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Enhanced hole injection in organic light-emitting devices by using Fe_3O_4 as an anodic buffer layer

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Hole injection improvement in organic light-emitting devices with Fe_3O_4 as a buffer layer on indium tin oxide (ITO) has been demonstrated. The luminance and the current density are significantly enhanced by using the Fe_3O_4/ITO anode, as well as the turn-on voltage is reduced by 1.5 V compared to the devices without the buffer. Results of atom force microscopy, x ray, and UV photoelectron spectroscopy studies reveal that the enhanced hole injection is attributed to the modification of the ITO surface and the reduced hole-injection barrier by the insertion of the Fe_3O_4 thin film between the ITO and hole-transporting layer. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3148657]

Organic light-emitting diodes (OLEDs) are attractive for their potential applications in flat-panel displays and solid-stated lighting.[1–3] Although significant progress has been achieved on the performance of OLEDs, further improvement is still needed for their commercial applications. It has been demonstrated that a buffer layer inserted between an electrode and an organic layer plays a crucial role,[4–7] which have shown their effects in reducing the holes injection barriers or balancing the concentrations of holes and electrons, for example, in the case of the interface between an anode and a hole-transporting layer. Among the reported anodic buffer layers, transition metal oxides, such as V_2O_5,[8] MoO_x,[9] WO_3,[10] CuO_x,[11] and NiO,[12] have attracted much attention due to their capability to lower the hole-injection barrier and improve the interface morphology. Reduced driving voltage and enhanced luminance, efficiency, and stability have been achieved by introduction of the thin transition metal oxides on anode. All of the above results motivate our works in exploring other transition metal oxides as the buffer and understanding the underlying physics.

Fe_3O_4 is a well-known ferromagnetic compound, known and widely investigated due to its potential application in spintronics. However, as a transition metal oxide, it has not been applied in OLEDs. In this letter, we demonstrated that holes injection from the indium tin oxide (ITO) anode to a hole-transporting layer is improved by evaporating the ITO anode with a very thin Fe_3O_4 layer. We carried out systematic studies on the role of Fe_3O_4 as the buffer on the ITO by *in situ* UV photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS) measurements, and atomic force microscopy (AFM). The studies on the ITO/Fe_3O_4/NPB interface show the reduced hole-injection barrier and better surface smoothness. As a result, the turn-on voltage is decreased, and the brightness and the current density of the OLEDs are improved.

The device structure in this study was as follows: (ITO)/Fe_3O_4 (x nm)/N,N'-diphenyl-N,N'-bis(1,1′-biphenyl)-4,4′-diamine(NPB) (50 nm)/tris-(8-hydroxyl quinoline)aluminum (Alq_3) (50 nm)/LiF (1 nm)/Al (100 nm). NPB was the hole-transporting layer and Alq_3 was used as the emitting layer. The thickness of the ultrathin film of Fe_3O_4 as the anode buffer varied from 0 to 2.5 nm. All layers were prepared by thermal evaporation in a high vacuum system with the pressure of less than 5×10^{-4} Pa. The electroluminescence spectra of the devices were measured by a PR655 spectroscan spectrometer, and the current density (J)-voltage (V)-luminance (L) characteristics were recorded simultaneously by combining the spectrometer with Keithley model 2400 programmable voltage-current source. The UPS data were measured with a Thermo ESCALAB 250, and during measurement the samples were biased at −4.0 V to observe the low energy secondary cutoff. The XPS measurements were performed with Mg *Ka* x-ray source (1253.6 eV, Specs XR50). AFM topography was measured using the tapping mode of a Digital Instruments Nanoscope IIIA scanning probe microscope to investigate the surface morphology of the ITO anode.

The atomic compositions of the deposited Fe_3O_4 thin films are analyzed by XPS, to which the spectra of Fe_3O_4 and Fe_2O_3 powders are referred. Fe_3O_4 powder was used for the evaporation to deposit the Fe_3O_4 film. Their Fe 2p core-level spectra are shown in Fig. 1. The spectra of Fe_3O_4 thin

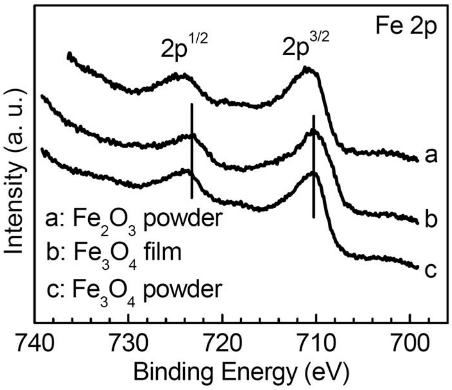

FIG. 1. XPS Fe 2p core-level spectrum of the Fe_3O_4 film with those from Fe_3O_4 and Fe_2O_3 powders as reference.

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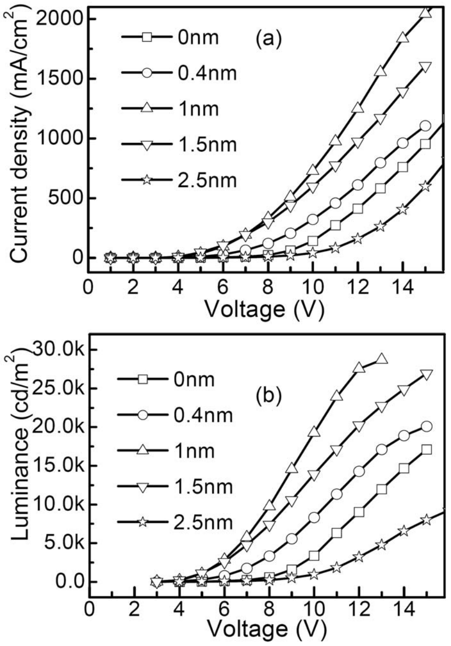

FIG. 2. Emission performance. (a) Current density-voltage and (b) luminance-voltage characteristics of devices with various thicknesses of Fe_3O_4 anodic buffer layer.

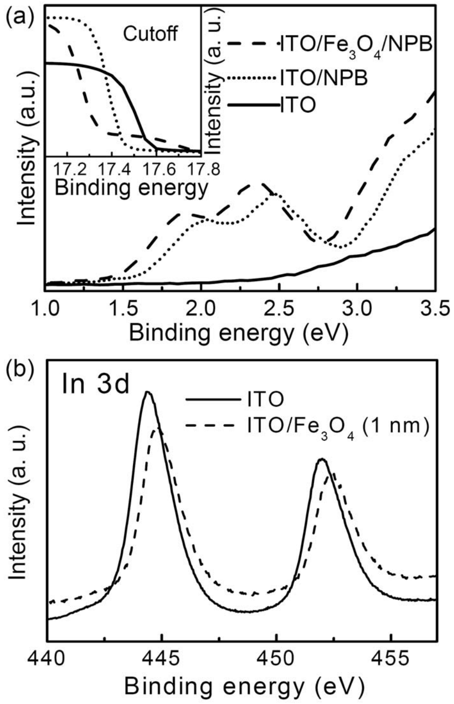

FIG. 3. Interfacial characteristics. (a) The measured UPS spectra of the HOMO region and the cutoff region (inset) of the ITO/Fe_3O_4 (1 nm)/NPB (15 nm) (dash), ITO/NPB (1 nm) (dot), and bare ITO (solid). (b) XPS spectra of ITO (solid) and ITO/NPB (1 nm) (dash) films.

film (curve b) coincides with that of the powder (curve c) very well, exhibiting typical Fe 2*p* peaks of Fe_3O_4 at 723.6 and 710.4 eV, while the typical Fe 2*p* peaks of Fe_2O_3 are at 724.1 and 710.7 eV (curve a).[13] Therefore, the thin film deposited by thermal evaporation under high vacuum from Fe_3O_4 powder is confirmed to stoichiometrically consist of Fe_3O_4.

Figure 2 shows the *J-L-V* characteristics of the devices with various thickness of Fe_3O_4 film. The *J-V* performance of the devices [Fig. 2(a)] is strongly dependent on the presence and the thickness of the Fe_3O_4 buffer layer. The current density markedly increases when increasing the Fe_3O_4 thickness, and reaches the maximum current density at 1 nm. With further increment in Fe_3O_4 layer thickness, current density is gradually decreased. The *L-V* performance [Fig. 2(b)] shows a similar behavior because luminance is determined by the current density. The turn-on voltage is reduced to 2.5 V of devices with 1 nm Fe_3O_4 from 4.0 V of devices without the buffer layer. The devices with a 1 nm Fe_3O_4 buffer layer also present much higher current density and luminance at the same driving voltage, and the luminance reaches 28710 cd/m^2 at 13 V, in contrast to that of only 11960 cd/m^2 for devices without Fe_3O_4. Among the reported improved performance of Alq_3 based OLEDs by using the different materials as the anodic buffer, MoO_x is one of the best candidates. The turn-on voltage of 2.6 V and 2.7 V have been observed from device structures similar to ours.[14,15] Compared to these reported results, the OLEDs with Fe_3O_4 as the anodic buffer shows lower turn-on voltage (2.5 V) and comparable luminance, showing that Fe_3O_4 is a highly competitive material for the anodic buffer of OLEDs.

The reduction in operation voltage can be explained by a lowered barrier for holes injection. UPS and XPS measurements were performed to determine the interfacial energy level. Figure 3(a) shows the evolution of the UPS spectra of ITO/Fe_3O_4 (1 nm)/NPB (15 nm), ITO/NPB (15 nm), and bare ITO, respectively. There is clear spectra change with the deposition of Fe_3O_4 and NPB on ITO. Both the highest occupied molecular orbital (HOMO) onset position and the cut off position of ITO/Fe_3O_4 (1 nm)/NPB (15 nm) shift towards the lower binding energy compared to that of ITO/NPB (15 nm). Combining the information of HOMO and vacuum level shifts as well as the band bending extracted from the UPS spectra, the hole-injection barrier at the ITO/NPB interface is reduced by 0.22 eV when the Fe_3O_4 buffer layer is inserted. The origin of the lower barrier of holes injection at the Fe_3O_4 modified interface could be well elucidated by the XPS core-level spectra. The indium 3*d* peak was measured from the bare ITO and ITO coated with 1 nm Fe_3O_4, as shown in Fig. 3(b). It can be seen that the indium 3*d* peaks shift towards higher binding energy after depositing Fe_3O_4 on ITO. The peak shift is a proof of an electron transfer from ITO to Fe_3O_4 at the interface.[15,16] The electron transfer across the interface results in a formation of a dipole layer at the interface, leading to an abrupt shift in the potential across the dipole.[17] The core-level shift shows a 0.3 eV up-shift in the vacuum level after depositing 1 nm Fe_3O_4, which results in a reduced energy barrier at the ITO/Fe_3O_4/NPB interface and accordingly reduced driving voltage.

In addition to the energetics, the morphology of the interface can play a role in determining the injection efficiency. The effect of the Fe_3O_4 on the interfacial morphology between the ITO anode and the deposited NPB films was investigated by AFM. The topographical images for ITO and surface obtained after depositing 1 nm of Fe_3O_4 film on ITO are shown in Figs. 4(a) and 4(b), respectively. These images reveal that the Fe_3O_4 capped ITO surface displays improved smoothness with a root-mean-square (rms) roughness of 0.72 nm compared to the bare ITO with a rms roughness of 1.04 nm. The Fe_3O_4 capped ITO demonstrates a better surface

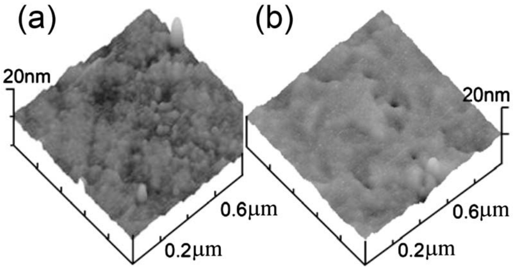

FIG. 4. AFM images of the (a) bare and (b) the 1 nm Fe_3O_4 modified ITO anodes.

roughness, which plays an important role in enhancing the OLEDs performance.

In summary, we demonstrated improved performance of OLEDs by using Fe_3O_4 as the anodic buffer. The brightness and the current density were highly enhanced with the optimum buffer layer thickness of 1 nm, and the turn-on voltage was lowered from 4 to 2.5 V. Dipole layer formation and resulted lower hole-injection barrier at the ITO/Fe_3O_4/NPB interface were observed by performing the XPS and UPS measurements, which resulted in the enhanced hole injection. In addition, better surface roughness of Fe_3O_4 coated ITO also contributed to the improved performance of the OLEDs. This result reveals that Fe_3O_4 is a practical valuable anodic buffer layer in reducing the driving voltage of the OLEDs.

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