Improvement of Characteristics of Ga-Doped ZnO Grown by Pulsed Laser Deposition Using Plasma-Enhanced Oxygen Radicals

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The authors report on the growth and characterization of Ga-doped ZnO films grown at a low temperature (100°C) by oxygen plasma-enhanced pulsed laser deposition (PE-PLD). The introduction of oxygen radicals during PLD growth remarkably improved the crystalline quality, surface morphology, and density of Ga-doped ZnO films. The PE-PLD grown Ga-doped ZnO film showed a maximum electron mobility of 46.2 cm²/V·s and a minimum resistivity of 3.5 × 10⁻⁴ Ω·cm at a radio-frequency input power of 100 W. Average visible (500–700 nm) transparency was improved from 83.7% in the Ga-doped ZnO grown without oxygen radicals to 93.1% in the samples grown with oxygen radicals. The use of oxygen radicals also increased the near-IR (800–3000 nm) transparency. The figure of merit of the Ga-doped ZnO film grown at a radio frequency input power of 100 W showed a maximum value of ~0.12 Ω⁻¹ at wavelengths of 580 nm in the visible range and 1100 nm in the near-IR range.

In recent years, transparent conductive oxides (TCOs) have attracted significant interest because of their application in flat panel displays, light-emitting diodes, photovoltaics, and architectural windows.1,4 Currently, tin-doped indium oxide (ITO) has been practically used in most TCO applications due to its high transmittance and low resistivity.5 However, the thermal instability and high cost of ITO attributed to limited availability of indium have hampered the industrial use of ITO in optoelectronic devices.6,7

ZnO is an n-type semiconductor with a wide and direct bandgap of 3.37 eV. Because ZnO has many advantages, such as relatively low material costs, nontoxicity, high conductivity, and high transmittance in the visible region, it is a promising replacement for ITO.8,9 Recently, significant research effort has been devoted to the realization of highly conductive and transparent group-III-element-doped ZnO, resulting in ZnO with optical and electrical characteristics comparable to ITO.9,11 Numerous deposition techniques, such as sputter deposition,12,13 chemical vapor deposition (CVD),14 spray pyrolysis,15 sol-gel,16 and molecular beam epitaxy,17,18 have been widely used to grow high-quality ZnO. However, most of the ZnO produced using these methods have serious problems that limit its use as an electrode in electronic devices. For example, in the most widely used sputter deposition, direct exposure of the device surface to the plasma induces plasma damage on the surface of the device.18

In the case of chemical-reaction-induced deposition, such as CVD, high deposition (400–600°C) or postannealing (400–700°C) temperatures are usually needed for recrystallization of the ZnO films. However, high-temperature processing causes surface roughness and decomposition of the underlying films, resulting in poor device performance and reliability due to nonuniform current flow at the damaged interface.19,20 Recently, pulsed laser deposition (PLD) has been known to provide several advantages over other deposition techniques, although it has the shortcoming that large-area scale-up is difficult due to the narrow forward angular distribution of the laser-induced plasma plume. In the PLD process, ionized and ejected species with high kinetic energies are generated in the laser-induced plasma plume, allowing good film quality and substrate adhesion at lower substrate temperature (<300°C) without surface damage.21 It has been reported that molecular oxygen partial pressure has a significant effect on the electrical and optical properties of ZnO during PLD growth,22,23 because ZnO thin films have oxygen deficiency-related intrinsic defects such as zinc interstitial (Zn_i) and/or oxygen vacancy (V_o) due to high vapor pressure of oxygen. Recently, Matsubara et al.24 reported that the use of an oxygen radical source during PLD growth of Al-doped ZnO is more effective in increasing the stoichiometry of the film than a molecular oxygen source. In the present study, we introduced radio-frequency (rf) plasma-induced oxygen radicals during PLD growth of Ga-doped ZnO on sapphire substrates to compensate for the shortage of oxygen atoms. The structural, electrical, and optical characteristics of Ga-doped ZnO grown by plasma enhanced (PE)-PLD at low temperature were investigated as a function of applied rf input power during film deposition.

Experimental

Ga-doped ZnO films were grown on (0001) sapphire substrates using PLD. A pulsed KrF excimer laser (wavelength 248 nm; pulse width at half maximum 25 ns) was focused on a rotating ZnO disk target (1 in. diameter) containing 3 wt % Ga₂O₃ at a repetition rate of 4 Hz. The distance between the substrate and the target was kept constant at 5.8 cm. The substrate temperature was 100°C and the laser energy density was 1.7 J/cm². The growth chamber was evacuated to a base pressure of 7.4 × 10⁻⁷ Torr. To alleviate the shortage of oxygen atoms during ZnO growth, an rf plasma cell (ALPHA PLUS AP-Plasma300) was used. Twelve sccm of oxygen gas flowed through the rf plasma cell while the oxygen working pressure in the PLD system was maintained at 10 mTorr. Highly reactive oxygen radicals were generated by applying rf power to a helical rf coil-surrounded discharge cell with an Al₂O₃ crucible. The rf plasma cell was located 15 cm from the substrate. The geometric picture inside the chamber is shown in Fig. 1. Figures 1a and b show the high-density plasma plume ablated from the target by excimer laser irradiation, with and without oxygen radicals, respectively. The applied rf input power during deposition was varied from 0 to 170 W at increments of 30–50 W. Table I shows the relation between rf input power and rf power density in the Al₂O₃ crucible of the rf plasma cell. Hall effect measurements were carried out in the van der Pauw configuration using a commercial system (BIO-RAD HL5500PC). The structural properties of the Ga-doped ZnO films were characterized using X-ray diffraction (XRD) (Rigaku Rint2000 with a Cu Kα X-ray source) and X-ray reflectometry with a high-resolution X-ray diffractometer (Philips XPert PRO MRD). UV-visible near-infrared spectrophotometry (Varian Cary5000scan) was

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Manuscript submitted March 31, 2008; revised manuscript received June 3, 2008. Published July 18, 2008.

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performed to investigate optical properties, and field-emission scanning electron microscopy (SEM) was used to measure film thickness.

Results and Discussion

Figure 2a shows a θ-2θ scan spectrum of the Ga-doped ZnO films grown by oxygen PE-PLD at 100°C as a function of applied rf input power. Figure 2a depicts the strong 0002 diffraction peaks at 34.4° of the Ga-doped ZnO layer and the 0006 peak at 41.7° of the sapphire, indicating that the films were highly c-axis oriented. The absence of additional peaks in the XRD spectrum excludes the possibility of any extra phases and/or large-sized precipitates in the films. Figure 2b shows the full width at half-maximum (fwhm) of the XRD rocking curve and the growth rate of the film as a function of rf input power. As rf input power increased from 0 to 100 W, the growth rate decreased. However, crystalline quality of the films improved as evidenced by the decrease of fwhm of the XRD rocking curve. However an additional increase in rf input power (≥130 W) caused the crystalline quality of the films to deteriorate.

Figures 3a-c illustrates the surface morphology of the Ga-doped ZnO films grown by oxygen PE-PLD at 100°C with rf input powers of 0, 100, and 170 W, respectively. Figures 3b and c clearly show that the surface morphology of Ga-doped ZnO was remarkably improved by the presence of oxygen radicals during film growth. As shown in Fig. 3b, the Ga-doped ZnO film grown at rf input power of 100 W did not show any surface hillocks, pits, or holes. The root-mean-square surface roughness of the Ga-doped ZnO films shown in Fig. 3a-c, measured by atomic force microscopy, were 15.1, 1.67, and 3.4 nm, respectively. The insets in Fig. 3a-c show that the growth rate of Ga-doped ZnO was decreased by rf plasma-induced oxygen radicals up to an rf input power of 100 W (see also Fig. 2b).

The crystal quality and surface morphology of Ga-doped ZnO, as shown in Fig. 2b, indicate that two-dimensional growth was facilitated on the surface by rf plasma-induced oxygen radicals during PLD growth. However, an additional increase in rf input power (170 W) caused structural quality to deteriorate, as evidenced by fwhm in the rocking curve (Fig. 2b) and SEM image (Fig. 3c).

Density of the Ga-doped ZnO film grown by oxygen PE-PLD at 100°C was determined by using X-ray reflectometry (XRR). A typical diffuse scan profile measured by XRR is shown in Fig. 4a, in which the specular peak at 0.8° and two Yoneda-wings (αi, αr) are evident. Yoneda-wings arise when the incident angle αi, or the exit angle αr, is equivalent to the critical angle of total reflection. The precise critical angle can be obtained using the equation θc = 0.8/(αi − αr)/2. Figure 4b shows the film density distribution, calculated using critical angles obtained from XRR as a function of rf input power. The film density of Ga-doped ZnO grown without rf power is 1.77 (W/cm²) at 50 W, 3.54 at 100 W, 4.60 at 130 W, 5.30 at 150 W, and 6.01 at 170 W.

Table I. The relation between rf input power and rf power density in the Al2O3 crucible of the rf plasma cell.

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<th>RF power (W)</th>
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<tr>
<td>50</td>
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input power was 4.83 g/cm³. As the rf input power increased, the film density also increased, reaching a maximum value of 5.49 g/cm³ at an rf input power of 100 W, which is close to the bulk ZnO density of 5.69 g/cm³ indicated by the dotted line in Fig. 4b.

Figure 5 shows the electrical properties of Ga-doped ZnO films grown by oxygen PE-PLD at 100°C as a function of biased rf input power. As the rf input power increased from 0 to 100 W, the electron concentration (curve a) gradually decreased from 3.1 \times 10^{21} to 5.6 \times 10^{18} cm⁻³. As the rf input power increased, electron mobility (curve b) increased, reaching a maximum value of 46.2 cm²/V s at an rf input power of 100 W, and then decreased again. The resistivity (curve c) decreased and reached a minimum value of 3.5 \times 10^{-4} Ω cm at an rf input power of 100 W and then dramatically increased at the rf input power over 100 W. Here, the decrease in electron carrier concentration with increasing rf input power also indicates that oxygen radicals effectively reduced oxygen deficiency-related donor defects, such as interstitial Zn (Znᵢ), oxygen vacancy (Vₒ), and Zn antisite (O₂Zn), by filling vacancies (Vₒ + 1/2 O₂ = Oᵢ) and/or forming ZnO (Znᵢ + 1/2 O₂ = ZnO).²⁹,³⁰

Deterioration of electrical properties of samples grown at rf input powers over 130 W could be explained by oxygen overabundance, such as Oᵢ, which can act as an acceptor. The dependency of film density and Hall data on the oxygen plasma power indicates that the optimum Ga-doped ZnO film density can be obtained at a plasma cell power of 100 W, where an adequate amount of oxygen radicals are provided for a good stoichiometry of Ga-doped ZnO.

Figure 6 shows the optical transmittance spectra of Ga-doped ZnO films grown by oxygen PE-PLD at 100°C as a function of rf input power. The average light transmittance of all samples grown in

![Figure 3](image3.png) SEM images of Ga-doped ZnO films grown by oxygen PE-PLD with biased rf input powers of (a) 0, (b) 100, and (c) 170 W. Insets show cross-sectional images of grown films.

![Figure 4](image4.png) (Color online) (a) Diffuse scan profiles for Ga-doped ZnO films measured by XRR. (b) Film density calculated using critical angles obtained by XRR as a function of rf input power.

![Figure 5](image5.png) (Color online) The rf input power dependence of (a) electron concentration, (b) mobility, and (c) resistivity in the Ga-doped ZnO films.
the presence of oxygen radicals was 93.1% in the visible range (500–700 nm), while the sample grown without oxygen radicals showed an average transmittance of 83.7% in the same wavelength range. In addition, near-IR transparency (800–3000 nm) of the samples grown in the presence of oxygen radicals was significantly improved compared to that of samples grown without oxygen radicals. The improvements were attributed to the fact that free carrier plasma reflectivity edges ($\lambda_{\text{plasma}}$) of the samples grown in the presence of oxygen radicals were shifted to the longer wavelength region.\textsuperscript{32} In doped semiconductors, the presence of impurities gives rise to new absorption mechanisms, which is related to $\lambda_{\text{plasma}}$.\textsuperscript{32} Reflectivity due to the presence of free carriers is zero at wavelengths just below $\lambda_{\text{plasma}}$, which can be determined using an equation given as:\textsuperscript{32}

$$\omega_p^2 = \frac{N e^2}{\varepsilon_{ZnO} \varepsilon_0 m^*}$$

where $\omega_p$ is the plasma frequency, $\varepsilon_0$ is the permittivity of empty space ($8.85 \times 10^{-12}\text{ F/m}$), $\varepsilon_{ZnO}$ is the refractive index of undoped ZnO, $m^*$ is the effective mass (0.28 $m_0$), $N$ is the carrier concentration, and $c$ is the velocity of light in a vacuum. The decrease in carrier concentration due to the reduction in native donor defects during oxygen PE-PLD growth can decrease $\omega_p$, shifting $\lambda_{\text{plasma}}$ to a longer wavelength region, as shown in Fig. 6.

Figure 7 shows the characteristics of ($\alpha h\nu$)$^2$ vs wavelength for Ga-doped ZnO films grown by oxygen PE-PLD at 100°C as a function of rf input power. The optical bandgap ($E_g$) can be determined by extrapolating the straight region in the plot of the square of the absorption coefficient term, ($\alpha h\nu$)$^2$, vs photon energy (eV) ($\alpha$ denotes the absorption coefficient).\textsuperscript{33} The $\alpha h\nu$ for allowed direct transitions at a given photon energy can be expressed as:

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

where $A'$ is a function of the index of refraction and effective hole and electron mass,\textsuperscript{33} $T$ is optical transmittance, $R$ is reflectance, and $d$ is film thickness. The obtained optical bandgap energies for films grown with biased rf input powers of 0, 50, 100, and 150 W were 3.67, 3.47, 3.42, and 3.44 eV, respectively. It is noteworthy that the determined optical bandgap was decreased with increasing the rf input power. The reduced optical bandgap energy of Ga-doped ZnO films grown in the presence of oxygen radicals could be explained in terms of a Burstein–Moss shift.\textsuperscript{36,37} When electron concentration exceeds the Mott critical density ($N_c$), which is defined as $N_c = (2\pi\varepsilon_0 m^*_e)^{1/2}$, where $m^*_e$ is the electron effective mass and $\varepsilon_0$ is the permittivity of empty space,\textsuperscript{36} the conduction band is partially filled. Consequently, the optical bandgap is increased, leading to a shift in the absorption edge toward the higher energy side in proportion to carrier density, as shown in the inset of Fig. 7.

Figure 8 shows the figure of merits (FOMs) for Ga-doped ZnO films grown by oxygen PE-PLD at 100°C as a function of biased rf input power. The films grown in the presence of oxygen radicals show higher FOMs compared to a film grown without oxygen radicals. FOMs of transparent conductors are defined as\textsuperscript{39}

$$\Phi_{\text{TC}} = \frac{\alpha t \exp(-10\alpha t)}{R_t}$$

where $\alpha$ is the absorption coefficient, $t$ is the film thickness, $T$ is the total visible transmittance, and $R_t$ is the sheet resistance. $R_t$ of the Ga-doped ZnO grown with an rf input power of 0, 50, 100, and 150 W was 13.54, 9.63, 8.23, and 58.18 $\Omega/\square$, respectively. A TCO with high FOM has high electrical conductivity and light transmittance, and higher FOM values mean better TCO performance. Ga-doped ZnO films grown with an rf input power of either 50 or 100 W showed much higher FOM compared to films grown without oxygen.
PLD are well-suited for long-visible wavelength optoelectronic devices that can emit in a visible wavelength of 580 nm and near-IR wavelength of 1100 nm. These results show that Ga-doped ZnO films grown by oxygen PE-PLD are well-suited for long-visible wavelength optoelectronic devices and solar cells that require high near-IR transparency.

Conclusions

Ga-doped ZnO films were grown at a low growth temperature of 100°C by using oxygen PE-PLD. Structural, electrical, and optical properties were investigated as a function of rf input power level. The XRD and SEM results showed that the structural quality of Ga-doped ZnO films has greatly improved by oxygen radicals. Electron mobility reached a maximum value of 46.2 cm²/V s and a minimum resistivity of 3.5 × 10⁻⁴ Ω cm at an rf input power of 100 W. Average visible (500–700 nm) transparency was improved from 83.7% in the Ga-doped ZnO grown without oxygen radicals to 93.1% in the samples grown with oxygen radicals. The electrical mobility also improved the near-IR (800–3000 nm) transparency. The FOM of the Ga-doped ZnO grown at an rf input power of 100 W reached a maximum value of −0.12 Ω⁻¹ at a visible wavelength of 580 nm and a near-IR wavelength of 1100 nm. These results show that Ga-doped ZnO films grown by oxygen PE-PLD have great potential as TCO electrodes for use in long-visible-wavelength organic solar cells.

Acknowledgments

This work was partially supported by the Center for Distributed Sensor Network at Gwangju Institute of Science and Technology, a Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MOST) (no. R17-2007-078-01000-0), and the Brain Korea 21 program.

Gwangju Institute of Science and Technology assisted in meeting the publication costs of this article.

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