

Surface modification of indium tin oxide by plasma treatment: An effective method to improve the efficiency, brightness, and reliability of organic light emitting devices

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We demonstrate the improvement of an indium tin oxide anode contact to an organic light emitting device via oxygen plasma treatment. Enhanced hole-injection efficiency improves dramatically the performance of single-layer doped-polymer devices: the drive voltage drops from >20 to <10 V, the external electroluminescence quantum efficiency (backside emission only) increases by a factor of 4 (from 0.28% to 1%), a much higher drive current can be applied to achieve a much higher brightness (maximum brightness $\sim 10,000$ cd/m² at 1000 mA/cm²), and the forward-to-reverse bias rectification ratio increases by orders of magnitude (from 10^2 to 10^6 – 10^7). The lifetime of the device is also enhanced by two orders of magnitude. © 1997 American Institute of Physics. [S0003-6951(97)00511-1]

Because of its transparency, high conductivity, and efficiency as a hole injector into organic materials, indium tin oxide (ITO) has been widely used as the anode contact for organic light emitting devices (OLEDs). These devices usually consist of a sandwich structure with the organic thin film deposited onto the ITO-coated glass substrate and covered by patterned top metal cathode contacts.^{1,2} Since the organic thin film is in direct contact with the ITO, the surface properties of the ITO are expected to directly affect the characteristics of the device. Abnormal device behaviors such as shorting, unstable I – V characteristics, and damage on the surface of the top cathode contact after continuous operation of the device have been observed in OLEDs built on bare cleaned ITO surfaces.^{3–5} Furthermore, as-grown ITO contacts have been found to be less efficient for hole injection than low work function metal cathodes for electron injection, resulting in hole-limited devices.^{6,7} The mitigation of these problems has so far involved changing the properties of the organic materials or introducing an intermediate stabilization layer with proper carrier injection/transport characteristics between the ITO and the active luminescent layers.^{7,8} The alternative of modifying the ITO itself, however, has not been extensively investigated. In this paper, we report that an oxygen plasma treatment is an effective way to modify the surface of ITO. We perform a comprehensive investigation of the correlation between ITO surface properties such as morphology and chemical composition, and the device characteristics. We demonstrate that ITO surface modification leads to good performance even in single layer polymer based OLEDs, where the ITO surface properties are more critical than in multilayer devices.

The ITO coated glass substrates used in this study were purchased from Donnelly Applied Films Co. The 1.1-mm-thick polished soda lime float glass was coated with a 200 Å SiO₂ barrier layer and a 1400 Å ITO film. ITO was sputtered from an In₂O₃–SnO₂ (90 wt %–10 wt %) oxide target in an Ar/O₂ ambient at an elevated temperature using a planar dc magnetron sputtering system. The ITO was annealed *in situ* during the deposition and no postdeposition annealing was performed. The sheet resistance and transmittance of the as-received ITO was 11 Ω/□ and 90% consistent with the ven-

dor's specification of 10–15 Ω/□ and 85%. Prior to their use, the ITO-coated glass substrates were cleaned by swabbing and sonification with detergent/de-ionized (DI) water, rinsing in DI water, degreasing by flushing the ITO surface with convection flow in warm TCE, and finally rinsing in acetone and methanol. The substrates were then used as cleaned or treated by either uv-ozone^{1,8} or a plasma before deposition of the organic layer. The uv-ozone treatment was carried out in a uv-ozone cleaning system with uv emission from low pressure quartz mercury vapor lamps and a 254 nm uv intensity of ~ 10 mW/cm² at a distance of one inch from the lamps. The uv radiation is absorbed by atmospheric oxygen, changing it to ozone and atomic oxygen. For the plasma treatment, the ITO samples were exposed to plasmas of different gases in a parallel-plate type plasma reactor configured in the reactive ion etching (RIE) mode. In this system, a rf power of 25 W corresponds to a power density of ~ 50 mW/cm².

The OLEDs tested in this study are single-layer doped polymer devices, in which the hole-transport matrix polymer poly(N-vinylcarbazole) (PVK) contains dispersed electron transport molecules, such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) or tris(8-hydroxy quinolate) aluminum (Alq), and fluorescent dyes as efficient emission centers.^{9–12} In this study, we used PVK:PBD:coumarin 6 (C6) (100:40:0.3 by weight) for green devices and PVK:Alq:nile red (100:40:0.2 by weight) for orange-red devices, both deposited by spin-coating onto the ITO-coated glass substrates. The organic film thickness was 1050 ± 25 Å. At 25 mA/cm², the variation of device drive voltage due to variations in blend film thickness was within ± 0.25 V. This difference is much smaller than the effect of different ITO treatments as will be shown below. After spin-coating, top metal cathode contacts consisting of 1200 Å Mg:Ag alloy and 800 Å Ag were deposited through a shadow mask with an array of 2 mm×2 mm holes. All spin-coating, device processing, including direct loading into the evaporator for metallization, and device characterization were carried out under a dry nitrogen atmosphere in a glove box.

The external EL quantum efficiency of OLEDs was mea-

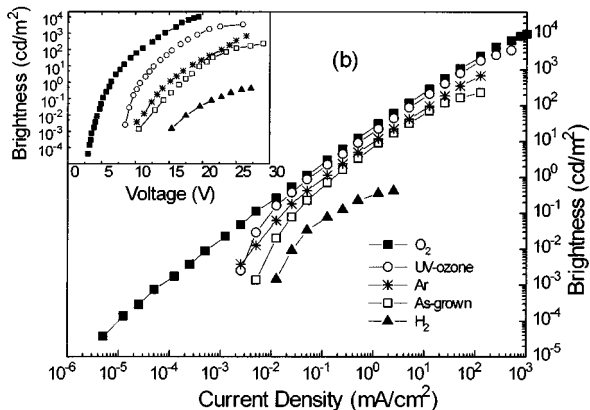
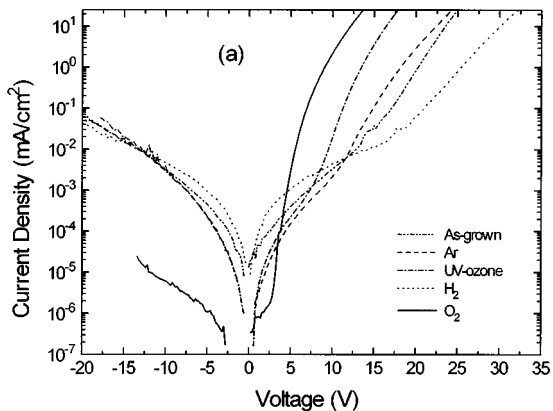


FIG. 1. (a) I - V characteristics, (b) brightness vs current and brightness vs voltage (the inset) of OLEDs built on ITO treated in different ways. The device structure is Ag (800 Å)/Mg:Ag (1200 Å)/PVK:PBD:C6 (100:40:0.3 by wt., 1050 Å)/ITO. ITO treatment conditions: uv ozone: 3 min; Ar plasma 150 mTorr, 25 sccm, 25 W, 3 min; H₂ plasma: 60 mTorr, 25 sccm, 20 W, 30 s; O₂ plasma: 150 mTorr, 25 sccm, 25 W, 4 min.

sured by detecting the light emission out of the bottom of the glass substrate with no corrections for absorption, waveguiding, or other effects that act to decrease the light emitted out of the backside of the glass substrate. The luminance (cd/m²) of the OLEDs was converted from the radiant power by assuming an angular distribution of Lambertian emission.¹³ For the continuous operation reliability test, a constant current source was used to drive the OLEDs in the dry nitrogen glove box, with the drive voltage and the light output monitored.

Figure 1(a) shows I - V characteristics for devices built on ITO treated in different ways. Figure 1(b) and its inset show corresponding brightness-current (L - I) and brightness-voltage (L - V) characteristics. Except for the hydrogen plasma treatment, each treatment is optimized for OLED performance by varying exposure time and power. In Fig. 1(a), all forward I - V curves have two regimes, a low current regime with a weaker voltage dependence and a high current regime with a steeper current rise with voltage. In all cases, the forward bias low current regime, henceforth referred to as "leakage," is always symmetrical to its reverse bias counterpart. Light emission is observed only in the high current regime, which we will refer to as the "bipolar" regime. The various ITO treatments considerably affect the turn-on voltage of the bipolar current, the leakage current, and the quan-

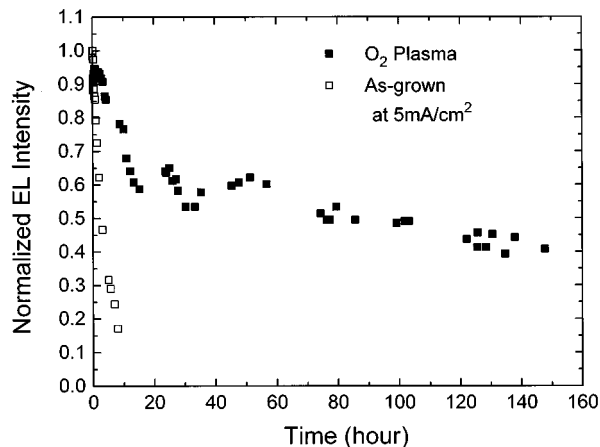


FIG. 2. Normalized EL intensity vs continuous operation time with a 5 mA/cm² dc current. The device structure is Ag (800 Å)/Mg:Ag (1200 Å)/PVK:Alq:niile red (100:40:0.2 by wt., 1050 Å)/ITO.

tum efficiency of light emission. Devices made on cleaned as-grown ITO have a turn-on voltage of ~ 12 V and an external quantum efficiency at 2.5 mA/cm² of 0.28% photon/electron. The Ar plasma treatment (25 W, 3 min) reduces the turn-on to 11 V and increases the efficiency to 0.35%. The optimal uv ozone treatment (~ 3 min) improves these parameters to 8 V and 0.7%, respectively. Most important, the oxygen plasma treatment (25 W, 4 min) dramatically reduces the turn-on voltage to 3 V and brings the efficiency to 1%. The hydrogen plasma treatment (20 W, 30 s), on the other hand, increases the turn-on to 17 V and reduces the efficiency to 0.007%. This poor performance is reversible and optimal performance can be recovered with a subsequent 8-min oxygen plasma treatment. In devices made on the hydrogen plasma-treated ITO, local sparks appear across the contact surface at current densities as low as 2.5 mA/cm² and quickly lead to open-circuited devices. In devices made on as-grown and Ar plasma-treated ITO, sparks appear around 100 mA/cm². In contrast, devices made on oxygen plasma-treated ITO can sustain currents as high as 1000 mA/cm² to achieve a maximum brightness of $\sim 10,000$ cd/m² around 19 V before the sparks appear and a rapid device deterioration occurs. A further consequence of improved OLEDs built on oxygen plasma treated ITO is an enhancement in reliability. As shown in Fig. 2, the lifetime of an OLED made on oxygen plasma treated ITO is at least two orders of magnitude longer than that of an OLED built on cleaned as-grown ITO.

None of the ITO treatments described in Fig. 1 changed the bulk properties of the ITO (sheet resistance and transmittance). We therefore conclude that changes in device performance are related to ITO surface properties. Previous studies of the degradation of ITO under severe hydrogen or other reducing gas plasma conditions, i.e., long exposure time (minutes), high temperature (100–500 °C) and high power (hundreds of mW/cm²)^{14–17} have shown large reduction in transmittance, increase in sheet resistance, substantial changes in surface morphology due to the formation of In rich hillocks, and large nonuniformity of surface compositions due to segregation and coalescence of In rich clusters.¹⁷ The conditions of exposure of ITO to different plasmas in our work are considerably milder (room temperature, ~ 50

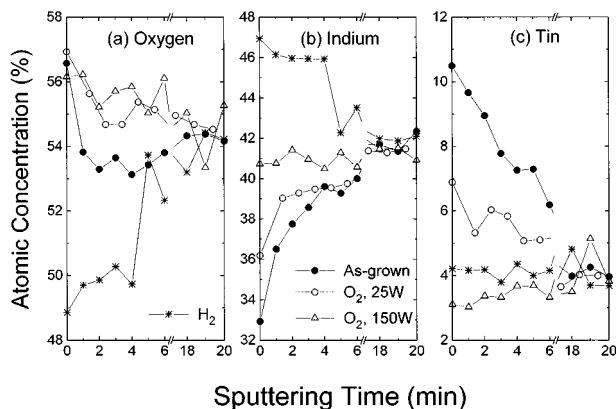


FIG. 3. (a) O, (b) In and (c) Sn atomic concentration profiles vs 1 keV Ar sputtering time for ITO treated in different ways. ITO treatment conditions: H₂ plasma: 150 mTorr, 25 sccm, 25 W, 3 min; O₂ plasma: 150 mTorr, 25 sccm, 25 W or 150 W, 4 min; clean as-grown ITO.

mW/cm², ~100 s, plasma potential of ~80–100 V). The rms surface roughness probed by atomic force microscopy (AFM) in 2 μ m by 2 μ m scans is 2.2 nm, 1.6 nm, and 1.7 nm for the as-grown, oxygen plasma-treated, and hydrogen plasma-treated ITO samples, respectively, indicating no significant impact of these treatments on surface roughness or morphology. However, the chemical profiles of the ITO layers near the surface measured by Auger electron spectroscopy depth profiling show considerable variation with different treatments (Fig. 3). The as-grown ITO is Sn-rich and In-deficient near the surface, as compared to the bulk. The Sn:In atomic ratio near the surface is ~1:3, while it is about 1:10 in the bulk. ITO films having good optical and transport properties tend to have Sn-rich surface layers due to the migration of Sn-rich phases to the surface.¹⁸ The 25 W, 4 min oxygen plasma treatment lowers the surface Sn:In ratio to 1:6 and increases the surface oxygen concentration, although less significantly. The hydrogen plasma also reduces the Sn surface atomic concentration, but substantially depletes the surface oxygen concentration. This is strong evidence for an electrochemical reduction-oxidation mechanism near the ITO surface in the reducing hydrogen plasma and the oxidizing oxygen plasma, respectively.

The lack of significant changes in surface morphology with different plasma treatments indicates that, within the conditions used here, morphology is not the determinant factor in the variations observed in device performance and reliability. However, the improvement of device performance with the oxygen plasma treatment suggests that the surface chemical composition might play a role in increasing the hole injection ability at the ITO/organic interface. ITO is generally considered as a heavily doped and degenerate *n*-type indium oxide with both Sn dopants and oxygen vacancies contributing to its conduction.¹⁸ The enhancement of hole injection may be due to an increase in the work function of the ITO as the surface Sn:In ratio is decreased and the oxygen concentration is increased. Indeed, our ultra-violet photoemission spectroscopy measurements on the oxygen plasma-treated ITO surfaces show an increase in the work function of 100–300 meV with regard to the cleaned as-grown ITO surfaces. The AES analysis also points out the

presence of carbon on the surface of the cleaned as-grown ITO, and its removal by the uv ozone or oxygen plasma treatment. The removal of the organic residue from the ITO surface could therefore also be partially responsible for the device improvement. The inert Ar plasma does not seem to chemically affect the ITO surface. The slight improvement in device made on Ar plasma-treated ITO could be due to a surface cleaning effect of Ar plasma or to residual oxygen in the RIE from venting to air for sample loading. Finally, the weakening of devices made on hydrogen plasma-treated ITO suggests that the uniformity of chemical composition across the ITO surface may also play a role in the reliability of OLEDs, in addition to changes in the average surface chemical composition.

In conclusion, we have shown that, without degrading the bulk properties of ITO, the chemical composition of ITO surface layers could be substantially modified by treatment in plasmas of different gases. As a result, the OLED device characteristics can be dramatically improved. The oxygen plasma is found to be the most effective in preparing the ITO surface for high performance OLEDs.

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