Enhanced hole injections in organic light-emitting devices by depositing nickel oxide on indium tin oxide anode

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An ultrathin layer of nickel oxide (NiO) was deposited on the indium tin oxide (ITO) anode to enhance the hole injections in organic light-emitting diode (OLED) devices. A very low turn-on voltage (3 V) was actually observed for the device with NiO on ITO. The enhancement of hole injections by depositing NiO on the ITO anode was further verified by the hole-only devices. The excellent hole-injection ability of NiO was also demonstrated by devising a device with patterned NiO on the ITO anode. Our results suggest that the NiO/ITO anode is an excellent choice to enhance hole injections of OLED devices. © *2002 American Institute of Physics.*
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Since Tang and Van Slyke reported the first high-efficiency organic light-emitting diode (OLED) in 1987,[1] indium tin oxide (ITO) has been the most common OLED anode material due to its high transparency, high conductivity, and, particularly, high work function. Other metal oxides have also been studied as the OLED anode materials including aluminum-doped zinc oxide,[2] zirconium-doped indium oxide,[3] fluorine-doped tin oxide,[4] and zinc-doped indium oxide.[5] The treatment of the ITO surface usually has a strong influence on the performance of the OLED device, suggesting that the interface between the ITO and the organic layer is quite important. Several approaches have been employed to pretreat the ITO surface including the wet treatment,[6] the low pressure plasma treatment,[7] the atmospheric plasma treatment,[8] the UV ozone treatment,[9] and the self-assembly monolayer coating treatment.[10] The most effective method until now is the atmospheric or low-pressure oxygen (O_2) plasma treatment. The O_2 plasma treatment increases the work function (by about 0.4 eV) of ITO as well as removes its surface contaminants, thus enhancing the hole injection.[11] Yet the work function of the O_2 plasma-treated ITO is not high enough, and the energy barrier exists for the hole injection from ITO to the organic layer. Another problem with the ITO anode is the diffusion of indium into the organic layer during device operations, which was found to be correlated with the decay of device performance.[12]

Nickel oxide (NiO) is a well-known *p*-type transparent conducting oxide,[13] which should exhibit a higher work function and is more favorable for hole injections into the organic than ITO. ITO/NiO film has been deposited on *p*-type gallium nitride (GaN) forming a highly transparent Ohmic contact.[14] J. Olivier *et al.* also reported that NiO has a higher work function (~5.0 eV) than ITO (~4.7 eV).[15] Yet no studies on the effects of NiO on the performance of the OLED has been reported. In this work, the performance of the OLED with NiO deposited on the ITO anode to enhance hole injections is studied and reported.

The ITO-coated glass (Merck-Taiwan Corp.) substrate was first cleaned by the ethanol-impregnated paper with mechanical rubbing and then cleansed sequentially with the detergent, methanol, and de-ionized water. After further O_2 plasma treatment of the ITO surface for 3 min, NiO was deposited on ITO by reactive magnetron sputtering with a Ni target (99.99% pure) using only O_2 gas at 10 mTorr. Triphenyl diamine (TPD), tris(8-hydroxyquinoline) aluminum (Alq_3), lithium fluoride (LiF), and aluminum (Al) layers were deposited consecutively in vacuum by thermal evaporation in a chamber with a base pressure of 10^{-6} Torr. The device structure is glass/ITO/NiO (<10 nm)/TPD (30 nm)/Alq_3 (50 nm)/LiF (1.5 nm)/Al (150 nm). Only an extremely thin layer of NiO was deposited considering that NiO is not as transparent as ITO. The deposition rates of the organic materials, LiF layer, and Al cathode were 1–2, 0.1–0.2, and 20 Å/s, respectively. The area of the active device was 8 mm^2. The $I-V$ characteristics of the devices were measured with a KEITHEY-2400 source meter and the luminance with a TOPCON BM-8 luminance meter. The device performance was measured in air. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Fison

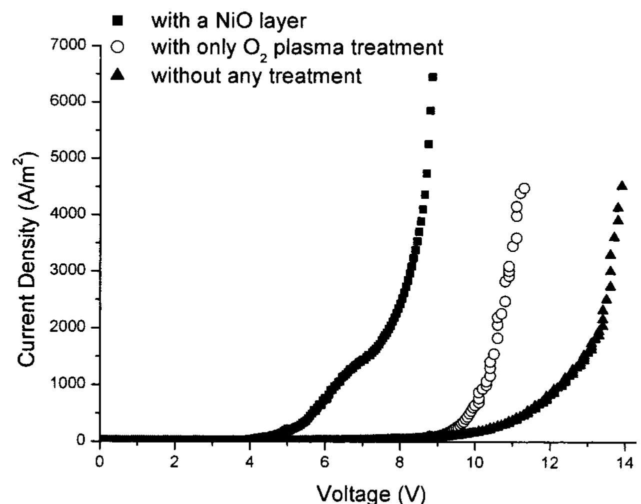

FIG. 1. $I-V$ characteristics of the OLED devices with various treatments of the ITO anode.

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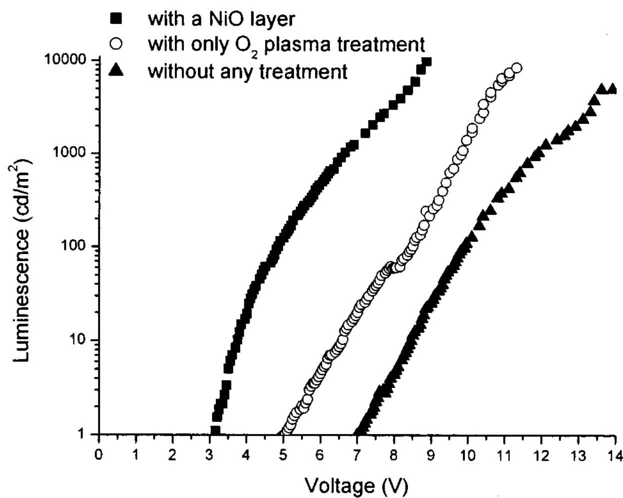

FIG. 2. $L-V$ characteristics of the OLED devices with various treatments of the ITO anode.

(VG) ESCA 21 system equipped with a monochromatic Al K_α source with photon energy of 1486.6 eV.

The XPS spectra of the as-deposited NiO film show a peak of Ni $2p_{3/2}$ with binding energy of 854.09 eV, consistent with the reported values of NiO.[16,17] $I-V$ characteristics of the OLED devices with various ITO treatments are shown in Fig. 1. Although the turn-on voltage of the device is effectively reduced by the O_2 plasma treatment of the ITO anode, it is most significantly reduced by the deposition of a NiO layer on the ITO surface. Figure 2 shows the luminescence intensity versus the applied voltage ($L-V$). The device with the deposition of NiO has the lowest voltage for the same emission intensity. The turn-on voltages at 1 cd/m^2 are 3, 5, and 7 V, respectively, for the devices with the NiO layer, with only the O_2 plasma treatment and without any treatment. The reduction of the turn-on voltage by the NiO layer might be attributed to the increase of the anode's work function, which reduces the energy barrier of hole injections into the organic layer.

The ITO/NiO device had a slightly lower efficiency in luminescence, i.e., 0.65 lm/W, than the ITO-only device, 0.7 lm/W. As pointed out by Parker,[18] the energy barriers for the electron and the hole injections are both important with the lower barrier determining the device current and the higher one determining the emission efficiency. The NiO layer lowered the hole injection barrier increasing the hole injection rate without affecting the electron injections, thus reducing the luminescence efficiency due to the lack of the corresponding increase of electrons. To compare the hole injection rates between the NiO/ITO and the ITO anodes, the hole-only devices (in which the currents are dominated by hole carriers) were prepared with the following structures: ITO/TPD (80 nm)/Al (150 nm), and ITO/NiO (<10 nm)/TPD (80 nm)/Al (150 nm).[18,19] The $I-V$ characteristics of the device are determined by holes only since the valence bands of both electrodes are close to the highest occupied molecular orbital of TPD. As clearly shown in Fig. 3, the hole injection is very difficult for the ITO anode without any surface treatment, becomes easier after the O_2 plasma treatment, and is most significantly enhanced by depositing a thin layer (<10 nm) of NiO.

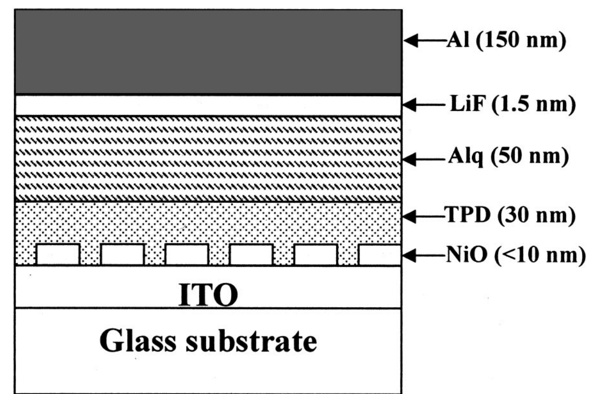

FIG. 4. The cross section of the OLED device with patterned NiO (multiple NiO lines) on the ITO surface.

An OLED device with patterned NiO on the ITO surface was further prepared to show the excellent hole-injection behavior of the NiO/ITO anode. Illustrated in Fig. 4 is the cross section of the device with patterned NiO. Multiple NiO lines were deposited on ITO using a shadow mask consisting of 0.25 mm metal lines with 0.5 mm spacing. Figure 5 shows the luminance of the device at a low forward bias (~6 V). Although both the ITO and NiO surfaces are in contact with

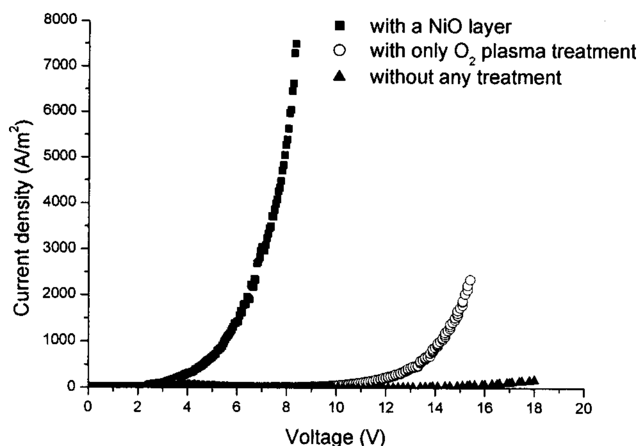

FIG. 3. $I-V$ characteristics of the hole-only devices (in which the currents are dominated by holes) with various treatments of the ITO anode.

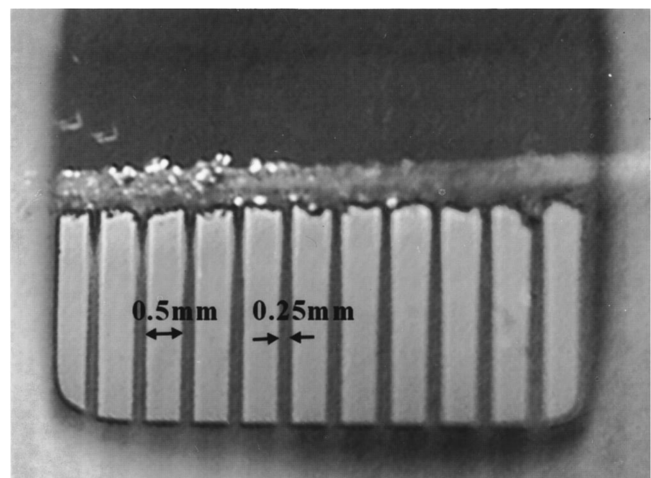

FIG. 5. Photographs of the luminance of the device described in Fig. 4 at a low forward bias (~6 V).

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TPD, only the NiO covered areas generate luminescence, demonstrating better hole-injection abilities of NiO.

Recently, Hu *et al.* also observed the lowering of the hole-injection energy barrier by depositing a nanometer-thick CuO_x layer on the ITO surface. Similar to our results with ITO/NiO anode, the ITO/CuO_x anode is effective to improve the hole injection into the organic layers, leading to a lowered operation voltage of the OLED device.[20] But, the ITO/NiO layer has higher transmittance (~88%) in the visible light region than the ITO/CuO_x layer (~80%).

In conclusion, we report that NiO is an excellent material for enhancing the hole injections. The turn-on voltage can be lowered down to 3 V by the NiO layer. The enhancement of hole injection by NiO was verified by the hole-only devices and the device with patterned NiO on ITO. However, slightly lower electroluminescence efficiency was observed for the device with a NiO layer. Higher efficiency is expected by simultaneously enhancing the electron injections.

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