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Characteristics of Organic Light Emitting Diodes with Al-Doped ZnO Anode Deposited by Atomic Layer Deposition

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Transparent conductive, Al-doped ZnO films (ZnO:Al) have been deposited by means of an atomic layer deposition method with the surface chemical compositions of ZnO (film A) and Al₂O₃ (film B). The sheet resistance, surface work function, and structure characteristics of ZnO:Al films have been investigated. Organic light emitting diodes (OLEDs) were fabricated on glass substrates using two different ZnO:Al anodes. The devices fabricated with them exhibited higher current and luminance with higher external quantum efficiencies below approximately 5000 cd/m², than those fabricated with a conventional tin-doped indium oxide (ITO) anode. The external quantum efficiencies of the devices with film A, film B, and ITO were 1.86, 1.97, and 1.74%, respectively. [DOI: 10.1143/JJAP.44.L242]

KEYWORDS: Al-doped ZnO, atomic layer deposition (ALD), organic light emitting diode (OLED), anode, work function

Transparent conductive oxide films (TCOs) have been extensively used in displays and optoelectronic devices. Among them, tin-doped indium oxide (ITO) is predominantly utilized due to the high conductivity, work function, and transparency.¹⁾ However, the chemical instability, the toxic nature of indium, and the high cost due to the scarcity of indium have led researchers to seek an alternative candidate for ITO.²⁾

Al- or Ga-doped ZnO has shown electrical and optical properties comparable with those of ITO films.³⁾ Recently, its low growth temperature has intrigued researchers with respect to its application for flexible displays and solar cells.^{4,5)} Undoped and doped ZnO films have been fabricated by several deposition techniques including chemical vapor deposition, reactive magnetron sputtering, electron-beam evaporation, and pulsed laser deposition.⁶⁾ A major focus of recent research on ZnO thin film deposition has been a technique of atomic layer deposition (ALD) which is capable of growing uniform and high quality thin film on a large area at low temperatures. Most ZnO thin films fabricated by means of the ALD method have been applied to the solar cell.^{7,8)}

Here, we present the application of ALD deposited ZnO:Al TCO for the anode film of organic light emitting diodes (OLEDs). Jiang *et al.* reported the use of ZnO:Al films having a surface work function between 3.7 and 4.4 eV, as the anode film of OLEDs by means of mid-frequency magnetron sputtering.⁹⁾ One of the main drawbacks of using the ZnO:Al film as the OLED's anode film was the reduction of luminescent performance compared with that of the device adapting ITO as the anode film, caused by the intrinsic low work function of the film. Therefore, a new concept for the fabrication of ZnO:Al anode film is needed to improve the characteristics of the OLED. Since the ALD method allows control of the film composition within atomic layer dimensions, it is very useful for modifying the surface composition of the thin film. Thus, we adapted a unique fabrication method for ZnO:Al thin films using ALD for the application of the OLED anode.

The growth of ZnO:Al films was carried out in a traveling

wave type hot wall reactor at the substrate temperature of 180°C. For the growth of ZnO film, diethylzinc (DEZ) and H₂O were used as the zinc and oxygen precursors, respectively. These precursors were alternatively injected into the reactor using nitrogen as a carrier gas with a flow rate of 100 sccm. With all other conditions fixed, the pulsing times were 1.65 second for the DEZ and H₂O, and 4.4 second for N₂ the purge. Two different methods were used for the deposition of ZnO:Al film. First, Al is doped into the ZnO film by the introduction of an Al precursor (trimethylaluminum) into the reaction chamber once in every 19 cycles of DEZ injection. This doping was repeated 49 times and was followed by the additional deposition of 19 cycles of ZnO growth (film A: ZnO). The second film (film B: Al₂O₃) was deposited by repeating 50 times doping of Al into a ZnO film as film A, followed by the additional deposition of 2 cycles of Al₂O₃ to form the ZnO:Al film having Al₂O₃ as the surface layer. ITO glass was used for the comparison. The crystallographic orientation of the ZnO:Al films was determined by an X-ray diffractometer (XRD) with CuK radiation, and the morphologies of the films were observed using a scanning electron microscope (SEM) and an atomic force microscope (AFM). UV-vis spectra were taken using a Hitachi U-3501 spectrophotometer. The surface work function of the ZnO:Al films and ITO film was measured using a photoelectron spectrometer surface analyzer (RIKEN AC-2). The sheet resistance was measured by means of the four-point probe method with the film thickness of 200 nm. The device structure of the OLED with the emitting area of 2 × 2 mm² was TCO/20 nm 4,4',4''-tris(3-methyl-phenylphenylamino)triphenylamine (MTDA-TA)/40 nm N,N'-bis-[1-naphthyl-(N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine)] (NPB)/60 nm tris-(8-hydroxyquinoline)aluminum (AlQ₃)/1 nm LiF/75 nm Al. Glass was used for the substrate of the OLED device.

The anode properties of OLED are mostly governed by the surface of the film. Treatment of ITO by oxygen plasma or ozone can greatly improve the OLED characteristics by changing the surface elemental composition to result in a change of the work function of ITO.¹⁰⁾ Therefore, we attempted to change only the elemental composition of the ZnO:Al film surface in the atomic layer dimension while

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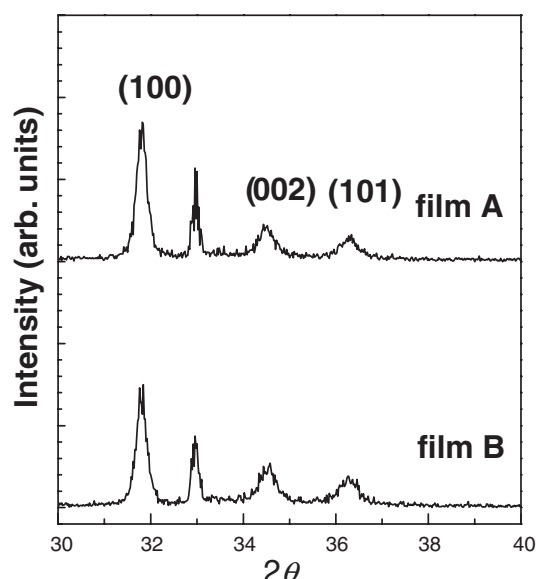


Fig. 1. X-ray diffraction patterns of ZnO:Al films (film A: ZnO surface; film B: Al₂O₃ surface).

keeping the bulk film properties unchanged.

Film A was fabricated with a ZnO layer as the surface layer, while film B was fabricated with an Al₂O₃ layer as the surface layer. The thickness of the surface Al₂O₃ is 3 Å, as estimated from the growth rate of the transient growth region of Al₂O₃ at 180°C. The material properties of film A and B were similar in terms of average sheet resistance, X-ray diffraction patterns, and surface images. The average sheet resistances of films A and B were 91.2 and 93.9 Ω/□, respectively. Figure 1 shows the X-ray diffraction patterns of ZnO:Al films on the Si wafer. They show XRD patterns that are typical for ALD deposited ZnO:Al films with the dominant orientation of the (100) direction. The surface morphologies of ZnO:Al films on the Si wafer were investigated with SEM and AFM. ALD-deposited ZnO:Al films have textured morphologies of wedge-like shaped crystallites even at low growth temperature as shown in Fig. 2. The surface roughnesses were 21.9 Å for film A and 23.5 Å for film B. The transparency was assessed on the basis of the transmittance measured using a UV-vis spectrophotometer from 300 to 800 nm. For the measure-

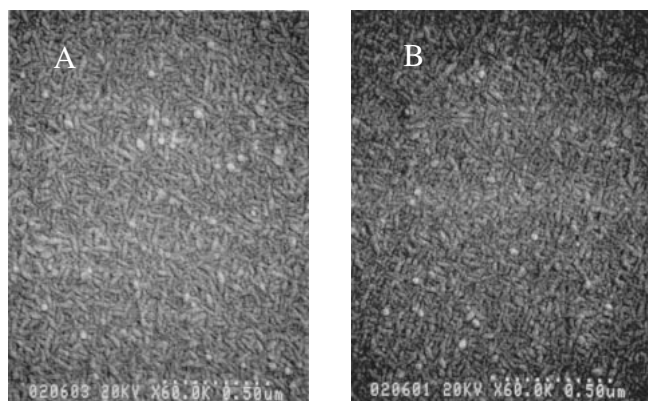


Fig. 2. SEM images of ZnO:Al films (film A: ZnO surface; film B: Al₂O₃ surface).

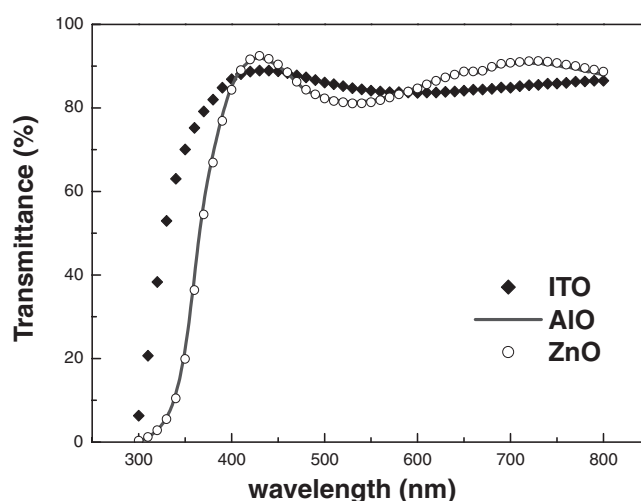


Fig. 3. Transmittance spectra of ZnO:Al films (film A: ZnO surface; film B: Al₂O₃ surface) and ITO film on a glass substrate.

ment, ZnO:Al films were grown on a glass substrate. As shown in Fig. 3, ZnO:Al films have a suitable transparency for OLEDs similar to ITO glass, although the transmittance onset is slightly higher than that of ITO glass.

The different characteristics of film A and film B were obtained from the work function measured at ambient pressure. While the work function of film A was 4.53 eV, film B showed the work function of 4.77 eV. On the basis of these results, it is clear that the surface layer of ZnO:Al can influence the work function of the film.

The change in the surface composition also changed the OLED characteristics. Commercially available ITO with a work function of 5.1 eV was used as an anode film of the OLEDs as well as the above two films. Figure 4 shows the electroluminescence (EL) spectra of the devices, and the EL spectrum of AlQ₃ was changed with the anodes. These spectral changes might be related to the changes of the optical fields with the anodes or the changes of the recombination zone due to the difference in the hole injection property.

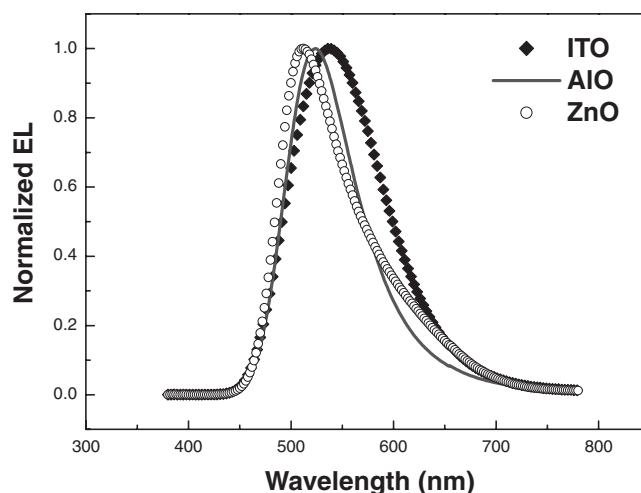


Fig. 4. EL spectra of OLEDs with ZnO:Al films (film A: ZnO surface; film B: Al₂O₃ surface) and ITO as anodes.

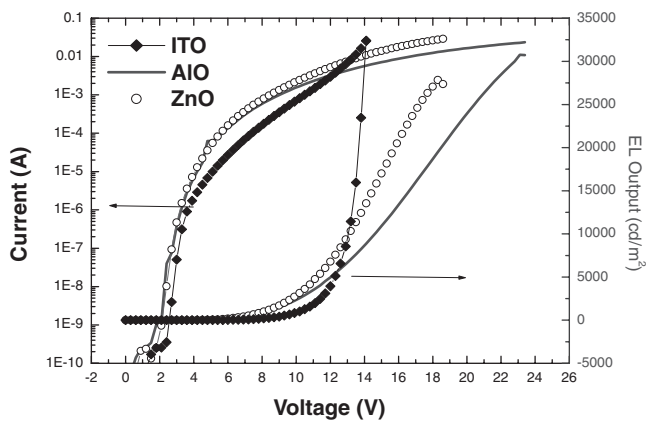


Fig. 5. *I*-*V*-*L* characteristics of OLEDs with ZnO:Al films (film A: ZnO surface; film B: Al₂O₃ surface) and ITO as anodes.

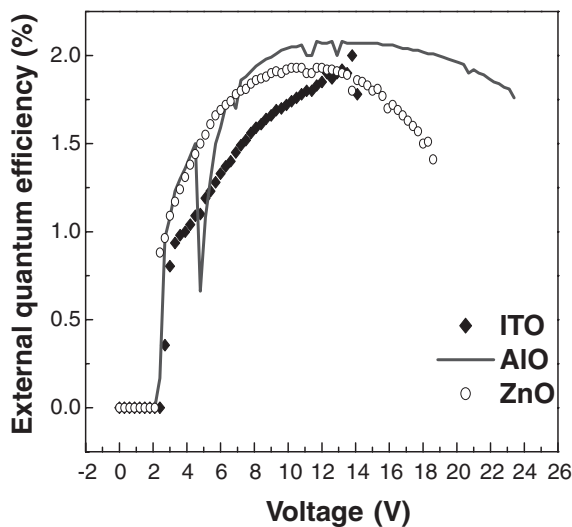


Fig. 6. External quantum efficiencies of OLEDs with ZnO:Al films (film A: ZnO surface; film B: Al₂O₃ surface) and ITO as anodes.

Figure 5 shows the current-voltage-luminance (*I*-*V*-*L*) characteristics of the devices. Although the devices with ZnO anodes showed slightly lower luminance maxima than that of device with the conventional ITO, they exhibited a higher current and luminance below approximately 12 V or 5000 cd/m². Moreover, a higher external quantum efficiency was achieved from the devices with an Al₂O₃-surfaced ZnO:Al anode (film B) as shown in Fig. 6. The external quantum efficiencies of the devices with film A, film B, and ITO were 1.86, 1.97, and 1.74% and the luminances were

990, 1170, and 1020 cd/m² at 20 mA/cm², respectively. The detailed device characteristics are shown in Table I. Although the devices with ZnO-based anodes have lower work functions than that with ITO-based anode, they showed better device performance in terms of practically applicable electric field or luminance. The enhanced current density might be attributed to the enhanced tunneling injection of holes at anodes. A previous report indicated that the enhancement of charge-injection efficiency in the presence of an ultrathin insulator could be explained by tunneling.¹¹⁾ According to that report, the bending of the energy band for the insulator layer causes the emission of the holes to overcome the reduced energy barrier between the anode and the organic layer, and tunneling across the insulator layer is allowed. Although we cannot clarify the mechanism of current increase, we suspect that the ZnO-based anodes having an insulating layer induce the hole injection by tunneling. Further studies are under way to establish the reason for the enhancement of the charge injection with the practically applicable electric field.

To achieve higher efficiency in OLEDs, it is important to balance the numbers of holes and electrons injected to the emitting layer.¹²⁾ Although the role of the surface Al₂O₃ of ZnO:Al in the hole injecting and transporting process is not clear, the enhanced efficiency of the OLED device with ZnO:Al film B might also be attributed to the balance of the hole and electron injections. Above approximately 12 V or 5000 cd/m², however, the higher sheet resistances of ZnO:Al films might cause the voltage drop across the anode to result in less current and luminance than the ITO anode at higher current densities. Qui *et al.* reported that insertion of a thin ZnO layer between the ITO and the copper (II) phthalocyanine (CuPC), instead of using a high resistance anode, resulted in not only the decrease of *V*_{on} but also the increase of the luminance at the higher current density. This result supports our explanation for the OLED behaviors at the high current density.¹¹⁾

In summary, the Al-doped ZnO (ZnO:Al) films were fabricated by means of an atomic layer deposition with the surface chemical compositions of ZnO and Al₂O₃. They showed slightly higher sheet resistances and lower work functions than ITO while the transmittance properties were similar in the visible region. Although the work functions of the ZnO-based anode films were lower than the conventional ITO films, we could obtain a higher luminance with a higher external quantum efficiency when OLEDs were fabricated with them. We believe that the surface insulating layers might play an important role in balancing hole and electron injections through the enhanced tunneling injection of holes.

Table I. EL characteristics of OLEDs with ITO, film A, and film B as anodes.

Anode	CIE Color Coord.	@ 20 mA/cm ²		@ 200 mA/cm ²		Maximum luminance (cd/m ²), V
		Ext. QE(%)	Luminance (cd/m ²)	Ext. QE(%)	Luminance (cd/m ²)	
ITO	0.363, 0.533	1.74	1020	1.92	11440	32400, 14.1
Film A	0.315, 0.546	1.86	990	1.90	10330	27830, 18.0
Film B	0.304, 0.576	1.97	1170	2.06	12360	30750, 23.1

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