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Liu Zugang†, Zhao Weiming†, Ji Rongbin†, Zhang Zhilin†, Jiang Xueyin†, Xue Minzhao‡ and Fang Bin‡

† School of Materials, Shanghai University, 201800 Shanghai, People's Republic of China
‡ Electrically Conducting Polymer Laboratory, East China University of Science and Technology, 200237 Shanghai, People's Republic of China

Abstract. Some organic thin film electroluminescent (EL) devices with aluminium-doped zinc oxide as the hole-injecting electrode have now been manufactured. Their EL spectra and J–V and B–V characteristics have been studied in detail. The work function and ionization potential of the materials composing the devices have been measured and their energy models given. The EL performance properties have been explained well.

1. Introduction

Many investigations of organic thin film electroluminescence have been made in recent years [1–9]. Many organic materials have been used as emission and carrier transportation layers, and different structures have been developed to increase the EL efficiency of the device. Studies on the mechanism of organic EL have also been reported, and the mechanism of organic EL is much better understood.

It is now clear that the electrode of the organic EL device plays an important role in the EL process. Stable material with a suitable work function may form the electrode. Material with a higher work function is better for a hole-injecting electrode and that with a lower work function is suitable for an electron-injecting electrode. Many low-work-function metals and their alloys such as aluminium [10], magnesium–silver alloy [11], magnesium–indium alloy [12] and calcium [13] have been used as the cathode, but for the anode the commonly used material is ITO, a transparent conducting thin film of complex oxide of indium and tin.

We found that transparent conducting aluminium-doped zinc oxide (AZO) has similar electrical conducting and optical transparent properties to ITO and possesses a higher work function than ITO. It is suitable for the anode in an organic EL device.

In this paper, we shall show some different structural organic EL devices with AZO and the interesting EL performances of these devices. In these devices, we chose 8-hydroxyquinoline aluminium (Alq3) as the emitting material because of its strong bright-green emission. Styryltriphenylamine (SA) derivative is a kind of conjugated large π molecular system containing the aryl amine group; we use it as hole-transporting material to improve the emitting efficiency of the device. We use a oxadizole derivative (PBD) between SA and Alq3 to obtain the blue emission from SA owing to its larger band gap and electron-transporting property. The purpose of the experiment is to determine whether AZO is a good anode material or not in an organic thin film EL device.

2. Experimental details

2.1. AZO thin film

A glass substrate was thoroughly cleaned with detergent and deionized water, ultrasonically treated with water, alcohol and acetone respectively and dried in acetone air. An AZO thin film was deposited on the substrate by the RF sputtering method at room temperature in Ar gas with 2 wt% Al_2O_3-doped ZnO sintered sheet as the target [16]. The square resistance of the AZO is about 150 $\Omega/\square$ and the transmission is 85–90% in the visible region. The electrical and optical properties of the AZO thin film are satisfactory for its use as an anode in an organic EL device.

2.2. Device preparation

The AZO thin film was etched with 10% HCl solution to a stripe 2 mm wide and cleaned by the same process described above. The organic layers were deposited by the heat evaporation method in a vacuum of 3×10^{-3} Pa. Then in a vacuum of 6×10^{-3} Pa, a 200 nm aluminium film was deposited on top of the organic layer. Thus we may have single-layer devices (SLDs), double-layer devices (DLDs) or triple-layer devices (TLDs) depending on the number of layers evaporated. Here Alq3 was used as the emitting layer in all devices, SA was used as the hole-transporting layer in DLDs and TLDs and PBD was sandwiched between the SA and Alq3 in TLD to ensure that there were holes in the SA layer in order to obtain emission from the SA. In SLDs and DLDs the thickness of all organic thin films was 75 nm. In TLDs the thicknesses of SA, PBD and Alq3 are 75 nm, 35 nm and 40 nm, respectively. The structures of the organic molecules and the devices are shown in figure 1.
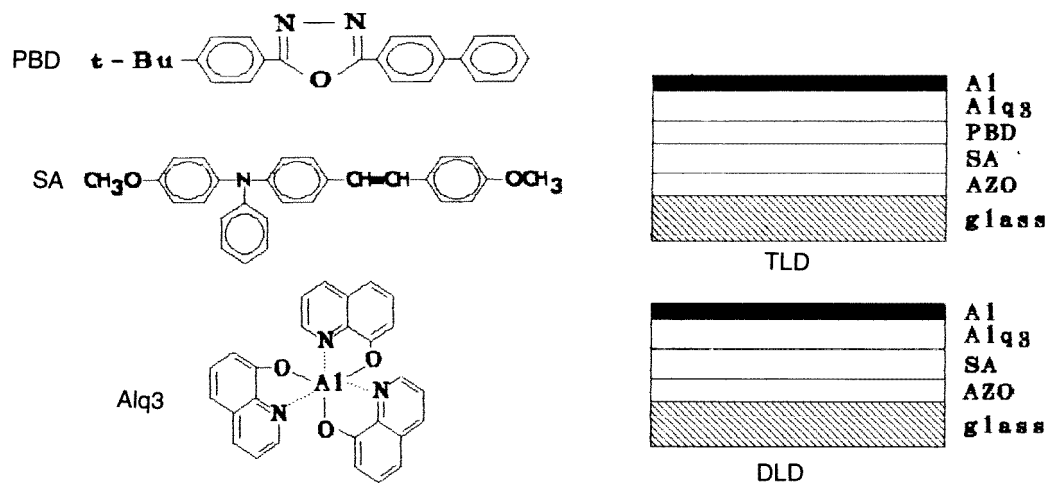

Figure 1. Structures of molecular SA, PBD and Alq3 and of the DLDs and TLDs.

2.3. Measurement

The EL spectra were measured with a Hitachi 850 fluorescence spectrophotometer. The J–V characteristics were measured with a Keithley 617 programmable electrometer and the brightness of the devices with an SL-801 brightness meter. The power source was a YJ82/2 DC regulated power supply. All the measurements were taken in air.
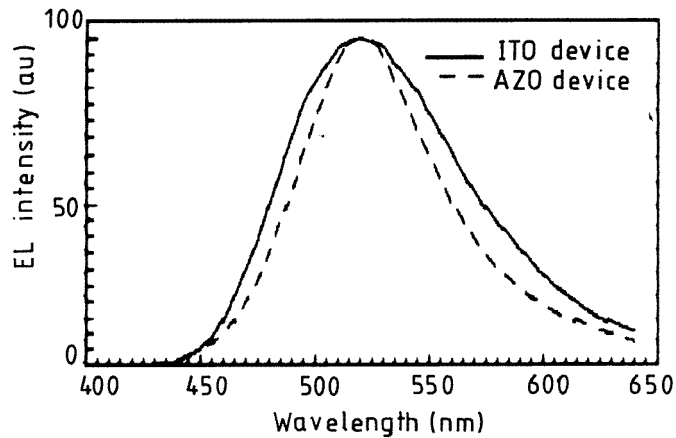

Figure 2. The EL spectra of AZO and ITO DLDs (a.u., arbitrary units).
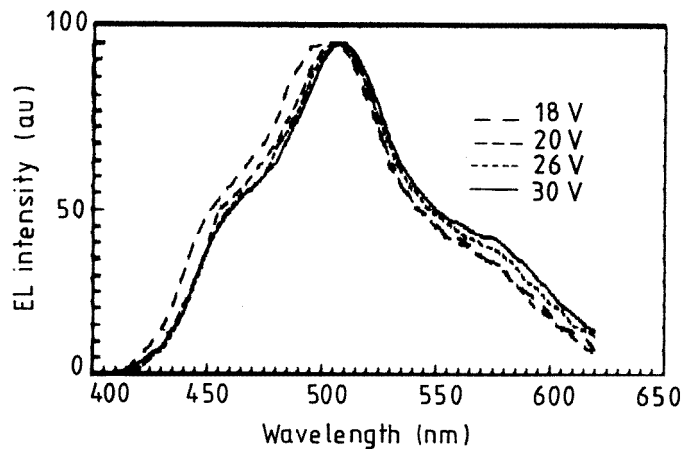

Figure 3. The EL spectra of AZO TLDs at different applied voltages (a.u. arbitrary units).

3. Results

3.1. EL spectrum

The Alq3 SLD emitted very weakly even at high applied voltages. Its EL spectrum was not easily obtained.

The AZO/SA/Alq3/Al DLD emitted a bright-green light; the peak position of the EL spectrum was 520 nm, the same as that of the DLD with ITO (ITO/SA/Alq3/Al). However, the width of the EL spectrum was much narrower than that of the latter device. Figure 2 showed the EL spectra of both DLDs. It can be seen that the half-width of the AZO device is 20% less than that of the ITO device. The narrowing of the spectrum is very interesting but the reason for this is not very clear.

For the AZO/SA/PBD/Alq3/Al TLD, the EL spectrum is much wider than that of the DLD and has three peaks (figure 3): a major peak at 506 nm and two shoulder peaks at 465 and 580 nm. The spectrum width is similar to that of the TLD with ITO. This might have arisen from the emission from SA and Alq3. In addition, the EL spectrum of the TLD has a 'red shift' of about 10–15 nm when the applied voltage was increased from 15 to 30 V. The reason will be discussed in detail in the next section.
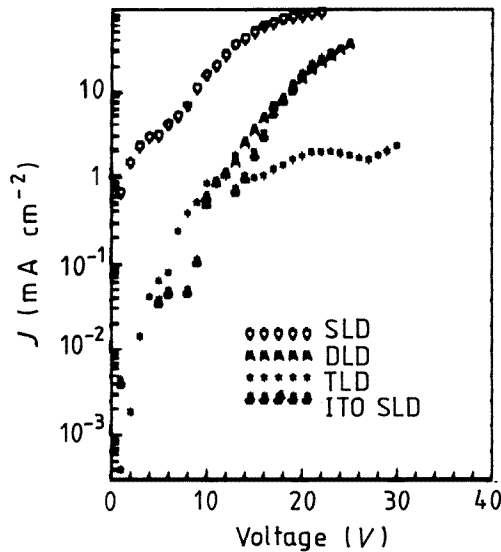

Figure 4. The J–V characteristics of AZO devices.

3.2. J–V and B–V characteristics

Current density–voltage (J–V) characteristics of three AZO devices are shown in figure 4. For the purpose of comparison, a J–V curve of an ITO SLD is shown in this figure too. It could be seen that the AZO device has a higher current density at low applied voltages but the current density rises more slowly than it does for the ITO device. This indicated that the AZO devices have a weaker rectification characteristic. It can also be seen that the current density of the SLD is much higher than those of the DLD and TLD and that of the TLD can no longer rise when the applied voltage is over 10 V.

The brightness–voltage (B–V) curves of the DLD and TLD are shown in figure 5. The SLD emitted too low an intensity for the B–V curve to be measured although its current is high. The B–V of the DLD is almost the same as that of the ITO DLD, and the AZO device had a much higher breakdown voltage. The brightness of the TLD is lower than that of the DLD by one order of magnitude.
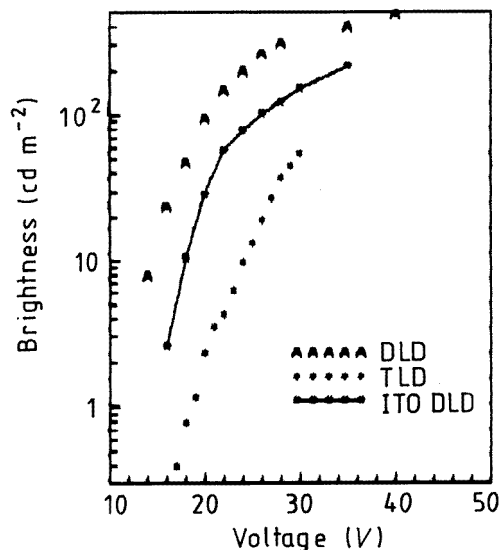
Figure 5. The B–V characteristics of AZO devices.

The internal quantum efficiencies η of AZO devices were calculated. For the SLD the EL brightness is very low, and the quantum efficiency is not easy to obtain. The η-values of the AZO DLD and TLD are 0.21% and 0.17%, respectively, at 24 V, about twice that of the ITO device. These quantum efficiencies are the highest for a device with aluminium as the cathode at present.

4. Discussion

4.1. Energy model

To obtain the energy levels of the devices, the work functions of the electrodes, the highest occupied molecular orbit (HOMO) levels and the energy difference between the lowest unoccupied molecular orbit (LUMO) and the HOMO should be obtained. We used the Kelvin method to determine the work function of the electrodes and the cyclic voltammetry method to obtain the approximate value of the HOMO levels of the organic materials.

For the work function, the electrode plate sample was fixed parallel to a reference plate metal such as pure Cu. When the plates vibrated at a certain frequency and the capacity of two plates was changed, an AC will flow in the circle. If an applied voltage is applied to the circuit to compensate for the potential difference between the sample and the reference metal, when the current is zero, the applied voltage is equal to the potential difference, and the work function of sample could be determined.

For the HOMO levels of the organic materials, the cyclic voltammetry method [17] was used to determine approximately the oxidation potential of the organic materials.

From the HOMO level and the band gap obtained from the optical absorption spectrum of organic material, the LUMO level can be obtained.

The work functions of the electrode materials AZO and aluminium measured by the Kelvin method and the approximate ionization potentials of the organic materials SA, PBD and Alq3 measured by cyclic voltametry were 5.2 eV, 4.3 eV, 5.2 eV, 6.2 eV and 5.7 eV,

respectively. The band gaps of these organic materials obtained from the lower-energy edge of absorption spectra of SA, PBD and Alq3 were 2.8 eV, 3.3 eV and 2.6 eV, respectively. We can find the approximate energy levels of the LUMO and the HOMO for the organic materials used. These are negative values because they are under the vacuum level which is considered as the zero level. The energy band schemes of the three devices are shown in figure 6.
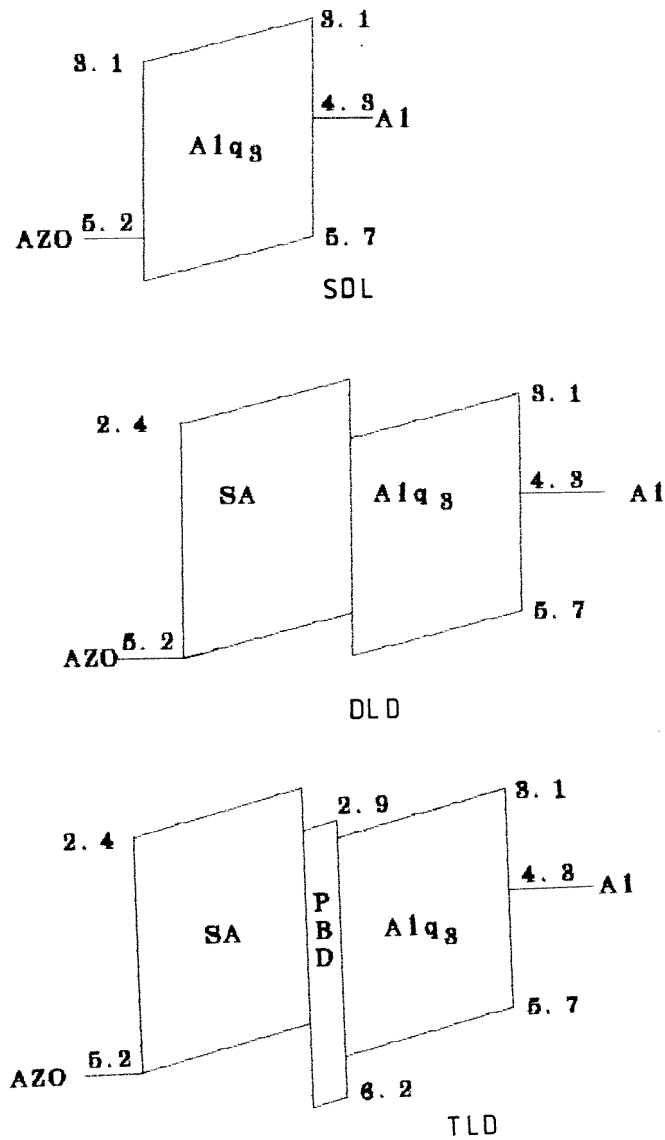

Figure 6. The energy band models of AZO devices.

4.2. Discussion

For carrier injection, there are two possible mechanisms: thermionic emission and tunnelling through the potential barrier. Two theories can be used to describe the injection current. However, in our experiment range, the injection current by thermionic emission is much less than the tunnelling current. The injection current described by the Fowler–Nordheim [14] tunnelling theory is

$$J = AF^2 \exp^{(-k\Phi^{3/2}F)} \tag{1}$$

where F is the field strength, A is the constant related to the material, $k = 8\pi(2m^*)^{1/2}/3qh$, Φ is the barrier height and m^* the effective mass of the carriers. According to equation (1), the injection current can be calculated roughly. For the AZO SLD, the hole barrier Φ_h is 0.5 eV and the electron barrier Φ_e is 1.2 eV; if we take $m_h^* = m_e^* = m_0$ and $F = 3 \times 10^8$ m^{-1}, according to equation (1), the ratio J_h/J_e of the hole to the electron current density is about 10^{10}, i.e. hole injection is much greater than the electron injection. So we can assume that the hole contribution dominates in the total current and the current is controlled by the number of injected holes. The work function of AZO (5.2 eV) is 0.2 eV higher than that of ITO (about 5.0 eV); so hole injection in the AZO device is easier than in the ITO device.

On the other hand, the quantum efficiency η_{EL} of the organic thin film EL device, if the light output efficiency of the device is ignored, is given by [15]

$$\eta_{EL} = \eta_{in}\eta_f \tag{2}$$

where η_{in} and η_f are the carrier injection efficiency of device and the fluorescence efficiency of the emitting material. η_{in} is the ratio of the minority current to the total current; if electrons are the minority carrier,

$$\eta_{in} = \frac{J_e}{J_h + J_e} = \frac{n\mu_e}{p\mu_h + n\mu_e} \tag{3}$$

where n and p are the numbers of electrons and holes, respectively, and μ_n and μ_h are the mobilities of electrons and holes, respectively. If $p \gg n$, then $\eta_{exc} \propto n/p$. This indicates that the efficiency is controlled by the number of injected electrons.

In the DLD, the thickness of two-layer organic materials is twice that of single-layer organic materials, the field strength F is reduced, and the majority carrier (the hole) will decay in the SA layer. So the current decreased. From figure 6 we can see the electron barrier at the Alq3–SA interface; the electrons will accumulate there. The number of electrons in the narrow zone in the Alq3 layer near the interface is large; so the exciton yield efficiency is larger, and therefore the efficiency of the DLD is larger than that of the SLD.

In the TLD, there is another high hole barrier present at the interface between SA and PBD, and the current will be reduced more. For the two barriers existing in the TLD, the exciton will be formed in the SA and Alq3 layers; so the EL spectrum is greenish blue at 500 nm, emitting from both SA and Alq3. At the same field strength as for the DLD, the quantum efficiency of the TLD is high (up to 0.4%) because two barriers coexist.

5. Conclusion

An AZO transmission conducting thin film can be used as the anode in an organic thin film EL device. The EL spectrum of the DLD with AZO is narrower than that of the ITO device, and that of the AZO TLD has three peaks. The current in the three kinds of AZO device is higher than that in an ITO device with the same structure. The quantum efficiency of the AZO DLD and TLD is twice that of the corresponding ITO devices.

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