Aluminum-doped zinc oxide formed by atomic layer deposition for use as anodes in organic light emitting diodes

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Aluminum-doped zinc oxide formed by atomic layer deposition for use as anodes in organic light emitting diodes

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Aluminum-doped zinc oxide films produced by atomic layer deposition were investigated for use as anodes in organic light emitting diode (OLED) devices. Al-doped ZnO (AZO) films (~200 nm thick) were deposited at temperatures of 200, 230, and 260 °C and the AZO film deposited at 260 °C demonstrated carrier mobility, carrier concentration, resistivity, and transmittance values of 16.2 cm² V⁻¹ s⁻¹, 5.18 × 10²⁰ cm⁻³, 7.34 × 10⁻⁴ Ω cm, and 90%, respectively. OLED devices with a DNTPD/TAPC/Bebq 2:10% doped RP-411/Bphen/LiF/Al structure on a glass substrate fabricated using an AZO anode formed at 260 °C showed turn-on voltage, maximum luminance, and current efficiency values of 5.3 V, 16680 cd/m², and 4.8 cd/A, respectively. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4738749]

I. INTRODUCTION

Currently, indium tin oxide (ITO) is the most widely used transparent conducting oxide (TCO) as an electrode material for optoelectronic devices because of its excellent features, low electrical resistivity (~2 × 10⁻⁴ Ω cm), high transparency (~90%) due to its wide optical bandgap (3.7 eV), and high work function (4.8 eV). However, ITO has many drawbacks, including its chemical instability, potential harm to humans, and high cost due to the relative scarcity of indium. ¹,² Therefore, in recent years new TCOs have been investigated as electrodes for optoelectronic devices in order to replace ITO, which is considered to be one of the key challenges to improve the optoelectronic performance. In particular, among the alternative TCO materials, zinc oxide (ZnO), which is typically an n-type semiconductor, is regarded as a good representative material and has excellent features, including high chemical stability, low material cost, high conductivity, and high optical transmittance.³,⁴ Moreover, the conductivity and optical transmittance of ZnO can be controlled by impurity doping with an electron donor from various III metal groups such as gallium,³ indium,⁴ and aluminum.⁵⁻¹⁰ Of these, Al-doped zinc oxide (AZO) films are considered to be a suitable TCO electrode material for optoelectronic devices.

AZO films can be fabricated using a variety of methods, including pulsed laser deposition (PLD),⁵⁻⁷ sputtering,⁶,⁹ and sol-gel¹⁰,¹¹ methods. In particular, AZO films deposited by PLD and sputtering methods have demonstrated a low resistivity of under 2.0 × 10⁻⁴ Ω cm and a high transmittance of over 85% with a wide optical energy bandgap compared to pure ZnO films.⁶⁻⁸ The possibility of TCO electrodes has been successfully demonstrated in optoelectronic device applications such as organic light emitting diodes (OLEDs),¹⁴,⁹ solar cells,¹⁷ and thin film transistors (TFTs).¹⁰ Recently, a novel deposition technique for AZO films was developed using atomic layer deposition (ALD),¹²⁻¹⁹ which is a cost efficient, low temperature deposition process. In addition, the electrical and optical properties of thin films deposited via ALD can be modified easily and exactly by controlling the deposition to under several angstroms per cycle.²⁰ Consequently, AZO TCOs deposited by the ALD method have been researched for use in optoelectronic devices such as organic solar cells,¹⁷ OLEDs,¹⁸ and TFTs.¹⁹ However, there is still a need for a comparative work with the AZO films deposited by sputtering and PLD methods.

In this work, therefore, we studied AZO films formed by ALD for application in OLED devices in order to ascertain their performance as a TCO anode. The AZO films were deposited on glass substrates at various deposition temperatures ranging from 200 to 260 °C and the variations of the electrical conductivity and optical transmittance as a function of the deposition temperature were analyzed. The prepared AZO films were also tested as a TCO anode in OLED devices. Finally, their luminance and current efficiency characteristics were investigated.

II. EXPERIMENT

The deposition of AZO films was carried out using a flow-type ALD reactor (Lucida D100, NCD). To investigate the effect of the deposition temperature, AZO films were deposited on high optical Corning 1737 glass substrates (>90% transmittance) with dimensions of 2.5 cm × 2.5 cm under different deposition temperatures ranging from 200 to 260 °C under a base pressure of 50 mTorr. AZO films composed of ZnO and Al₂O₃ were formed using a “super cycle”
process of 39 total super cycles where each super cycle was composed of 29 ZnO cycles followed by 1 AlOx cycle. Under these deposition cycle conditions, the doping concentration of Al was controlled to be 2.2 at.%. Diethyl zinc (C2H5)2Zn, DEZ) and de-ionized water (H2O) were used as the precursor reactants for ZnO, while tri-methyl aluminum (Al(CH3)3), TMA) and H2O were used for AlOx. High purity nitrogen (99.999% N2) gas was used as the purge gas. The pulse times for each DEZ, TMA, and H2O cycle were 0.1, 0.05, and 0.1 s, respectively, and the N2 purge time was 8 s. The AZO film thickness target was around 200 nm and the maximum deposition temperature was limited to 260°C based on the ALD process window. The growth rates per cycle (GPC) of ZnO and AlOx were calculated from the prepared film thicknesses to be 1.70 and 1.1 Å/cycle at a deposition temperature of 200°C and 1.66 and 1.09 Å/cycle at 250°C, respectively.

In order to use the TCO as an anode for OLED devices, the prepared AZO films were cleaned using acetone, methanol, H2O, and isopropyl alcohol in an ultrasonic bath. Then, AZO anodes were patterned by conventional photolithography and were etched over the 2 × 2 mm2 emitting area by a wet process using a mixed etchant solution of MA-SO2 methanol, H2O, and isopropyl alcohol in an ultrasonic bath. After this etching process, AZO anodes were moved to a higher diffraction angle than ZnO. The crystallinity of the AZO film also changed with increasing deposition temperature. The c-axis parameter of the AZO films increased with increasing deposition temperature. The c-axis lattice parameters of AZO films fabricated at deposition temperatures of 200, 230, and 260°C were calculated to be 5.276, 5.258, and 5.252 Å, respectively, which are smaller than the lattice parameter of ZnO (5.290 Å), and which lead us to surmise that higher deposition temperatures enhance the occupation probability of Al1+ ions into ZnO. However, the a-axis lattice parameters calculated from the 001 diffraction peak of the ZnO film and AZO films deposited at 200 and 230°C were found to be 3.299, 3.296, and 3.293 Å, respectively, demonstrating a much smaller decrease than the c-axis parameter. This enhanced shrinkage along the c axis induces a preferred growth orientation along the c axis.

The crystal structure properties of AZO films were analyzed by x-ray diffractometry ([XRD], D/MAX-2000, Rigaku) with Cu Kα radiation and field emission scanning electron microscopy ([FE-SEM], S-4800, Hitachi). The optical properties, including the transmittance and UV absorption of the AZO films, were inspected using a UV-visible-near-infrared spectrometer (V-570, Jasco). The electrical properties consisting of the sheet resistance and resistivity of the AZO films, were inspected using a UV-visible-near-infrared spectrometer (V-570, Jasco). The electrical properties consist-

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction spectra of the AZO films deposited onto glass substrates at various deposition temperatures ranging from 200 to 260°C. The main x-ray diffraction spectrum of the ZnO film deposited at 200°C was observed to have 100, 002, and 110 peaks at 2θ angles of 31.28°, 33.86°, and 56.11°, respectively, with a hexagonal structure. The AZO films also showed identical diffraction peaks as the ZnO film. However, upon increasing the deposition temperature from 200 to 260°C, the AZO films showed a preferred c-axis growth orientation, i.e., an increase in the intensity of the 002 diffraction peak, whereas the intensities of the 100 and 110 diffraction peaks gradually decreased and finally vanished at a deposition temperature of 260°C. This change in growth orientation was suggested to be due to the much smaller ionic radius of Al3+ (0.53 Å) than Zn2+ (0.74 Å), and therefore this substitutional effect of Al3+ ions occupying Zn2+ sites can lead to shrinkage of the ZnO lattice. The 002 diffraction peak of AZO deposited at 200°C moved to a higher diffraction angle than ZnO. The c-axis lattice parameters of AZO films fabricated at deposition temperatures of 200, 230, and 260°C were calculated to be 5.276, 5.258, and 5.252 Å, respectively, which are smaller than the lattice parameter of ZnO (5.290 Å), and which lead us to surmise that higher deposition temperatures enhance the occupation probability of Al1+ ions into ZnO. However, the a-axis lattice parameters calculated from the 001 diffraction peak of the ZnO film and AZO films deposited at 200 and 230°C were found to be 3.299, 3.296, and 3.293 Å, respectively, demonstrating a much smaller decrease than the c-axis parameter. This enhanced shrinkage along the c axis induces a preferred growth orientation along the c axis.
deposited at temperatures of 200, 230, and 260 °C were calculated using Scherrer’s formula to be 17.3, 20.8, and 23.1 nm, respectively. The lattice parameter, c, and grain size of the AZO films deposited at various temperatures are shown in the inset in Fig. 1.

Figure 2 shows the surface morphologies of the ZnO film and AZO films fabricated at deposition temperatures of 200, 230, and 260 °C, as visualized by FE-SEM. The ZnO film deposited at 200 °C had a cylindrical morphology, but the AZO film deposited at 200 °C had a less sharp cylinder particle shape due to the change in the preferred growth orientation along the c axis. The particle shape in the AZO film deposited at 230 °C became almost spherical and the AZO film deposited at 260 °C had a flat and uniform surface morphology with a highly crystalline state, as shown in the XRD pattern in Fig. 1.

Figure 3 shows the electrical properties including the carrier concentration, mobility, and resistivity of the AZO films fabricated at the various deposition temperatures ranging from 200 to 260 °C. All of the prepared AZO films showed n-type semiconductor properties, and the carrier concentration of ZnO deposited by ALD at 200 °C was measured to be $8.44 \times 10^{19}$ cm$^{-3}$, whereas the carrier concentrations of the AZO films increased up to $5.18 \times 10^{20}$ cm$^{-3}$ with increasing deposition temperature. This increasing carrier concentration behavior with increasing deposition temperature agrees well

![Figure 3](http://example.com/fig3.png)

**FIG. 3.** (Color online) Electrical properties of the ZnO film deposited at 200 °C and AZO films deposited at (b) 200 °C, (c) 230 °C, and (d) 260 °C.
with the decreasing behavior of the c-axis parameter, as shown in the XRD spectra in Fig. 1. Otherwise, the carrier mobility of the AZO films decreased compared to ZnO, which appears to be due to the enhanced carrier scattering probability from the substitutional Al3+ ions. However, the carrier mobility in the AZO films increased slightly with increasing deposition temperature due to the enhanced crystallinity as shown in Fig. 1. Therefore, the resistivity of the AZO films decreased from 9.94 to 7.34 × 10−4 Ω cm (corresponding average sheet resistances of 93 and 52 Ω/sq) with increasing deposition temperature from 200 to 260 °C.

Figure 4(a) shows the optical transmittance and absorption spectra (inset) in the visible region from 350 to 800 nm and Fig. 4(b) shows plots of the optical bandgap (Eg) vs (zhv)² of the ZnO and AZO films. The average transmittance of the ZnO and AZO films was in the range of 80%–90%. The optical absorption edge for the ZnO and AZO films was determined by extrapolation of the plot of (zhv)² vs Eg, as shown in Fig. 4(b). The optical absorption edge of the AZO films was blueshifted compared to that of the ZnO film, which increased with increasing deposition temperature. Specifically, the Eg value was 3.22 eV for the pure ZnO film and it increased to 3.27, 3.37, and 3.43 eV for the AZO films deposited at 200, 230, and 260 °C, respectively. That is, the Fermi level can be raised with increasing carrier concentration and can be moved into the conduction band. Therefore, the Eg of the AZO film increased with increasing carrier concentration, as observed in Fig. 3. This Eg widening of AZO

![Fig. 4](image_url)

**Fig. 4.** (Color online) (a) Optical transmittance spectra in the visible range (inset corresponds to absorption behavior), (b) plots of the optical bandgap (Eg) vs (zhv)² and (c) plots of Eg vs n^(2/3) for the ZnO film deposited at 200 °C and AZO films deposited at 200, 230, and 260 °C.

film can be explained by the Burstein–Moss effect as shown as follows:

$$\Delta E_g = \left( \frac{\hbar^2}{2m^*_e} \right) \left( \frac{3\pi^2}{2} \right)^{2/3} (n)^{2/3} \text{(eV)}.$$  \hspace{1cm} (1)

In Eq. (1), $\Delta E_g$ is the widened optical band edge of the semiconductor with increased carrier concentration, $n^{2/3}$, $\hbar$ is Planck’s constant, and $m^*_e$ is the reduced effective mass ($1/m^*_e = 1/m^*_0 + 1/m^*_h$). The relationship between $\Delta E_g$ and $n^{2/3}$ is shown in Fig. 4(c), where the dashed line corresponds to the calculated Burstein–Moss shift values where $m^*_e = 0.38 m_0$, and $m^*_h = 1.8 m_0$. The $E_g$ values of pure ZnO and AZO deposited at 200 °C are in accord with the calculated $\Delta E_g$ values. On the other hand, the $E_g$ values of the AZO films deposited at 230 and 260 °C were inconsistent with the $E_g \propto n^{2/3}$ relationship in the Burstein–Moss model. The $n^{2/3}$ value linearly increased with increasing deposition temperature, which can provoke more Al$^{3+}$ ions to diffuse and substitute at Zn$^{2+}$ sites at higher deposition temperatures. As a result, this may influence the crystallinity, surface morphology, and optical properties of the AZO films.

In order to determine the performance of our AZO films as a TCO anode for OLED devices, a figure of merit ($\eta = T^{10}/R_S$) value was calculated, where $T$ is the optical transmittance at 550 nm and $R_S$ is the sheet resistance, which is a common rating method for TCO films to determine their possible use in optoelectronic applications. The figure of merit values of the AZO films, representing both their electrical and optical properties, are summarized in Table I. The highest figure of merit of the AZO films was 6.71 × 10$^{-3}$ cm$^2$/V$^2$ for the film deposited at 260 °C, which had the lowest sheet resistance and highest optical transmittance.

Figure 5(a) shows the current density versus voltage ($J-V$) and Fig. 5(b) shows the luminance versus voltage ($L-V$) characteristics of the OLED devices with ZnO and AZO anodes. The schematic energy band of the OLED devices with AZO/DNTPD/TAPC/Bebq2:10% doped RP-411/Bphen/LiF/Al structure is presented in the inset in Fig. 5(a). The OLED device with the ZnO anode showed lower current density and luminance characteristics, while the maximum luminance value was found to be 15 cd/m$^2$ at 18 V. The maximum current density value for the OLED test device with ZnO was 72 mA/cm$^2$, whereas the OLEDs with AZO anodes all had similar maximum current densities of approximately 400 mA/cm$^2$. The maximum luminance values of the OLED devices with AZO anodes deposited at 200, 230, and 260 °C increased to 8296, 11 210, and 16 680 cd/m$^2$ (at 18 V), respectively. On the other hand, the turn-on voltage (at 10 cd/m$^2$) of the OLED devices decreased to 5.7, 5.4, and 5.3 V with increasing deposition temperature. From the luminance and current density results, the current efficiency was calculated, and the current efficiency versus current density ($\eta$ vs $J$) characteristics of the OLED devices with ZnO and AZO anodes are shown in Fig. 6. The current efficiency of the device with the ZnO anode was nearly zero. The maximum current efficiencies in the turn-on voltage region of the OLED devices with AZO anodes grown at deposition temperatures of 200, 230, and 260 °C were 2.3, 2.9, and 4.4 cd/A, respectively. The lowest turn-on voltage and the highest luminance and current efficiency values were obtained for the device with the AZO anode deposited at 260 °C, corresponding to the AZO film with the lowest sheet resistance and highest optical transmittance. These results can be correlated with the figure of merit values of the AZO films. With decreasing figure of merit values of the AZO TCOs, the luminance and current efficiency values of the OLED device increased, as shown in Table I. Another factor to consider is the work function of the anode, which is one of the key issues for improving the electrical and optical characteristics of OLED devices. Since a lower energy barrier between the anode and HIL layer can allow the carrier transmission to occur more easily and effectively. The work function of the ZnO film is 3.74 eV. Jiang et al. reported a

<table>
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<tr>
<th>Condition</th>
<th>Carrier mobility (cm$^2$/V·s)</th>
<th>Carrier concentration (× 10$^{20}$/cm$^3$)</th>
<th>Resistivity (× 10$^{-4}$/Ω·cm)</th>
<th>Sheet resistance (Ω/sq)</th>
<th>Transmittance (% at 550 nm)</th>
<th>Figure of merit (× 10$^{-3}$/Ω$^{-1}$)</th>
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<tr>
<td>ZnO 200 °C</td>
<td>34.9</td>
<td>0.84</td>
<td>21.25</td>
<td>257</td>
<td>83</td>
<td>0.60</td>
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<tr>
<td>AZO 200 °C</td>
<td>14.4</td>
<td>3.41</td>
<td>9.94</td>
<td>93</td>
<td>80</td>
<td>1.15</td>
</tr>
<tr>
<td>AZO 230 °C</td>
<td>15.9</td>
<td>4.49</td>
<td>8.72</td>
<td>79</td>
<td>88</td>
<td>3.53</td>
</tr>
<tr>
<td>AZO 260 °C</td>
<td>16.4</td>
<td>5.18</td>
<td>7.34</td>
<td>52</td>
<td>90</td>
<td>6.71</td>
</tr>
</tbody>
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FIG. 6. (Color online) Current efficiency vs current density ($\eta$ vs $J$) characteristics of the OLED devices containing ZnO deposited at 200 °C and AZO deposited at 200, 230, and 260 °C.
work function of 4.4 eV of AZO films doped with 2.1 at. % Al by a sputtering method, and Meyer et al. reported the work function of AZO films deposited by the ALD method to be 4.2 eV. Therefore, the hole injection barrier between the AZO anode and DNTPD is lower than that of a ZnO anode. Accordingly, in the case of OLED devices with AZO anodes, the hole injection into the DNTPD was greater than in the case of OLEDs with a pure ZnO anode because a large amount of hole–electron (exciton) recombinaiton was gener-

ated in the case of OLEDs with a pure ZnO anode due to a large amount of hole–electron (exciton) recombinaiton was generated with the Bebq3:RP-411 EML. Therefore, the OLED devices with AZO anodes show a higher luminance and current efficiency than those with a ZnO anode due to their reduced sheet resistance and hole injection barrier.

Figure 7 shows the electroluminescence (EL) characteristics of OLED devices with ZnO and AZO anodes at maximum luminance. All prepared OLED devices showed good red emission and their EL intensity was consistent with their luminance. The main peaks of the EL spectra of the OLED devices with AZO anodes deposited at temperatures ranging from 200 to 260 °C were slightly shifted from 623 to 628 nm, which also agrees well with the absorption behavior shown in the inset in Fig. 4(a).

IV. CONCLUSION

In this work, AZO films deposited at various temperatures by the ALD method were studied for use as TCO anodes in OLED devices. The AZO films showed enhanced electrical conduction with increasing deposition temperature because the electron carrier concentration increased due to successful substitution of Zn$^{2+}$ with Al$^{3+}$. The best transmittance and resistivity results were 90% and $7.34 \times 10^{-4}$ Ω cm, respectively, found in the AZO film deposited at 260 °C, corresponding to the best figure of merit. Consequently, the best performance of the OLED devices was achieved with this AZO anode material where the maximum luminance and current efficiency values were 16 680 cd/m$^2$ and 4.4 cd/A, respectively. From these results, it can be concluded that AZO films deposited by ALD at a controlled deposition temperature are a promising electrode material for low-temperature-deposition OLED devices.

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