Effects of microcavities on the spontaneous emission of organic light-emitting diodes with ZnO:Al as the anode

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Abstract.   Organic light-emitting diodes (LED) with a microcavity structure and an aluminium-doped zinc oxide ZnO:Al (AZO) anode have been fabricated. Effects of microcavities on the spontaneous emission of the organic LED, such as spectral narrowing, intensity enhancement and angle dependence of the emission, have been observed. Different emission colours have been obtained by changing the thickness of the AZO layer and that of a TiO$_2$ filler layer. The wavelengths of the cavity modes can be explained on the basis of the calculated total optical thickness of the individual cavities.

1. Introduction

Organic light-emitting diodes (LEDs) have been attracting more and more interest because of their potential application in the flat-panel displays [1]. But the emission spectra of most organic LEDs are too broad to provide the pure primary colours necessary for full-colour displays, because of the vibronic sidebands and the strong inhomogeneous broadening of the transitions.

On the other hand, a kind of micro-Fabry–Perot vertical cavity has been successfully used for controlling the spontaneous and stimulated emission of inorganic semiconductors [2–7]. The effect of microcavities on the spontaneous emission has been especially fully investigated [8].

In recent years, organic microcavities have been widely studied by several groups [9–21]. Some organic emission materials have been sandwiched between two mirrors to produce effects of microcavities on their emissions following light [9, 12] or electric excitation [13–15]. In the case of light excitation, the effects of cavities on both spontaneous emission and stimulated emission have been observed. The effects on spontaneous emission are spectral narrowing, intensity enhancement and angular dependence of the emission, and the effect of cavities on the stimulated emission is to cause a lasing from the organic microcavity [12]. In the electrically driven case, only the effects of cavities on the spontaneous emission of organic LEDs have been reported and discussed [16–21], and a potential method for obtaining pure primary colours for full-colour display has been suggested. Dodabalapur's group [20] use a filler layer, and Cimrova's group [14] and Zhang's group [26] use the

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thickness of the organic layer itself to adjust the optical thickness of the cavity and obtain tunability of the emission colour of the cavity-based device.

All of the microcavity-based organic light-emitting diodes reported so far use ITO or a gold [22, 23] or silver [10] thin film as the anode. In our previous work, we found that an aluminium-doped zinc oxide (AZO) metallic layer can be used as the anode instead of ITO in a noncavity organic LED and noted a spectral narrowing in the AZO device [24]. This spectral narrowing may be due to a cavity effect in that AZO may also act as a half-reflective mirror. The wish to discover what the effect of the AZO is in a real cavity-based structure was the original motivation for the present work.

In this paper, we report on an organic LED using AZO as the anode, with a planar Fabry–Perot microcavity, to investigate the further cavity effects of this kind of organic LED. We use the thickness of the AZO layer as well as that of the anode of the LED, in comparison with that of a TiO_2 filler layer, to adjust the total optical thickness. We will discuss the effects of cavities on the spontaneous emission of such organic LEDs and compare the theoretical cavity modes calculated from the given equations with the experimental results.

2. Experimental procedure

The molecular structure of the organic materials used in the experiment and a schematic diagram of the structure of the microcavity-based LED are shown in figure 1. There are two layers of organic thin film between a transparent conducting layer of an aluminium-doped zinc oxide ZnO:Al (AZO) anode and a metallic aluminium layer cathode in the LED. One layer of organic material is a styryltriphenylamine (SA) derivative, to allow hole transportation, and the other is an aluminium chelate of 8-hydroxylquinoline (Alq3), to allow emission. A quarter-wave stack (QWS) consisting of three layers of TiO_2/SiO_2 is used as a half-reflective mirror, and the metallic aluminium cathode of the organic LED is used as a full reflective mirror for the cavity. Another layer of TiO_2 is deposited between the AZO electrode and the QWS layer as a filler layer, to change the total thickness of the cavity. The microcavity is designed in such a way that the Alq3 layer is located at one maximum of the *E*-field of a standing-wave cavity mode.

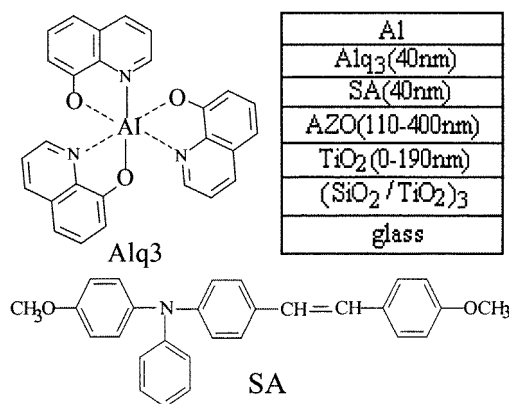The organic LEDs with microcavity structure were fabricated in the following steps. The

Figure 1. Molecular structures of the organic materials and a schematic diagram of the organic LED with microcavity structure.

TiO$_2$ and SiO$_2$ layers were deposited by electron beam evaporation onto a glass substrate. AZO layers with different thicknesses were then deposited by a r.f. sputtering method on top of the TiO$_2$. A detailed description of the deposition of the AZO was given in our previous work [24]. On top of the AZO, SA and Alq3 were deposited subsequently by thermal evaporation. Finally, aluminium metal was deposited on top of the organic layers.

By changing the thickness of the AZO anode with no filler layer and changing the thickness of the filler layer with the thickness of the AZO layer fixed at 110 nm, different devices were made, in order to investigate the cavity effects as a function of the optical thickness of the cavity.

3. Results and discussion

3.1. Spectral narrowing

Typical electroluminescence (EL) spectra of organic LEDs with and without a microcavity structure measured perpendicular to the surface are shown in figure 2. An effect of spectral narrowing and an enhancement of the emission intensity of the LEDs with the cavity structure are clearly observed. It can be seen that the spectrum of a normal organic LED without cavities is a wider band, whereas that of a LED with a cavity takes the form of a sharp major peak centred at 540 nm with two weaker peaks at 460 nm and 670 nm. The full width at half-maximum of the main peak of the EL spectrum of a LED with a microcavity is much smaller than that of a LED without cavities. The former is about 14 nm, and the latter is about 100 nm. We can also see that the intensity of the sharp peaks of a LED with a microcavity is more than twice that of the spectrum of an LED with no cavity. This result is similar to that of Jordan *et al* [18], who measured both the bidirectional emission and the net efficiency enhancement.
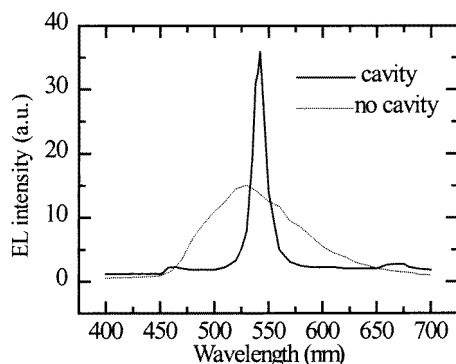

Figure 2. EL spectra of organic LEDs with (——) and without (- - - -) a cavity.

3.2. Spectrum variation with the optical thickness of the cavity

3.2.1. Spectrum variation with the thickness of the filler layer. By fixing the thickness of the AZO layer at 110 nm, and setting the thickness of the TiO$_2$ filler layer as 0 nm, 63 nm, and 190 nm, three organic LEDs emitting different colours were obtained. The electroluminescence spectra of these LEDs are shown in figure 3(a). For the case with no filler layer, the cavity emits a narrow peak at 517 nm. For the case with a TiO$_2$ filler layer

63 nm thick, the cavity emits two narrow peaks instead of one peak. The two peaks are centred at 565 nm and 475 nm, while there are two peaks at 593 nm and 485 nm emitted from the cavity with a filler layer 190 nm thick.
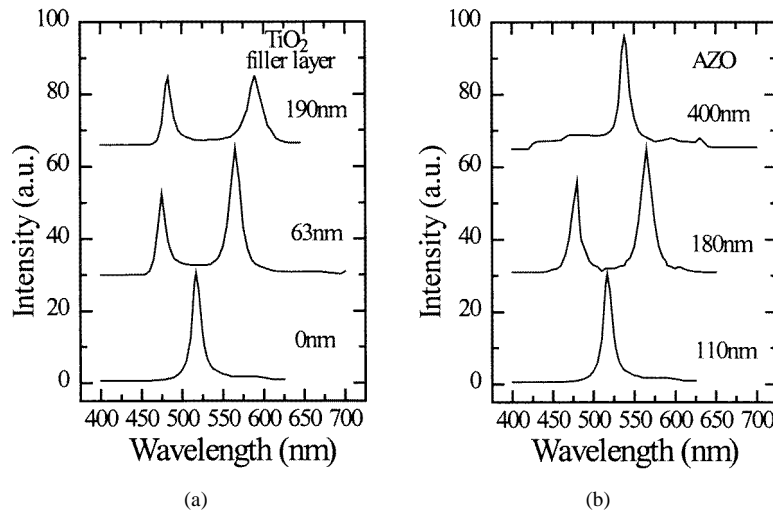

Figure 3. (a) EL spectra of LED cavities with different thicknesses of the filler layer. (b) EL spectra of LED cavities with different thicknesses of the AZO layer.

3.2.2. Spectrum variation with the thickness of the AZO anode.   With no filler layer, i.e., just by changing the thickness of the AZO anode, some devices emitting different colours were also obtained. The EL spectra of the LED cavity with no filler layer but different thicknesses of the AZO layer (110 nm, 180 nm, and 400 nm) are shown in figure 3(b). For an AZO layer 110 nm thick, the device emits one peak at 517 nm. For AZO layers 180 nm and 400 nm thick, both devices emit two peaks. The former emits at 570 nm and 480 nm, while the latter emits at 538 nm and 630 nm; the peak at 630 nm is very weak.

3.2.3. Calculation of the cavity mode of the LED with microcavity structure.   As is known, the emission from a Fabry–Perot cavity is determined by the resonance modes of the cavity, and the spectral position of the cavity modes is determined by the optical thickness of the cavity:

$$L = k(\lambda_k/2) \tag{1}$$

where $k = 1, 2, 3 \ldots$ is the mode index, L is the optical thickness of the cavity, and λ_k is the mode wavelength of the cavity. In this case, the optical thickness of the cavity can be calculated from

$$L = \frac{\lambda}{2}\left(\frac{n_{eff}}{\Delta n}\right) + \left|\frac{\Phi_m}{4\pi}\lambda\right| + \sum_i n_i d_i + n_{\text{TiO}_2} d_{\text{TiO}_2} + n_{\text{AZO}} d_{\text{AZO}}. \tag{2}$$

The first term is the effective penetration depth in the QWS, λ is the vacuum wavelength, n_{eff} is the effective refractive index of the QWS, and Δn is the difference between the indexes of the materials of the QWS.

The second term is the optical thickness contributed by the phase shift at the interface of the metal layer and the organic layer, and Φ_m is the phase shift at the interface, depending on the refractive indexes of the metal and the organic layer at the interface:

$$\Phi_m = \arctan\left(\frac{2n_m k_m}{n_s^2 - n_m^2 - k_m^2}\right). \tag{3}$$

Here n_s is the refractive index of the organic material in contact with the metal, and n_m, k_m are the real and imaginary parts of the refractive index of the metal.

The last three terms of equation (2) are the optical thicknesses of the organic layers, the TiO_2 filler layer, and the AZO layer in the cavity, respectively. n_i, n_{TiO_2}, and n_{AZO} are the refractive indexes of the organic materials, the TiO_2 filler, and the transparent AZO electrode respectively, and d_i, d_{TiO_2}, and d_{AZO} are their thicknesses.

When the first three terms were kept unchanged, the total optical thickness of the cavity could be changed by changing the thickness of the AZO layer or the TiO_2 layer. Here $n_{AZO} = 2.0$ [25], $n_{TiO_2} = 2.2$, $n_{eff} = 1.79$, $\Delta n = 0.74$, the indexes of the organic materials are both 1.65, and the real and imaginary parts of the refractive indexes of the metal aluminium are 0.956 and 6.69. The thicknesses of the organic layers are 40 nm; the vacuum wavelength (symbol λ) of the QWS was set as 550 nm in the process of deposition of the TiO_2 and the SiO_2.

In the case in which the cavities had a fixed thickness of AZO of 110 nm but different thicknesses of the filler layer, 0 nm, 63 nm, and 190 nm, the optical thicknesses L were 1030 nm, 1167 nm, and 1448 nm, as calculated from equation (2). The calculated theoretical mode position of the cavity with no filler layer, within the emissive spectral range of Alq3, is 515 nm, with a mode index of 4, which fits well with the experimental value of 517 nm. For the cavity with a filler layer 63 nm thick, the theoretical mode positions are 584 nm (index 4) and 467 nm (index 5), corresponding to the observed wavelengths 565 nm and 475 nm. For the thickness of the TiO_2 filler set at 190 nm, the theoretical positions are 597 nm for index 5 and 483 nm for index 6, also fitting well to the experimental positions of 593 nm and 485 nm.

For the case of cavities with no filler layer but different thickness of the AZO layer of 110 nm, 180 nm, and 400 nm, the total optical thicknesses of the cavities, as calculated from equation (2), are 1030 nm, 1170 nm, and 1610 nm, respectively. For an AZO layer thickness of 110 nm, the position of the theoretical mode (index 4) within the emission spectral range of Alq3 is 515 nm, fitting well with the experimental value of 517 nm. For 180 nm thickness of the AZO layer, the calculated positions of mode index 4 and mode index 5 are 585 nm and 486 nm, compared with the observed values of 570 nm and 480 nm. The theoretical positions of mode index 5 and mode index 6 are 644 nm and 537 nm for an AZO layer thickness of 400 nm, and the observed positions are 630 nm and 538 nm respectively. The peak at 630 nm is weak because this cavity mode is located at the edge of the emission band of Alq3.

3.3. Angular dependence of the emission spectra

Figure 4 shows the angle dependence of the emission of the LEDs with optical microcavity structure. The numbers in the figure denote the detection angle, relative to the normal to the diode surface. It can be seen that all of the emission peaks of the cavity shift to shorter wavelengths when the detection angle is increased, and that the intensity of a peak on the longer-wavelength side increases more when it has shifted to about 600 nm. For a 0° detection angle, the main emission peak is at 530 nm; at 30°, it shifts to 520 nm and
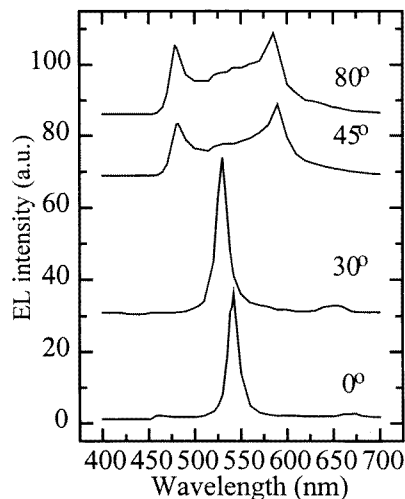
Figure 4. EL spectra of a cavity-based organic LED detected in different directions.

a weak peak appears at 650 nm. When detecting at an angle larger than 45°, the major emission peak shifts to a wavelength shorter than 480 nm, and the long-wavelength peak shifts to about 570 nm and becomes more intense.

The enhancement of the emissive intensity in allowed cavity modes and the spectral narrowing as well as the angular dependence of the emission wavelengths and intensity are assumed to be due to the redistribution of the photon density of states when the microcavity structure is introduced.

This angular dependence of the emission wavelength is unfavourable for the display applications of the organic microcavity-based LED. However, it is possible to reduce it. Becker [11] achieved a considerable reduction of the angular dependence of the resonance wavelength in the microcavity structure by choosing the appropriate metallic mirror.

4. Conclusion

In summary, we have made a new kind of microcavity-based organic LED with aluminium-doped zinc oxide layers of different thicknesses as the anode. We demonstrated effects of microcavities on the spontaneous emission of the LEDs, such as spectral narrowing, intensity enhancement, and angle dependence of the emission wavelength. We also showed that the thickness of the AZO layer and the filler TiO_2 layer could be used for adjusting the cavity modes to produce different emission colours. Using the equations given for the total optical thicknesses of the cavities, the observed wavelength could be explained as emission from cavity modes.

Acknowledgments

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