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Thermally stable transparent conducting and highly infrared reflective Ga-doped ZnO thin films by metal organic chemical vapor deposition

J.L. Zhao [a], X.W. Sun [a,b,*], H. Ryu [c], Y.B. Moon [d]

[a] Department of Applied Physics, College of Science, Tianjin University, 92 Weijin Road, Tianjin 300072, People's Republic of China
[b] School of Electrical & Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore
[c] Department of Nano Systems Engineering, Center for Nano Manufacturing, Inje University, Obang-dong, Gimhae, Gyeongnam 621-749, Republic of Korea
[d] THELEDS Co., Ltd., Yongin-si, Gyeonggi-do 449-871, Republic of Korea

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ABSTRACT

Highly transparent conductive Ga-doped ZnO (GZO) thin films have been prepared on glass substrates by metal organic chemical vapor deposition. The effect of Ga doping on the structural, electrical and optical properties of GZO films has been systematically investigated. Under the optimum Ga doping concentration (~4.9 at.%), *c*-axis textured GZO film with the lowest resistivity of $3.6 \times 10^{-4}\ \Omega$ cm and high visible transmittance of 90% has been achieved. The film also exhibits low transmittance (<1% at 2500 nm) and high reflectance (>70% at 2500 nm) to the infrared radiation. Furthermore, our developed GZO thin film can well retain the highly transparent conductive performance in oxidation ambient at elevated temperature (up to 500 °C).

1. Introduction

Transparent conducting oxide (TCO) thin films have a large variety of applications in optoelectronic industry, such as transparent electrodes for light-emitting diodes (LEDs), liquid crystal displays (LCDs), photodetectors and solar cells [1–5]. TCO films can also show high reflectance to infrared radiation due to the resonance plasma effect induced by high density carriers, which is promising for the infrared/heat reflective coating for energy saving glasses/windows [6–8]. Currently the most developed TCO technology for practical applications is based on indium-tin-oxide (ITO). However, ITO will be difficult to meet the fast growing demand in the optoelectronics industry due to the scarcity of indium. As a result, indium-free TCOs have recently attracted much attention as a substitute for ITO [9,10]. Doped ZnO is one of the most promising candidates for replacing ITO [10–21]. ZnO has a direct wide band gap of 3.4 eV, which can be used for optoelectronic devices operating in the blue to UV region. The most important advantage of ZnO over ITO is the abundance of Zn element and the lower cost. To increase its electrical conductivity, ZnO is usually doped with group III elements including B, Al, Ga or In as effective donors. Al-doped ZnO (AZO) [7,16–18] and Ga-doped ZnO (GZO) [8,10–16] are the most widely developed TCOs for transparent electrode and infrared insulator applications. Furthermore, previous efforts suggest that GZO has better conduction stability than AZO because Ga is less reactive and more resistant to oxidation than Al [16].

Many deposition techniques have been employed to deposit ZnO based thin films, including magnetic sputtering [5,10–13,16–18], metal organic chemical vapor deposition (MOCVD) [1,2,15,19–23], pulsed laser deposition (PLD) [4,14,16], molecular beam epitaxy (MBE) [24], e-beam evaporation [25], chemical spray pyrolysis [26], sol–gel [27], etc. Among these methods, sputtering and MOCVD are preferred for practical use as the two are easily scalable for large area deposition with high film quality. Furthermore, MOCVD can also enable on-line glass coating (integrating the deposition process with floating glass production line) [28], which is very promising for development of low cost large area TCO glasses. In this paper, we shall report a systematically study on the Ga doping dependency, electrical conduction, transmittance and infrared reflectance properties for GZO thin films by MOCVD. Low resistivity, high visible transparency, high infrared reflectance, and high thermal stability have been achieved in the optimized GZO film.

2. Experimental procedure

The GZO thin films were deposited by a home-made showerhead injector MOCVD system on amorphous glass substrates. Trimethylgallium (TMGa), dimethylzinc (DMZn) and oxygen were

* Corresponding author at: School of Electrical & Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore.
E-mail address: exwsun@ntu.edu.sg (X.W. Sun).

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used as precursors and nitrogen was employed as the carrier gas for the metal organics. The flow of N_2 and O_2 was controlled at 500 and 200 standard cubic centimeter per minute (sccm). The flow of TMGa and DMZn were controlled at 0–5 sccm and 2 sccm, respectively, where the Ga content in the film was adjusted by varying the TMGa flow. The GZO films were grown at a relatively low temperature of 300 °C with a chamber pressure of ~25 Torr. The thickness of ZnO film is about 600 nm. To study the thermal stability, the GZO film was also deposited on quartz substrate under the aforementioned growth conditions, which was further annealed in air ambient at temperature of 400–600 °C with the duration of 2 h.

The Ga content in GZO films was determined by energy dispersive X-ray spectroscopy (EDX) analysis attached to a JSM- 5600LV scanning electronic microscope (SEM). The film crystal quality was investigated by X-ray diffraction (XRD) with a Siemens X-ray diffractometer at 45 kV and 40 mA under $\theta/2\theta$ scan mode. The surface morphology was characterized by atomic force microscopy (AFM, DIGITAL INSTRUMENTS NanoScope IIIa). The electrical properties including resistivity, carrier concentration and Hall mobility was measured by van der Pauw method using a Hall effect measurement system (HL5500PC) with the magnetic field strength of 0.326T. The optical transmittance and reflectance properties were obtained using a UV–VIS-NIR spectrophotometer (PERKIN ELMER, Lambda 950).

3. Results and discussion

Fig. 1 shows the XRD patterns ($\theta/2\theta$) of GZO thin films with various Ga doping concentration. All the films show well defined wurtzite ZnO phase with no other impurity crystal phases. Undoped ZnO film exhibits a strong *c*-axis texture with only (0 0 2) diffraction in XRD scan. With the doping of Ga, some other peaks from different planes emerge. Here we introduce a texture coefficient $T_{(hkl)}$ to quantitatively represent the degree of preferred orientation (texture), which is defined as [29].

$$T_{(hkl)} = \frac{I_m(hkl)}{I_0(hkl)} \div \frac{1}{n}\sum_{1}^{n}\frac{I_m(hkl)}{I_0(hkl)} \quad (1)$$

where $I_m(hkl)$ is the measured relative intensity of the reflection from the (hkl) plane, $I_0(hkl)$ is that from the same plane in a standard reference sample (JCPDS 36-1451), and n is the total number of reflection peaks from the film. In present analysis, $n = 6$ since 6 major directions are involved (100, 002, 101, 102, 110, and 103). For the undoped ZnO film, the $T_{(0\,0\,2)}$ reaches the maximum value of 6 since only (0 0 2) peak detected in XRD.

The dependence of (0 0 2) diffraction intensity, full width at half maximum (FWHM), and the (0 0 2) texture coefficient ($T_{(0\,0\,2)}$) on the Ga content is shown in Fig. 2. The GZO thin films with Ga content below ~6 at.% exhibit relatively good crystal quality with strong (0 0 2) preferred orientation ($T_{(0\,0\,2)} > 5.5$). The FWHM increases with Ga doping, which indicates that the crystallite size along (0 0 2) plane becomes smaller. With the further increase of Ga concentration (>6 at.%), the (0 0 2) diffraction intensity significantly decreased by more than 10 times. Meanwhile the (0 0 2) texture degrades significantly with the increasing Ga content (>6 at.%). The degradation of the crystal quality in high density Ga doped films originates from the residual stress, distortion and dislocations owing to the difference in ionic radii between Zn (0.074 nm) and Ga (0.062 nm) [30,31].

The $4 \times 4\ \mu m^2$ AFM images for GZO films with various Ga contents are shown in Fig. 3. The films show densely packed polycrystalline structures. The crystallite size decreases with the increasing Ga doping concentration from 0 to 7.2 at.%, which is in good agreement with the XRD FWHM analysis. The crystallite size of GZO film

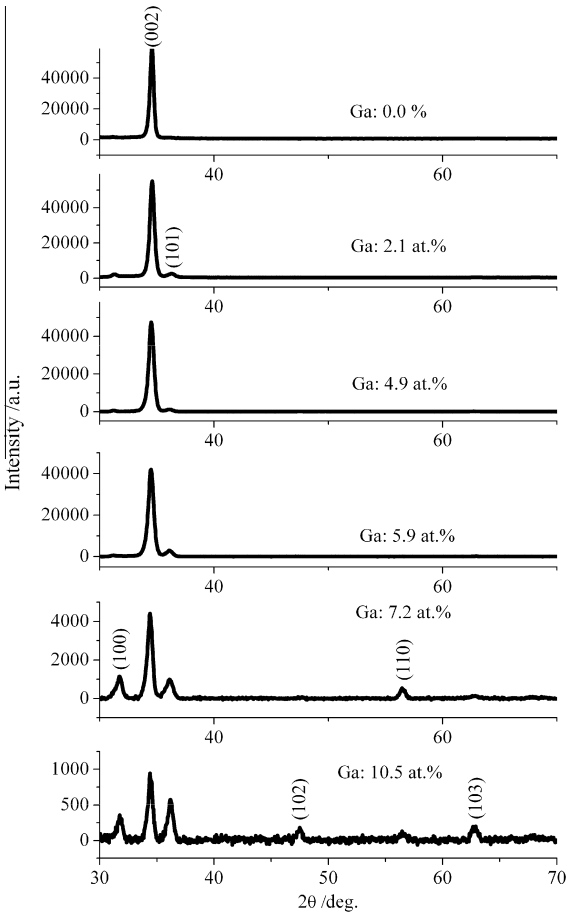

Fig. 1. XRD $\theta/2\theta$ scan of GZO thin films with various Ga content. All the peaks belong to wurtzite ZnO phase.

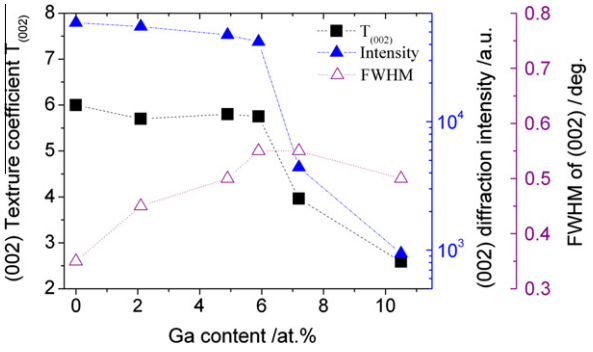

Fig. 2. Dependence of (0 0 2) texture coefficient $T_{(0\,0\,2)}$, (0 0 2) diffraction intensity and FWHM on the Ga content of GZO thin films.

with the highest Ga concentration of 10.5 at.% is not uniform, and the crystallite shape is not very clear due to the poor crystal quality. The surface root-mean-square roughness (rms) becomes higher with the increase of Ga concentration. The reason is that high concentration Ga doping degrades the (0 0 2) texture and thus the surface is composed of different oriented crystallites. Relative smooth and uniform GZO film can be obtained under a moderate Ga doping concentration. The rms is below 10 nm for the 600 nm-thick film containing ~4.9 at.% Ga.

Fig. 4 shows the dependence of resistivity, carrier concentration and Hall mobility of GZO films on the Ga content. Undoped ZnO shows *n*-type conductivity due to the intrinsic donor defects such