High transmittance–low resistivity ZnO:Ga films by laser ablation

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High transmittance, low resistivity, and *c*-axis highly oriented ZnO:Ga thin films on glass were obtained by laser ablation at different deposition temperatures. The surface morphology, crystalline structure, and optical and electrical properties were found to depend directly on substrate temperature. From optical and electrical analyses we observed that the optical transmittance, carrier concentration, and optical energy gap of the ZnO:Ga transparent conductive oxides increased when the deposition temperature is raised from 150 to 300 °C. Films grown on 300 °C substrates showed a low resistivity value of 3.6×10^{-4} Ω cm, a carrier concentration of 8.7×10^{20} cm^{-3}, a band gap of 3.81 eV, and a visible transmission of 85%. These films were deposited with an excimer (KrF) laser beam of $\lambda=248$ nm operated under optimized conditions of 2.7 mJ/cm^2 energy density and 30 Hz repetition rate.

I. INTRODUCTION

Transparent thin films with low electrical resistivity are materials of considerable interest because of their potential applications in optoelectronic systems such as flat panel displays,[1] electroluminescent (EL) devices,[2] thin film transistors (TFTs),[3] and solar cells.[4] For operation of these systems it is essential to improve the physical properties of their individual components. As an example, in an EL device the electroluminescent layer is sandwiched between two electrodes, one of which is the transparent conducting oxide (TCO) which is usually damaged during the fabrication of the active layer. Thus, a TCO that offers more stable properties under degrading environments, good visible transmittance, and electrical conductivity is a very important material that needs to developed in order to improve performance in optoelectronic devices. In the past few years zinc oxide thin films doped with any of the group IIIB elements (Ga, Al, B, or In) have been proposed as transparent electrode materials. Aluminum-doped ZnO in particular is more chemically (thermally) stable than indium tin oxide (ITO) under hydrogen plasma processes that are commonly used for the production of solar cells,[5] and EL devices.[6]

In the last decade, a number of experimental techniques such as rf sputtering,[7] metalorganic chemical vapor deposition,[8] spray pyrolysis,[9] and ion implantation[10] have been employed to grow (B, Al, or Ga)-doped zinc oxide transparent conducting thin films. More recently, a new physical vapor deposition method has emerged that is more suitable for obtaining thin films of complex chemical compounds with excellent stoichiometric transfer of the target material[11] than other methods.

In this study we demonstrate that excimer-based pulsed laser deposition can be used to deposit Ga-doped zinc oxide (ZnO:Ga) thin films on glass substrates at relatively low temperatures. The ZnO:Ga films obtained in this work by laser ablation showed excellent physical properties with better conductivities than those grown by other techniques.[7,10]

II. EXPERIMENTAL TECHNIQUES

In this article we report on a reliable method to deposit thin films of gallium-doped zinc oxide (ZnO:Ga) transparent electrodes on glass substrates by pulsed laser deposition (PLD). The ablation targets employed during thin film growth were fabricated by the combustion synthesis reaction technique in which appropriate amounts of zinc nitrate, gallium nitrate, carbohydrazide (fuel), and water are mixed together in a Pyrex combustion dish and reacted at low temperatures.[12] The resulting mixture is introduced into a muffle furnace maintained at 500 °C until it reacts (3–5 min). In the combustion synthesis process, an exothermic reaction is utilized to obtain crystalline, high purity, fine grain size powders. The exothermic reaction occurs between metal nitrates and carbonaceous reductive fuel materials in a rapid and self-sustaining manner. By calcination, the metal nitrates can be decomposed into metal oxides upon heating to or above the phase transformation temperature. In this case an external heat supply is needed; however, with the presence of a reductive fuel material, the internal energy released from the exothermic reaction between the nitrates and the fuel can rapidly heat the system to a high temperature for a short period of time without the external heat supply. The exothermic reaction is usually ignited at a temperature that is much lower than the actual phase transition temperature.[13]

Combustion synthesized ZnO:Ga powders (30–50 nm particle size) with 5 at. % Ga were cold pressed at 30 MPa in a steel dye to obtain pellets 13 mm in diameter and 5 mm in thickness. The pellets were heat treated at 1000 °C for 1 h to obtain structurally robust targets.

ZnO:Ga transparent-conductive thin films were evaporated in a laser ablation ultrahigh vacuum system having a base pressure of 5×10^{-10} Torr. All the substrates were 7059

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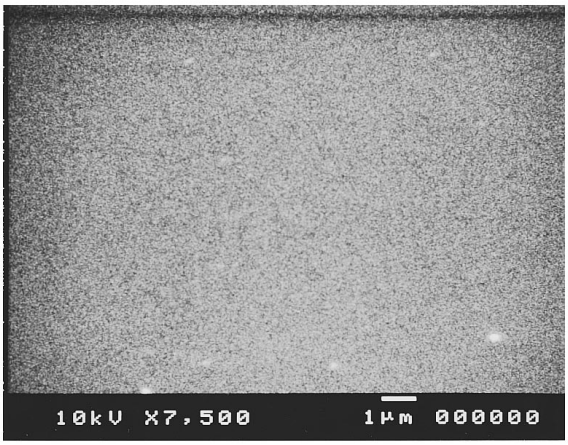

FIG. 1. SEM micrograph taken on the surface of a ZnO:Ga thin film deposited on glass at 300 °C by PLD.

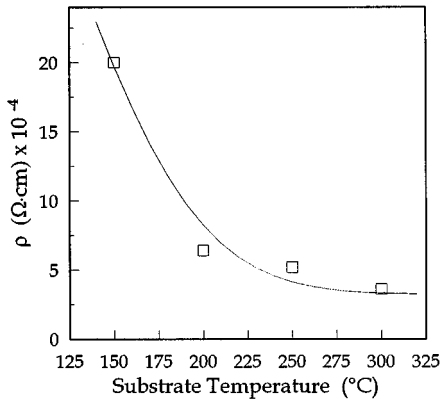

FIG. 3. Resistivity values of ZnO:Ga films as a function of substrate temperature.

Corning glass cleaned in an ultrasonic bath with acetone and dried in hot air. Deposition temperatures were varied from 150 to 300 °C. A KrF excimer laser with an ultraviolet (UV) wavelength of 248 nm, a repetition rate of 30 Hz, and a 2.7 mJ/cm^2 energy density was focused on the target to obtain the films.

The ZnO:Ga films obtained were characterized for surface morphology and crystallinity by scanning electron microscopy (SEM) and x-ray diffractometry (XRD), respectively. The electrical resistivity and Hall mobility measurements were performed by the van der Pauw method at room temperature. Optical transmission through the films was measured in the wavelength range 300–1000 nm by means of a spectrophotometer. The optical energy gap was estimated by extrapolating the square of the absorption coefficient versus the wavelength energy.

III. RESULTS AND DISCUSSION

A representative SEM of the laser ablated ZnO:Ga thin films is shown in Fig. 1. This SEM picture corresponds to a 200 nm thin film grown at 300 °C. It can be observed that a homogeneous distribution of small grains yields a uniform and smooth film deposited on the glass substrate.

X-ray analyses indicated that the ZnO:Ga films deposited at 150, 250, and 300 °C exhibited a strong *c*-axis orientation perpendicular to the substrate surface, as can be seen in Figs. 2(a)–2(c), respectively. The crystallinity evaluated from the intensity and full width at half-maximum of the (002) diffraction peak improved as the substrate temperature was increased. The sharpening of this peak also indicates that the grains are increasing in size, even over this narrow temperature range.

Electrical resistivities as a function of deposition temperatures are plotted in Fig. 3. All samples had the same thickness (200 nm) as measured by a conventional stylus surface roughness detector. As can be observed from Fig. 3, the resistivity decreases as the substrate temperature increased from 150 to 300 °C. Similar behavior has been reported for Al- or Ga-doped zinc oxide TCOs deposited by other techniques.[7,14]

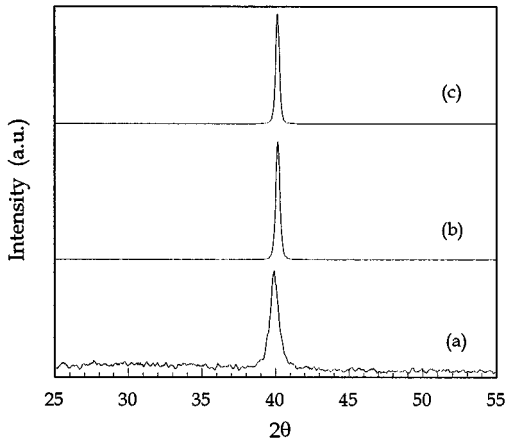

FIG. 2. X-ray diffraction patterns measured on ZnO:Ga films deposited at (a) 150, (b) 250, and (c) 300 °C substrate temperatures, respectively.

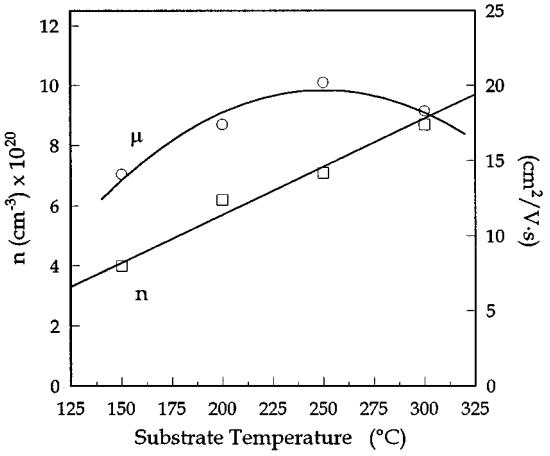

FIG. 4. Electron concentration and Hall mobilities for ZnO:Ga films deposited by PLD at different temperatures.

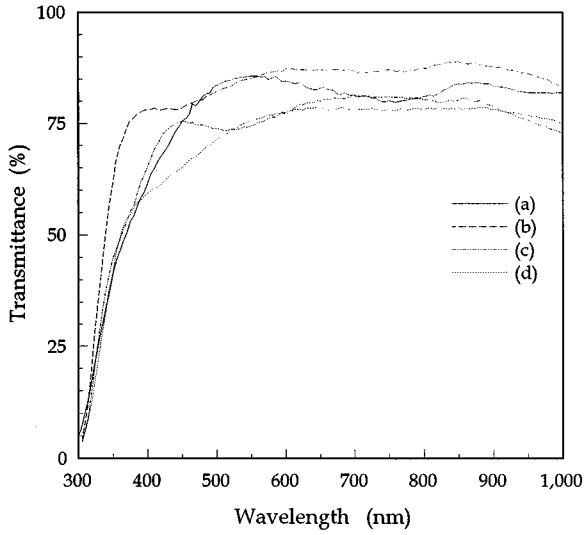

FIG. 5. Transmittance spectra of 200 nm films of (a) ITO and three ZnO:Ga films grown by PLD at (b) 300, (c) 250, and (d) 150 °C, respectively.

Carrier concentration and Hall mobilities measurements as a function of substrate temperature are plotted in Fig. 4. The free electron concentration increases with deposition temperature and the Hall mobility reaches a maximum at 250 °C. These values are favorably compared with those reported in the literature[7,14] for the same composition fabricated by other techniques.

The transmittance characteristics for three ZnO:Ga thin films were measured in the visible range (300–1000 nm wavelength) and the results are shown in Fig. 5. Figure 5(a) shows a 200 nm ITO grown by rf magnetron sputtering that is included for comparison. A noticeable improvement in the transmittance in the blue–green interval is obtained for PLD ZnO:Ga films grown at 150, 250, and 300 °C as can be observed in Figs. 5(b)–5(d), respectively.

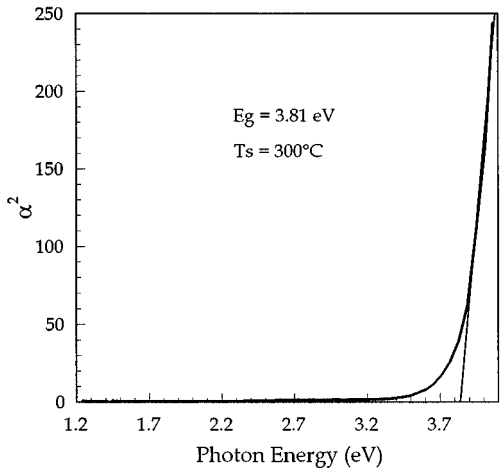

FIG. 6. Optical energy gap determined by extrapolation of absorption coefficient squared vs photon energy curve of a ZnO:Ga film grown at 300 °C.

TABLE I. Resistivities and band gap values for ZnO:Ga grown at four different deposition temperatures.

T (°C)	$\rho(\Omega\ \mathrm{cm})\times10^{-4}$	E_g (eV)
150	20.0	3.68
200	6.4	3.71
250	5.2	3.78
300	3.6	3.81

The optical absorption coefficient α near an absorption edge is given by

$$\alpha=(h\nu-E_g)^{1/2}, \tag{1}$$

where h is the Planck's constant, ν is the frequency, and E_g is the intrinsic band gap of the semiconductor.

The optical energy gap was estimated by extrapolating the square of the absorption coefficient given in Eq. (1) versus the photon energy curve, as illustrated in Fig. 6 for the ZnO:Ga film deposited on the 300 °C substrate. The band gap values for other deposition temperatures are listed in Table I. It can be seen that the band gap increases as the temperature is raised from 150 to 300 °C.

It has been reported that the increase in the optical band gap with an increase in electron concentration is related to increases in the Fermi level in conduction bands in degenerate semiconductors. This phenomenon is known as the "blueshift," and the relationship between ΔE_g and the carrier concentration (n) was proposed by Burstein[15] in the following expression:

$$\Delta E_g=(h^2/8m^*)(3/\pi)^{2/3}n^{2/3}. \tag{2}$$

Thus, our films obey this relationship as we observe an increase in E_g with an increase in n.

IV. CONCLUSIONS

It was determined that the pulsed laser deposition technique is an excellent method to deposit Ga-doped zinc oxide thin conductive oxides at low temperatures. Transparent, low resistivity, c-axis, highly oriented ZnO:Ga thin films were grown on glass substrates by laser ablation at different deposition temperatures. The degree of crystallinity, optical absorption, and electrical properties is strongly dependent on deposition temperature. From optical and electrical analyses it was concluded that the optical transmittance, electron concentration, and optical energy gap of ZnO:Ga transparent conductive oxides increased when the deposition temperature was raised from 150 to 300 °C. Films grown on 300 °C substrates showed a low resistivity value of $3.6\times10^{-4}\ \Omega$ cm, a carrier concentration of $8.7\times10^{20}\ \mathrm{cm}^{-3}$, a band gap of 3.81 eV, and a transmittance of about 85% in the visible range.

ACKNOWLEDGMENTS

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