Improved Performance of Organic Light-Emitting Diodes with MgF_2 as the Anode Buffer Layer *

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Organic light-emitting diodes (OLEDs) based on N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) and tris (8-hydroxyquinoline) aluminium (Alq_3) are improved by using a thin MgF_2 buffer layer sandwiched between the indium tin oxide (ITO) anode and hole transporting layer (HTL) of NPB. The current-voltage curves of the OLEDs with MgF_2 buffers shift to lower voltages, which can be explained by the tunnelling effect. Under 10 V bias, the current density and brightness for the optimized OLED with a 1.0-nm MgF_2 are 196 A/m^2 and 517 cd/m^2, respectively, while for the OLED without anode buffer layer are only 109 A/m^2 and 156 cd/m^2. The atomic force microscopy shows that the rms roughness of NPB on ITO/MgF_2 is only 1/3 of NPB on bare ITO. The improved morphology of the HTL would lead to more robust OLEDs. The OLED with a 1.0-nm MgF_2 layer has a long lifetime of more than five times of the MgF_2-free reference device due to the combined electrical and morphological effects of the MgF_2 layer.

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Since Tang and VanSlyke first demonstrated highly efficient electroluminescence from organic light-emitting diodes (OLEDs),[1] great effort has been taken to improve their performance. Insertion of a buffer layer between the ITO anode and hole transporting layer (HTL) of NPB is one of the widely adopted ways to improve the stability and/or efficiency of OLEDs. Many organic materials such as copper phthalocyanine (CuPc),[2] starburst triphenylamines[3] and organic siloxanes[4] have been used as buffer layers in OLEDs. By using CuPc as the buffer layer, better performance of OLEDs could be achieved mainly due to the two factors: (a) the improved balances in electron and hole injection and (b) the improved wetting property of organic materials on ITO.[5,6] Recently, there are many reports on inorganic anode buffer layers such as CuO_x,[7] LiF,[8] Al_2O_3,[9] SiO_2,[10] Si_3N_4,[11] Ta_2O_5,[12] and MgF_2.[13] However, most of the reports focused the electrical properties of the inorganic buffer layer and the effect of a thin inorganic buffer layer on the morphology of the HTL remains unstudied.

In this work, we test the OLEDs with a thin MgF_2 buffer layer between the anode and the HTL. We also study the effect of a MgF_2 layer on the morphology of the HTL by atomic force microscopy (AFM). It is found that the combined electrical and structural characteristics of the MgF_2 layer would lead to more robust OLEDs.

OLEDs with the device structure of ITO/MgF_2 (d nm)/NPB(40 nm)/Alq_3 (60 nm)/Mg:Ag10:1 (50 nm)/Ag (50 nm) were prepared by conventional thermal deposition in vacuum of around 10^{-3} Pa. Prior to the thermal deposition, ITO glass substrates with rms roughness $R_{\rm rms}$ smaller than 0.5 nm were cleaned by ultrasonication in organic solvent and deionized water successively, and then were dried for 2 h before use. We varied the thickness of the MgF_2 layer from 0.5 nm to 3.5 nm. The device without MgF_2 was also fabricated for reference. The emitting areas were defined by a mask with $5\times 7\,\mathrm{mm}^2$ patterns. The luminance-current-voltage characteristics and lifetime results were measured using a Keithley 4200 semiconductor characterization system. All the measurements were carried out in air without encapsulation of the devices. We also prepared ITO/NPB (40 nm) and ITO/MgF_2 (d nm)/NPB (40 nm) samples for the morphology studies using our Seiko instrument SPA 400 AFM system.

The current–voltage (I–V) and luminance-current (L–I) characteristics of the OLEDs are illustrated in Fig. 1. As can be seen from Fig. 1(a), the device with a submonolayer of MgF_2 (0.5 nm) shows the steepest I–V curve among the five devices due to improved hole injection. The devices with 1.0-nm and 2.0-nm MgF_2 buffer layers also show lower driving voltages than the reference. However, further increase of the MgF_2 thickness to 3.5 nm shifts the I–V curve to higher voltages. This result is somewhat different from the previous work of Chen *et al.*[13] They found

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that a 1.0-nm MgF_2 buffer layer between the ITO anode and HTL would decrease the hole injection and increase the driving voltages. This discrepancy can be explained by the tunnelling model reported by Zhao *et al.*,[14] who found that the effects of LiF inserted at the ITO/NPB interface on the hole injection are dependent strongly on the initial barrier height (IBH) existing at the interface. Only for a large IBH (1.2 eV, for the devices using H_2 plasma treated ITO, H-OLEDs), will the introduction of a LiF buffer show beneficial effect for hole injection. For a small IBH (0.5 eV, for devices using O_2 plasma treated ITO, O-OLEDs), the presence of the LiF buffer will block the hole injection. In the work of Chen *et al.*,[13] the authors used an oxygen plasma treated ITO substrate, which would certainly reduce the IBH and make their device to perform in O-OLED manners.

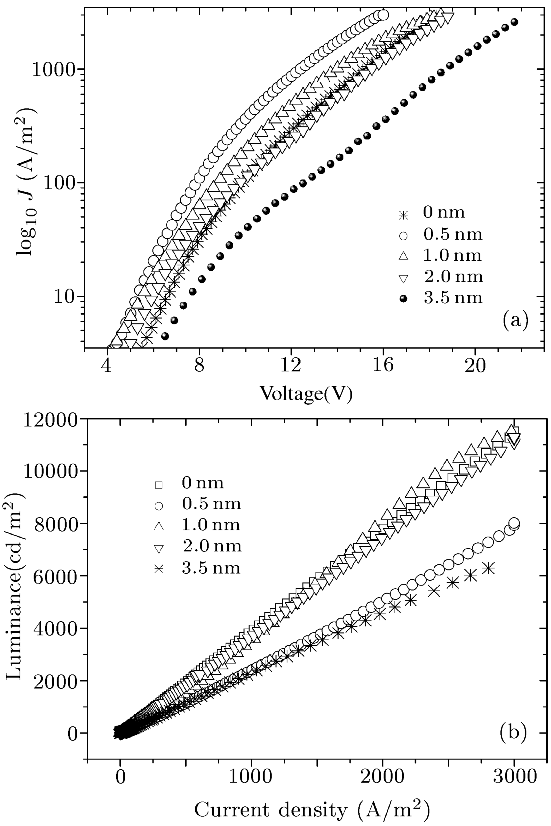

Fig. 1. (a) Current density J in logarithm versus voltage V for the devices with different thicknesses of the MgF_2 buffer layer. (b) Luminance-current characteristics for the OLEDs with different thicknesses of the MgF_2 buffer layer.

It is clear from Fig. 1(b) that the device with a 0.5-nm MgF_2 buffer layer shows the efficiency lower than the reference device on bare ITO. With the increase of the MgF_2 thickness, the efficiency is gradually recovered. The devices with 1.0-nm and 2.0-nm MgF_2 layers show almost the same efficiency as the reference though hole injection is improved. It is evident that the MgF_2 buffer between the ITO anode and HTL will alter the internal electric field distribution and lead to a change in both the hole and electron injections. However, with further increase of the MgF_2 thickness up to 3.5 nm, the device efficiency decreases again.

The lifetime curves of the OLEDs are shown in Fig. 2. It is clear that the lifetimes of devices with MgF_2 buffer layers are all longer than the MgF_2-free reference device at the initial luminance of 1000 cd/m^2. It is generally believed that the charge balance factor plays an important role in the long-term stability of OLEDs. Aziz *et al.*[15] reported that the dominant contribution to OLED degradation comes from instability of Alq_3 cations which are generated when excessive holes are injected into Alq_3. However, since all of the OLEDs with MgF_2 show similar or lower efficiencies than the reference, other factors may also contribute to this lifetime enhancement.

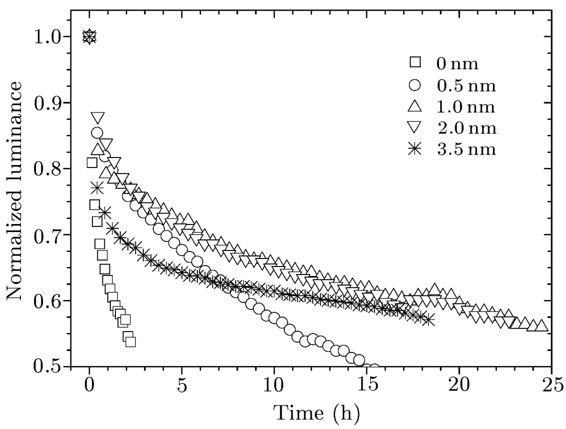

Fig. 2. Lifetime curves of the devices with different thicknesses of the MgF_2 buffer layer.

In order to understand the role of MgF_2 better, we also study the effect of MgF_2 on the morphology of the NPB layer. Figure 3(a) shows that the ITO substrate we used is very smooth. R_{rms} is as low as 0.408 nm and the height from the maximum peak to the valley is about 2.309 nm. However, 40-nm NPB on ITO shows rather poor surface morphology. R_{rms} is 1.568 nm and the height from the maximum peak to the valley is 10.89 nm. Forsythe *et al.*[5] reported that NPB has sufficient energy to move on ITO surface and can form islands during deposition, which ultimately coalesces to form a continuous film. This mechanism is applicable to our observations. For the evaporated MgF_2 films, MgF_2 dots scatter randomly on the ITO substrate when the average MgF_2 thickness is low, and the full coverage of ITO surface is observed at an average MgF_2 thickness of 2.0 nm with R_{rms} = 0.549 nm, as shown in Fig. 3(c). The MgF_2 film is very smooth because MgF_2 has a lower mobility on ITO than NPB at the same temperature and the growth of large island is not favoured by statistic rules.

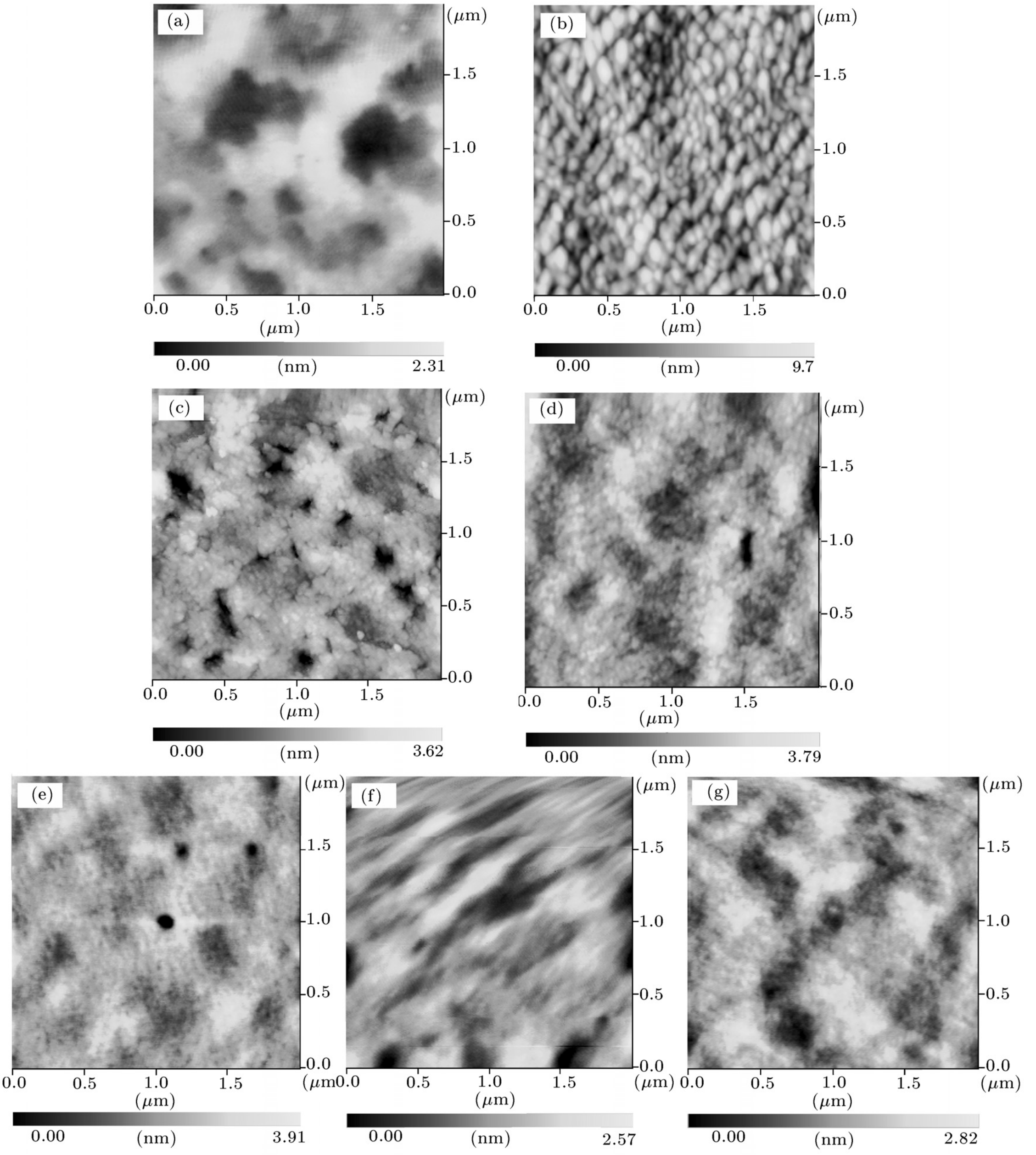

Fig. 3. AFM images observed from various films with structures: (a) bare ITO, (b) ITO/NPB (40 nm), (c) ITO/MgF_2 (2.0 nm), (d) ITO/MgF_2 (0.5 nm)/NPB (40 nm), (e) ITO/MgF_2 (1.0 nm)/NPB (40 nm), (f) ITO/MgF_2 (2.0 nm)/NPB (40 nm), (g) ITO/MgF_2 (3.5 nm)/NPB (40 nm).

The NPB film on MgF_2-modified ITO is shown in Figs. 3(d)–3(g). All the films are smooth and uniform with $R_{\rm rms}$ = 0.591, 0.516, 0.401, 0.475 nm for MgF_2 buffer layer thicknesses of 0.5–3.5 nm. These $R_{\rm rms}$ values are equivalent to those of bare ITO and ITO/MgF_2 surfaces, indicating that insertion of MgF_2 is favoured for NPB growth. Forsythe *et al.*[5] found that NPB growth mode can be altered from an island-like mode on bare ITO to a layer-by-layer mode on ITO/CuPc due to improved wetting. For our MgF_2 buffer, we observe that the movement of NPB on ITO surface is hindered by the presence of the MgF_2 layer and the morphology of NPB is therefore improved. As is well known, the ITO anode and the HTL interface is the weakest link in the OLED structure. The morphological change of the HTL during device operation, caused by Joule heating, would reduce the lifetime or even lead to sudden failure.[16−18] This improved ITO/NPB contact by the insertion of a MgF_2 buffer is essential for improved device lifetime.

In summary, we have successfully improved the stability of OLEDs by insertion of a thin inorganic buffer layer of MgF_2. AFM study shows that the NPB film grows better on ITO/MgF_2 than on bare ITO as the wetting property of NPB on ITO is improved by the presence of the MgF_2 buffer. The improved morphology of the HTL would lead to more robust OLEDs. The optimized OLED with a 1.0-nm MgF_2 layer shows a long lifetime of more than five times of the MgF_2 buffer-free reference device due to the combined electrical and morphological effects of the MgF_2 layer.

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