Structure and properties of transparent conductive doped ZnO films by pulsed laser deposition

Sang-Moo Park a,*, Tomoaki Ikekami a, Kenji Ebihara b, Paik-Kyun Shin c

a Graduate school of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan
b Department of Electrical and Computer Engineering, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan
c School of Electrical Engineering, Inha University, 253 Yonghyun-Dong Nam-Gu, Incheon 402-751, Korea

Article history:
Received 23 September 2005; received in revised form 8 February 2006; accepted 17 February 2006
Available online 3 April 2006

Abstract

High quality transparent conductive ZnO thin films were deposited on quartz glass substrates using pulsed laser deposition (PLD). We varied the growth conditions such as the substrate temperature and oxygen pressure. X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS), and atomic force microscopy (AFM) measurements were done on the samples. All films show n-type conduction, the best transparent conductive oxide (TCO) performance (Al-doped ZnO = 1.33 x 10^4 Ω cm, Ga-doped ZnO = 8.12 x 10^5 Ω cm) was obtained on the ZnO film prepared at pO2 = 5 mTorr and Ts = 300 °C.

© 2006 Elsevier B.V. All rights reserved.

Keywords: ZnO; XPS; Electric and optical properties; TCO; PLD

1. Introduction

Zinc oxide (ZnO) is an inexpensive optical material that has attention recently [1,2]. It is a II–VI semiconductor which is highly transparent in the visible region with a wide and direct band gap of about 3.37 eV at room temperature and a high exciton binding energy of 60 meV [3]. ZnO is a promising material because it could be applied to many fields such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin films transistors and other [4,5]. Generally, undoped ZnO thin films typically exhibit n-type conduction and are transparent conducting oxides (TCO) with a background electron concentration as high as 10^21 cm^-3 [6]. When doped with group-III element, such as Al, Ga and In, its resistivity could be reduced to 2–4 x 10^{-3} Ω cm [7,8]. ZnO can be grown as a thin film by many deposition techniques including chemical vapor deposition, radio frequency sputtering, magnetron sputtering, sol–gel method, ion-beam-assisted deposition, molecular-beam epitaxy, and pulsed laser deposition [4,9–12]. Among the fabrication techniques, pulsed laser deposition (PLD) has attracted much attention because the fabrication process is quite suitable for optoelectronic devices using the ZnO as a transparent electrode. Furthermore, the composition of films grown by PLD is quite close to that of the target, and it is true even for a multi component target. PLD films may be crystallized at lower deposition temperatures in comparison to other physical vapor deposition techniques due to the high kinetic energies of the ionized and ejected species in the laser plumes [13]. However, it is difficult to make the transparent layer on the optoelectronic devices because the electrical and optical properties of doped ZnO films depend drastically on the PLD condition. In this work we report results obtained from nominally undoped ZnO, Al doped ZnO (AZO) and Ga doped ZnO (GZO) films grown by KrF excimer (λ = 248 nm, 25 ns pulse width) pulsed laser deposition (PLD) at different substrate temperatures and background pressure of oxygen gas. Several critical issues on how to control the growth conditions in order to get good-quality ZnO films are addressed in this paper. In particular, the crystallographic structure and the electrical and optical properties of the films prepared at different growth parameters will be discussed.

2. Experimental

Fig. 1 shows a schematic diagram of the PLD system. Transparent conductive ZnO films were prepared by pulsed
laser deposition on quartz glass substrates. The laser source was a KrF excimer laser ($\lambda = 248$ nm, 25 ns pulse width) with an energy fluence of 2 J/cm$^2$. The nominally undoped ZnO films were deposited by ablating a 99.99% pure ZnO target. The AZO and GZO films were produced by ablating ZnO targets containing 2 wt.% $\text{Al}_2\text{O}_3$ and 5 wt.% $\text{Ga}_2\text{O}_3$, respectively. A substrate was placed at 40 mm away from the target and heated up to temperature of 1000 °C. The typical growth process was done with 9000 laser shots and a repetition rate of 10 Hz. All of the films were deposited on quartz glass cleaned in an ultrasonic bath using acetone and then ethanol for 5 min. The deposition chamber was initially evacuated to 4 $\times$ 10$^{-5}$ Torr using a turbo molecular pump and then oxygen gas was introduced into the chamber so that the pressure was controlled to be 1–100 mTorr. The as-grown and doped ZnO films were characterized by X-ray diffraction (XRD, Rigaku, RINT 2100/PC). Surface and atomic composition analyses were performed by X-ray photoelectron spectrometer (XPS, VG Scientific, Sigma Probe). The surface morphology was observed by atomic force microscopy (AFM, Seiko Instrument, SPI 3800N). The growth rate and the thickness of the samples were determined by cross-sectional scanning electron microscopy (SEM, JEOL JSM-T200). The transmission through the films was measured using an UV–vis spectrophotometer in the wavelength range from 200 to 800 nm. Electrical properties of the doped ZnO films were measured by van der Pauw method at room temperature.

The emission spectra of the plasma plumes produced during the deposition process of AZO and GZO ZnO films were recorded using monochromater (Acton Research, Spectra Pro-308i) equipped with an ICCD (Intensified Charge Coupled Device, Princeton Inc., ICCD-576G) and a detector controller (Princeton Inc., ST-138S) connected to a digital oscilloscope. Plasma emission was recorded at distance of 10 mm from the target surface at laser fluence of 2 J/cm$^2$.

3. Results and discussion

The optical emission of a plasma plume generated in the laser ablation process for GZO, AZO and ZnO were measured at a distance $d = 10$ mm from the target surface. Fig. 2 shows the spectrum of plasma produced at $p_{\text{O}_2} = 5$ mTorr. Strong emission lines at 328.2, 330.3, 334.6, 468.0, 472.2, 481.1, 518.2 and 633.2 nm are due to the Zn atomic lines (Zn I). Emission from the Ga atomic lines (Ga I) at 403.3 and 417.2 nm, Al (Al I) at 394.4 and 396.2 nm, and O (O I) at 777.2 nm are also observed.

<table>
<thead>
<tr>
<th>$p_{\text{O}_2}$ (mTorr)</th>
<th>Crystal size (nm)</th>
<th>c-Axis length (Å)</th>
<th>Roughness (nm)</th>
<th>T (%) (400–800 nm)</th>
<th>Band gap (eV)</th>
<th>Resistivity ($\Omega \cdot \text{cm}$)</th>
<th>Carrier concentration ($\times 10^{20}$ cm$^{-3}$)</th>
<th>Carrier mobility (cm$^2$/V s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.15</td>
<td>5.178</td>
<td>5.062</td>
<td>88.66</td>
<td>3.36</td>
<td>5.14 $\times 10^{-4}$</td>
<td>1.25 $\times 10^{21}$</td>
<td>9.74</td>
</tr>
<tr>
<td>3</td>
<td>22.8</td>
<td>5.173</td>
<td>7.142</td>
<td>90.97</td>
<td>3.36</td>
<td>4.97 $\times 10^{-4}$</td>
<td>1.16 $\times 10^{21}$</td>
<td>10.87</td>
</tr>
<tr>
<td>5</td>
<td>34.02</td>
<td>5.176</td>
<td>7.97</td>
<td>93.37</td>
<td>3.35</td>
<td>3.92 $\times 10^{-4}$</td>
<td>1.14 $\times 10^{21}$</td>
<td>14.03</td>
</tr>
<tr>
<td>10</td>
<td>25.3</td>
<td>5.182</td>
<td>7.354</td>
<td>95.46</td>
<td>3.34</td>
<td>7.5 $\times 10^{-4}$</td>
<td>1.04 $\times 10^{21}$</td>
<td>8.01</td>
</tr>
<tr>
<td>50</td>
<td>23.5</td>
<td>5.187</td>
<td>7.227</td>
<td>94.63</td>
<td>3.32</td>
<td>1.75 $\times 10^{-3}$</td>
<td>9.92 $\times 10^{20}$</td>
<td>3.55</td>
</tr>
<tr>
<td>100</td>
<td>21.3</td>
<td>5.185</td>
<td>6.634</td>
<td>95.14</td>
<td>3.26</td>
<td>5.22</td>
<td>1.25 $\times 10^{19}$</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Fig. 3a shows effect of oxygen pressure \( (p_{O_2}) \) on the crystallinity of the AZO films. The ambient oxygen pressure was changed from 1 to 100 mTorr at substrate temperature of 500 °C. XRD 2θ scans in the vicinity of the ZnO (0 0 2) reflection were performed on these films. The strong peak signal of the (0 0 2) diffraction was observed for the 5 mTorr film, while the film prepared at 1 mTorr shows fine evidence of crystallinity. Similar sets of samples were prepared using the Ga containing targets and XRD 2θ scans were also carried out on these films. These results showed the same trend with \( p_{O_2} \) as the Al doped ZnO films. Table 1 shows that the crystal size of the AZO films increases from 10.15 nm at 1 mTorr to 34.02 nm at 5 mTorr and then decreases gradually for samples prepared up to 100 mTorr. The facts suggest that the crystalline quality of the AZO films degraded from single-oriented crystal to polycrystalline with the increase of the oxygen content. The excess oxygen might induce defects in the films, which influenced the nucleation and growth of the films, and resulting

![Fig. 2. Optical emission spectra at \( d = 10 \) mm of plasma plumes originating from (a) the GZO target, (b) the AZO target and (c) ZnO target in 5 mTorr of \( O_2 \) pressure. The plasma plumes were generated at \( E_L = 2 \) J/cm².](image)

![Fig. 3. XRD 2θ scans of ZnO films grown on quartz substrates in the vicinity of ZnO (0 0 2) peaks. (a) AZO films as function of \( p_{O_2} \). (b) GZO films as function of \( T_s \).](image)

![Fig. 4. XPS spectra of (a) the GZO target and (b) the AZO target in 5 mTorr of \( O_2 \) pressure at 500 °C.](image)
in the degradation of the crystalline quality (see also Table 1). These results also confirm that a pressure of 5 mTorr will cause the better epitaxy (as seen from 2θ scan), better texture, and larger crystal size (34 nm using Scherrer’s formula) for the AZO films. Fig. 3b shows effect of substrate temperature on the crystallinity of the GZO films. Two diffraction peaks corresponding to (0 0 2) and (0 0 4) reflections are predominant and indicate that the film has a c-axis direction with an out-of-plane lattice parameter around 5.2 Å. At higher substrate temperatures the intensity of (0 0 2) peaks increased. The FWHM (full width half maximum) values decreased from 0.36° to 0.198° as the growth temperature increased from 100 to 500 °C.

In order to find the Al and Ga elements in the doped films, we performed a surface and atomic composition analysis for the samples by X-ray photoelectron spectroscopy (XPS). Fig. 4 shows the XPS spectra, for which the calculated atomic composition percentages are (a) Ga-doped sample at \( p\text{O}_2 = 5 \text{ mTorr} \) and \( T_s = 500 \text{ °C} \): Ga = 4.75, C = 3.89, O = 8.47 and Zn = 82.84; (b) Al-doped sample at \( p\text{O}_2 = 5 \text{ mTorr} \) and \( T_s = 500 \text{ °C} \): Al = 0.6, C = 2.98, O = 8.51 and Zn = 87.89. The Ga-doped ZnO sample prepared using the 5 wt.% Ga\textsubscript{2}O\textsubscript{3}–95 wt.% ZnO target reveals 4.75% Ga on the surface of the films, whereas the Al-doped ZnO sample prepared using the 2 wt.% Ga\textsubscript{2}O\textsubscript{3}–98 wt.% ZnO target shows the presence of only 0.6% Al on the surface.

The morphology and the surface roughness determined by AFM measurement are shown in Fig. 5. The roughness seems to increase with the increase of substrate temperature and in the same time, the grain size on the surface is varied. For the film grown at low temperature (100 °C), the grain size is around 90 nm. Furthermore, the roughness of this film is about 9 nm. On the contrary, the film grown at higher temperature (300 °C) has the grain size of around 115 nm and the roughness of the film slightly decrease to about 8 nm. The sample prepared at up to 500 °C shows the grain size of around 230 nm and the roughness of about 8 nm.

Fig. 6 shows optical transmittance of the ZnO, AZO and GZO thin films prepared at a substrate temperature of 500 °C and at an oxygen pressure of 5 mTorr. The transmittances obtained are around 90% at the wavelength from 400 to 800 nm. We also find the transmission edge shift around 350–390 nm toward higher energies either by doped material. This shift is confirmed by representing absorbance squared versus the excitation energy \( h\nu \). The optical absorption coefficient \( \alpha \) is related to the threshold absorption energy \( E_g \) by \( \alpha = A(h\nu - E_g)^{1/2} \) (A is a constant). The band gap energy \( E_g \) can be determined by extrapolation of the linear part of the plot of \( \alpha^2 \) versus \( h\nu \). The band gap of ZnO, AZO and GZO films are 3.23, 3.36 and 3.51 eV, respectively. The high-energy shift of the optical band gap of GZO and AZO films compared to the ZnO films are due to the much higher carrier concentration of these
doped films and filling of electronic states of the conduction band (Burstein-Moss-Shift) \[14\]. According to this Burstein-Moss-Shift, the band gap would increase with increasing carrier concentration. With increasing \(p_{O_2}\), the optical band gap is gradually decreased from 3.36 to 3.26 eV by the relaxation of built-in strain in AZO (see also Table 1). According to the Burstein-Moss effect, the broadening of the optical band gap is

\[
\Delta E_g = \left( \frac{\hbar^2}{2m^*_{cv}} \right) (3\pi^2 n)^{2/3}
\]

where \(\Delta E_g\) is the shift of the doped semiconductor with respect to the undoped semiconductor, \(m^*_{cv}\) the reduced effective mass \((1/m^*_{cv} = 1/m^*_c + 1/m^*_v)\), \(m^*_c = 0.38\, m_0\) and \(m^*_v = 1.8\, m_0\), \(\hbar\) the Plank’s constant and \(n\) is the carrier concentration, respectively [15]. According to this equation, the band gap would increase with carrier concentration. Carrier concentration in the AZO films was observed to gradually decrease from 1.25 \(\times 10^{21}\) to 1.25 \(\times 10^{19}\) cm\(^{-3}\) as oxygen pressure was increased.

The carrier concentration in the AZO films was observed to gradually decrease from 1.36 \(\times 10^{21}\) to 9.92 \(\times 10^{20}\) cm\(^{-3}\) as the oxygen pressure was increased (see also Table 1). A maximum in the carrier mobility was observed for an oxygen pressure of 5 mTorr. For ratios O and Zn (oxygen flow rates of 1–5 mTorr) incorporation of interstitial Zn leads to a worsening of crystalline quality and creation of electron scattering centers. Consistent with this, the carrier mobility was found to increase with increasing oxygen flow rate below the optimum oxygen pressure of 5 mTorr. For ratios O and Zn higher than the optimum oxygen pressure of 5 mTorr, excess oxygen on the growth surface presumably induces changes in growth mode and crystal quality, resulting in increased carrier scattering and lower mobility. Carrier mobility thus decreases with increasing oxygen pressure of 5 mTorr.

Fig. 7a shows the variation of resistivity, carrier concentration, and carrier mobility as a function of the oxygen pressure of the GZO films grown at an oxygen pressure of 5 mTorr. As the substrate temperature increases from 100 to 300 °C, the resistivity decreases from 3.69 \(\times 10^{-4}\) to 1.25 \(\times 10^{-4}\) Ω cm as the \(p_{O_2}\) was increased from 1 to 5 mTorr. A drastic increase in the resistivity is observed as the \(p_{O_2}\) is further increased from 5 to 100 mTorr. Electrical property of GZO films has close relationship to oxygen content in the film. GZO is an oxide semiconductor having n-type conduction. High conductivity of the GZO might result from Ga-doping effect. Since electrons in the GZO films are supplied from oxygen vacancy and gallium atoms in the film, it can be thought that an increase of oxygen content might cause a decrease of the oxygen vacancy, resulting in increase of resistivity. Fig. 7b shows the variation of the resistivity, carrier concentration, and carrier mobility as a function of the deposition temperature of the GZO films grown at an oxygen pressure of 5 mTorr. As the substrate temperature increases from 100 to 300 °C, the corresponding resistivity becomes 1.25 \(\times 10^{-4}\) Ω cm. The slight increase in resistivity of the films grown at higher substrate temperatures from 300 to 500 °C may be due to contamination by alkali ions from quartz glass substrates and increase of C contamination with increasing substrate temperature [16]. The C contaminants were found to be
increased with increasing growth temperature maybe due to the remainder on quartz glass substrate after cleaning process. The oxygen vacancies play more important role on the electrical properties of transparent conductive films. The decrease of carrier mobility with higher substrate temperature was due to the decrease of oxygen vacancies with increasing C contamination. Therefore, the increase in the resistivity from 300 to 500 °C is attributed to the increase of C contamination and the decrease in the carrier mobility.

The carrier concentration in the GZO films was observed to gradually increase as the deposition temperature was increased. This increase in carrier concentration may be due to an increase in diffusion of Ga atoms from interstitial locations and grain boundaries into the Zn cation sites [17]. The carrier mobility increases from 19.12 cm²/V s at 100 °C to 33.36 cm²/V s at substrate temperature 300 °C, then decreases to 26.42 cm²/V s. Moreover, the observed low resistivity of the 1.46 × 10⁻⁴ Ω cm at 100 °C suggests that film deposition into the semiconductor devices would be possible.

4. Summaries and conclusion

High quality transparent conductive doped ZnO thin films were grown using the PLD technique on quartz glass substrates starting from ZnO target containing 2 wt.% of Al₂O₃ and 5 wt.% of Ga₂O₃, respectively. The growth was performed under wide oxygen pressure range of 1–100 mTorr in the different substrate temperature range of 100–500 °C. We have studied the influence of the growth conditions (oxygen pressure, substrate temperature) on the structural properties that are directly related to essence of films, such as out of plane alignments, in plane epitaxy, crystal size, grain size, and so on. The resistivity and the carrier concentration of the films were decreased due to the decrease of the oxygen vacancy with increasing the oxygen pressure. With increasing the deposition temperature, the resistivity of the films was decreased and the carrier concentration was increased due to the grain growth and the enhancement of the impurity diffusion.

Acknowledgment

This work is supported in part by a Grant-in-Aid for Scientific Research (2003-2006, No. 15360171) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References