Effects of Doping Concentration on the Structural and Optical Properties of Spin-Coated In-doped ZnO Thin Films Grown on Thermally Oxidized ZnO Film/ZnO Buffer Layer/Mica Substrate

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Abstract: ZnO buffer layers were deposited on mica substrates using a sol-gel spin coating method. Then, a thin film of metallic Zn was deposited onto the ZnO buffer layer/mica substrate using a thermal evaporator, and the deposited Zn thin films were then thermally oxidized in a furnace at 500 °C for 2 h in air. Finally, In-doped ZnO (IZO) thin films with different In concentrations were grown on the oxidized ZnO film/ZnO buffer layer/mica substrates using the sol-gel spin-coating method. All the IZO films showed ZnO peaks with similar intensities. The full width at half maximum values of the ZnO (002) peak for the IZO thin films decreased with an increase in the In concentration to 1 at%, because the crystallinity of the films was enhanced. However, a further increase in the In concentration caused the crystal quality to degrade. This might be attributed to the fact that the higher In doping resulted in an increase in the number of ionized impurities. The Urbach energy ($E_U$) values of the IZO thin film decreased with an increase in the In concentration to 1 at% because of the enhanced crystal quality of the films. The $E_U$ values for the IZO thin films increased with the In concentration from 1 at% to 3 at%, reflecting the broadening of localized band tail state near the conduction band edge of the films.

(Received March 4, 2016; Accepted July 22, 2016)

Keywords: thin films, sol-gel, optical properties, x-ray diffraction, Zn-deposited mica substrate

1. INTRODUCTION

ZnO has a wide direct band gap (3.36 eV), high transparency in the visible region, high thermal stability, and a large exciton binding energy (60 meV) at room temperature (RT) [1]. Due to these unique properties, ZnO is one of the most promising candidate materials for optoelectronic devices operating in the ultraviolet (UV) region and for transparent conducting oxide (TCO) films [2-4]. To realize ZnO-based devices for optoelectronic applications, the crystal quality of the ZnO films must be improved, and structural, optical, and electrical properties must be controlled by appropriate doping. Group III elements, such as B, Al, Ga, and In, can be used as donor dopants for ZnO. In particular, In is an important dopant since it changes the conductivity of n-type materials; therefore, ZnO is doped with In to control resistivity for electrical applications, notably in UV sensors, gas sensors[5], field-effect transistors, and solar cells [6]. Moreover, In-doped ZnO (IZO) films show higher conductivity and optical transmittance than other metal-doped ZnO films [7]. IZO thin films can be prepared by using the sol-gel method[8,9], which has several advantages, such as ability to control the chemical composition, low growth temperature, simplicity, safety, and low cost. The structural, optical, and electrical properties of sol-gel-derived IZO thin films are strongly affected by various substrates [10-13]. The substrate type is a very important factor because different flexible substrates have different characteristics, and it is important to choose one that is chemically and thermally stable, transparent, perfectly insulating, and lightweight. Muscovite mica sheets are cheap and flexible, and exhibit heat resistance at temperatures higher than 600 °C as compared to other substrates [14-17]. Therefore, they are a suitable alternative to polymer substrates for synthesizing flexible TCO films [18].

In this study, IZO thin films were deposited by sol-gel spin-coating on thermally oxidized ZnO film/ZnO buffer layer/muscovite mica substrates, and the effects of In doping (0, 1, 2, and 3 at%) on the structural and optical properties of the IZO thin films were investigated.

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2. EXPERIMENTAL PROCEDURES

The precursor solution for the ZnO buffer layer (Solution 1) was prepared by the dissolution of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, ACS Reagent, >98%, Sigma-Aldrich) in 2-methoxyethanol (99.8%, Sigma-Aldrich). The precursor solution for the IZO film (Solution 2) was formed by dissolving zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, ACS Reagent, >98%, Sigma-Aldrich) and indium acetate dihydrate (ln(CH₃COO)₃·2H₂O, 99%, Sigma-Aldrich) in 2-methoxyethanol (99.8%, Sigma-Aldrich). The total volume of the two precursor solutions was 40 mL and the concentration of the metal precursor was 0.5 M. Monoethanolamine (C₂H₇NO, MEA, ACS Reagent, >99.0%, Sigma-Aldrich) was used as the stabilizing agent to improve the solubility of the precursor salt. The molar ratio of MEA to the metal salt was 1.0 (1.204 mL), and the In-to-Zn ratio was varied from 0 to 3 at%. The stabilized sol solutions were stirred at 60 °C for 2 h, after which they became clear and homogeneous. They were subsequently cooled to RT and aged for 24 h before being used as coating solutions to deposit the ZnO seed layer and IZO film. The mica plates (highest-grade V1 muscovite mica) used as substrates were chemically cleaned by using the piranha method. They were then rinsed with distilled water and subsequently blow-dried with ultrahigh-purity N₂ gas (99.9999%) before the spin-coating process. Solution 1 was spin-coated onto the cleaned mica substrate at 2,000 rpm for 20 s. After the deposition by spin-coating, the ZnO buffer layers were pre-heated at 200 °C for 10 min to evaporate the solvent and to remove any residual organic materials.

Metallic Zn source (99.999%) was cleaned ultrasonically for 10 min in methanol and acetone, respectively, and then rinsed with deionized water, followed by blow drying with ultrahigh-purity N₂ gas (99.9999%). Next, the prepared substrates and Zn source were placed in a substrate holder and a tungsten boat, respectively, and then moved to the reaction chamber. The Zn metal source was evaporated and a thin film of metallic Zn was deposited onto the ZnO buffer layer/mica substrate by heating the tungsten boat. The thickness of all the deposited Zn thin films was 200 nm; this was accomplished by controlling the shutter, and was measured by monitoring the quartz crystal resonator inside the chamber. The deposited Zn thin films were then thermally oxidized in a furnace at 500 °C for 2 h in air. Solution 2 was spin-coated onto the thermally oxidized ZnO film/ZnO buffer layer/mica substrate at 2000 rpm for 20 s. After the deposition process, the spin-coated IZO thin films were pre-heated at 200 °C for 10 min to evaporate the solvent and to remove any residual organic materials. These spin-coating and drying processes were repeated seven times. Next, the IZO film was annealed in a furnace at 500 °C for 1 h.

Structural and optical properties of the IZO films grown on the thermally oxidized ZnO film/ZnO buffer layer/mica substrates were investigated by X-ray diffraction (XRD) and UV-visible spectroscopy (SCINCO Ltd.). The thicknesses of the films were determined using profilometry (Tencor Alpha Step).
Table 1. Values of FWHM and average grain size with different In concentrations.

<table>
<thead>
<tr>
<th>In Concentration (at%)</th>
<th>FWHM(002)</th>
<th>Average grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.2406</td>
<td>34.56</td>
</tr>
<tr>
<td>1</td>
<td>0.1751</td>
<td>47.50</td>
</tr>
<tr>
<td>2</td>
<td>0.1817</td>
<td>45.78</td>
</tr>
<tr>
<td>3</td>
<td>0.1824</td>
<td>45.59</td>
</tr>
</tbody>
</table>

Table 2. Values of the optical band gap (E_g) and Urbach energy (E_U) for In concentrations.

<table>
<thead>
<tr>
<th>In Concentration (at%)</th>
<th>Optical band gap (E_g)</th>
<th>Urbach energy (E_U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.15 eV</td>
<td>215 meV</td>
</tr>
<tr>
<td>1</td>
<td>3.25 eV</td>
<td>140 meV</td>
</tr>
<tr>
<td>2</td>
<td>3.24 eV</td>
<td>145 meV</td>
</tr>
<tr>
<td>3</td>
<td>3.23 eV</td>
<td>153 meV</td>
</tr>
</tbody>
</table>

Fig. 2. Optical transmittance spectra in the 200 to 800 nm range for the IZO thin films with different In concentration; the inset shows the absorption spectra of the films.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD patterns of the mica substrate between 25° and 65°, which are marked with the symbol “*” and were observed at 26.81°, 36.03°, 45.49°, and 55.22° (JCPDS card No. 6-263). Figure 1(b) reveals the magnified XRD pattern of the IZO thin films with increasing In concentration for the range 30°–35°. The peaks at 31.3°, 31.4°, 32.4°, 33.85°, and 33.9° correspond to the mica substrate, while the ones for the IZO thin films are observed at 31.7° and 34.4°, which correspond to the (100) and (002) directions of a hexagonal ZnO structure with lattice parameters of a=0.323 nm and c=0.519 nm (JCPDS card No. 36-1451). All the IZO films showed ZnO peaks at similar intensities. All samples exhibited preferred orientation along (002), indicating that all the films were preferentially grown with a c-axis orientation. It is well-known that the preferred c-axis orientation is due to high atomic density and the minimal surface energy along the (002) plane [19,20]. The values of the full width at half maximum (FWHM) in the 0 at% to 3 at% range for the (002) peak were evidently dependent on the In concentration, as shown in Table 1. The FWHM values for the IZO thin films decreased when the In concentration was increased to 1 at% because the crystallinity of the films was enhanced. However, a further increase in the In concentration caused the crystal quality to degrade, which might be attributed to the fact that the higher In doping concentration resulted in an increase in the number of ionized impurities. The average grain size of the ZnO thin films was determined using the Debye Scherrer formula [21].

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]

where \( \beta \) is the FWHM of the (002) diffraction peaks, \( \theta \) is the Bragg angle of the X-ray diffraction peaks, \( \lambda \) is the wavelength of CuKα, \( K \) is constant (about 0.9), and \( D \) is the average grain size. The calculated average grain size values are shown in Table 1. The larger grain size and lower FWHM values indicate the improved crystal quality of the ZnO film [22]. Thus, the IZO film with 1 at% In doping is most effective for the growth of IZO thin films with high c-axis orientation and good crystallinity.

Figure 2 shows the optical transmittance spectra of the IZO thin films in the wavelength range between 200 and 800 nm. All the films exhibited an average transmittance higher than 70% in the visible region and a sharp absorption edge at about 370 nm. The highest optical transmittance in the visible region was observed for the undoped ZnO film. The absorption edge in the 370 to 400 nm range for the IZO thin films shifted toward higher wavelengths with increasing In concentration. The absorption edge for IZO thin films for the
range 0-3 at% was red-shifted. There are mainly two reasons to explain the red-shift: (1) It can be attributed to the increase in optical scattering; (2) The red-shift was induced by splitting the conduction band into an upper and lower conduction band. As In\(^{3+}\) replaces Zn\(^{2+}\), the excess electron reduces the band gap [23-25]. Accordingly, the calculated absorption coefficients in the UV region were found to decrease with decreasing In concentration, as shown in the inset of Fig. 2. The absorption edge of the films corresponds to electron transitions from the valence to the conduction band and can be used to obtain detailed information about the energy band gaps. The relationship between the absorption coefficient and the photon energy for a direct transition can be expressed as follows [26]:

\[
\alpha h\nu = A (h\nu - E_g) \frac{1}{2}
\]

where A is an energy-independent constant, \(E_g\) is the optical band gap, and \(\alpha\) is the absorption coefficient.

Figure 3(a) reveals plots of \((\alpha h\nu)^2\) vs. \(h\nu\) for IZO thin films with different In concentration. The optical band gap values, as shown in Table 2, were determined from the intercept of the \((\alpha h\nu)^2\) vs. \(h\nu\) plots. The \(E_g\) value of the undoped ZnO thin film (3.15 eV) was lower than that of the IZO thin films. This effect can be attributed to the improvement in the crystallinity of the films [27]. \(E_g\) of IZO thin films was found to gradually decrease from 3.25 to 3.23 eV in the range from 1 to 3 at%. This decrease can possibly be attributed to the existence of In impurities in the ZnO structure, which induce the formation of new recombination centers with lower emission energy [28,29]. Figure 3(b) shows the Urbach energy values for the films extracted from the \(\ln \alpha\) vs. \(h\nu\) plots. The absorption coefficient reveals an exponential dependence on the photon energy near the band edge, which follows the empirical Urbach rule [30],

\[
\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_U} \right)
\]

where \(\alpha_0\) is a constant and \(E_U\) is the Urbach energy calculated from the reciprocal gradient of the linear portion of \(\ln \alpha\) vs. \(h\nu\) curves. As shown in Table 2, the Urbach energy \((E_U)\) values of the IZO thin films decreased with an increase in the In concentration to 1 at% because of enhanced crystal quality. This enhancement was possibly due to an increase in the affinity between Zn and O caused by the incorporation of In. The dynamic affinity of the Zn for bonding with O might be improved by the incorporation of a suitable amount of In, because the oxygen affinity of In is greater than that of Zn. The relatively stronger bond between In and O leads to the existence of more oxygen, and more stoichiometric ZnO crystals were therefore generated in the IZO thin films. The \(E_U\) values in the range from 1 at% to 3 at% for the IZO thin films increased with In concentration, reflecting the broadening of the localized band tail state near the conduction band edge of the films. There are several factors that possibly affect the Urbach band tail in a semiconductor, including carrier–impurity or carrier–phonon interaction, and structural disorder [31]. Thus, the increased number of defects
introduced by In doping may be responsible for the increase in the $E_U$ values of the films. Therefore, according to the structural properties of the XRD and optical band gaps, the best properties were observed for the 1 at% IZO thin film.

4. CONCLUSION

The smallest FWHM values for the (002) peak in the XRD pattern, and the smallest average grain sizes were obtained at 1 at% In concentration. The crystal sizes of the IZO thin films with 0, 1, 2, and 3 at% In concentrations were found to be 34.56, 47.50, 45.78, and 45.59 nm, respectively. The optical band gap of the IZO thin films were found to decrease from 3.25 to 3.23 eV in a range from 1 to 3 at%. The values of the Urbach energy for the films were found to be 215, 140, 145, and 153 meV. From the calculated Urbach energy, we demonstrated that the 1 at% IZO thin film exhibited the best crystallinity. Thus, the optimal In concentration was 1 at% for growing IZO thin film with good structural and optical properties on a mica substrate. We expect that the results of this research will contribute to the development of flexible and transparent IZO-based devices.

ACKNOWLEDGEMENT

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2015R1D1A1A01058131).

REFERENCES