of the GZO single layer films.

Also, GZO/TiO_2 bi-layered films show a higher work function than that of the GZO single layer films. These results indicate that the 5-nm-thick TiO_2 buffer layer in the GZO/TiO_2 films results in better performance than GZO single layer films.

Acknowledgement

This work was supported by 2012 Research Fund of University of Ulsan.

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