

# Characterization of treated indium–tin–oxide surfaces used in electroluminescent devices

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The influence of oxidative and reductive treatments of indium–tin–oxide (ITO) on the performance of electroluminescent devices is presented. The improvement in device performance is correlated with the surface chemical composition and work function. The work function is shown to be largely determined by the surface oxygen concentration. Oxygen-glow discharge or ultraviolet–ozone treatments increase the surface oxygen concentration and work function in a strongly correlated manner. High temperature, vacuum annealing reduces both the surface oxygen and work function. With oxidation the occupied, density of states (DOS) at the Fermi level is also greatly reduced. This process is reversible by vacuum annealing and it appears that the oxygen concentration, work function, and DOS can be cycled by repeated oxygen treatments and annealing. These observations are interpreted in terms of the well-known, bulk properties of ITO. © 1999 American Institute of Physics. [S0021-8979(99)07815-9]

## I. INTRODUCTION

Indium–tin–oxide (ITO) is routinely used as a transparent, hole-injecting electrode in organic electroluminescence (EL) devices. When used without some type of surface modification, the cells constructed with ITO usually exhibit poor reproducibility in device performance criteria, such as efficiency and lifetime. It has been known for some time that an oxidative surface treatment, such as oxygen glow discharge (O-GDT) or ultraviolet (UV)–ozone, could enhance the temporal stability of cells constructed from ITO and, at the same time, significantly lower the required drive voltage.<sup>1–3</sup> Alternatively, it is possible to improve the stability and drive voltage by inserting a thin buffer layer, such as copper–phthalocyanine (CuPc),<sup>4</sup> polyaniline (PANI),<sup>5,6</sup> poly(3,4-ethylene dioxathiophene) (PEDOT),<sup>6,7</sup> or carbon<sup>8</sup> between the ITO anode and the hole-transporting layer. The exact mechanism, whereby these treatments render such a beneficial effect, remains unknown. However, it has been suggested that the effect of oxidative treatments is to increase the work function of the anode and thus lower the barrier to hole injection.<sup>9</sup>

## II. EXPERIMENT

In this article we will present the results of two studies aimed at elucidating surface characteristics (such as chemical composition, densities of states, and work function), and correlating these properties with measured cell stability and drive voltages. In both sets of experiments, the ITO (Applied Films Inc.) was coated on glass to a thickness of about 30 nm and had a sheet resistance of about 100  $\Omega/\square$ . The routine cleaning procedure included sonication in a detergent, rinsing in de-ionized water and isopropyl alcohol, vapor degreasing in toluene, and final treatment by UV–ozone exposure or

O-GDT. In the first series of experiments, duplicate substrates were prepared. One set was used to produce devices while the other was analyzed by x-ray and ultraviolet photoelectron spectroscopy (XPS) and (UPS) for surface characterization. The ITO substrates were treated by either UV–ozone or O-GDT just prior to analysis or deposition of the organic layers. The devices had a multilayer structure of ITO/(CuPc)/NPB/Alq/MgAg, where the optional (CuPc) serves as a buffer layer, NPB is a hole-transport layer, and Alq is the emissive as well as electron transport layer. All organic layers were prepared by conventional vapor deposition with the substrates maintained at ambient temperature. The thicknesses were about 15 (0), 60, and 75 nm, for CuPc, NPB, and Alq, respectively. The top electrode was prepared by simultaneous deposition of Mg and Ag to give a 10% Ag alloy layer. The EL devices were completed with encapsulation in a dry argon box. Light–current–voltage characteristics were measured using a radiometer and a digital voltmeter.

The substrates for surface characterization were mounted into a VG, ESCALAB Mark II spectrometer for XPS and UPS analysis. The XPS spectra were recorded using monochromatic Al  $K_{\alpha}$  excitation (1486.6 eV), while the UPS used He I radiation (21.218 eV) from an unfiltered, windowless, gas discharge lamp. The UPS spectra were biased at  $-4$  V to observe the low energy secondary cutoff. The work function was taken as the excitation energy less the difference between the Fermi level and the low energy cutoff.<sup>10,11</sup> The second set of experiments was carried out in a custom built instrument that allowed for *in situ* glow discharge treatment, high temperature annealing, UPS and Auger analysis. This instrument used a similar source for UV excitation and a double-pass, cylindrical mirror analyzer for the UPS and Auger energy analysis.

Detailed characterization of the surface chemical composition of commercial ITO can be very challenging and not particularly enlightening. Significant surface and bulk contamination by carbon is common, as are smaller amounts of nitrogen and sulfur. All of these impurities exist in at least partially oxidized states, which confounds attempts to accurately determine the amount of oxygen bounded to indium and tin. Significant variations in composition are often found even within a given sample of material. While most of the surfaces we have investigated do show a very slight Sn enrichment at the surface, the phenomenon is, by no means, universal and is much less pronounced than reported by other workers.<sup>8</sup> For this reason, the XPS results will serve only as a qualitative guide when comparing results from different samples or, more particularly, changes within a given sample after various treatments.

### III. RESULTS AND DISCUSSION

In an organic EL device, the barrier to hole injection from a metallic electrode is normally taken as the energy difference between the Fermi level of the metal and the highest occupied molecular orbital of the organic. In the simplest model of heterojunction formation, this barrier to injection is simply the difference between the metal work function and the ionization potential of the organic.<sup>12,13</sup> This model is strictly correct only if “the interface charge density is exactly equal to a linear superposition of the respective surface charge densities.”<sup>14</sup> This is generally a very poor approximation for any heterojunction involving a metal and has been shown to be quantitatively incorrect for many interfaces involving EL materials.<sup>12,13</sup> Even so, the empirical fact remains that, in the case of electron injection, efficiencies scale reasonably well with the work function of the cathode.<sup>15</sup> Much less is known about the hole injection dependence on the anode work function. The anode is normally chosen to be the transparent electrode and most studies of hole injection have been limited to anodes made of ITO. Hence, the work function dependence of anode injection is not well established. However, from the limited data that does exist, the barrier to hole injection does appear to qualitatively track the anode work function.<sup>16</sup> Whereas work function is a surface property, there is some latitude in “engineering” its value even for a given bulk material. Our experience and that of others is that reducing treatments, such as hydrogen plasma, increases the required drive voltage whereas oxidative treatments, such as UV-ozone or O-GDT, decrease it.<sup>9</sup> This is consistent with the generally observed result that oxygen adsorption increases metallic work functions.<sup>17</sup>

#### A. Films prepared for devices

The forward bias, current–voltage ( $I$ – $V$ ) characteristics of the prepared EL devices are shown in Fig. 1. Curve A is for a device built on an ITO substrate that had undergone only the conventional, chemical cleaning described above. It exhibited a relatively high drive voltage and had a mean time to half-brightness (or half-life) of only several hours when operated at 20 mA/cm<sup>2</sup>. In comparison, the inclusion of CuPc or an oxidative treatment lowered the drive voltage significantly and increased the half-life to about 4000–5000

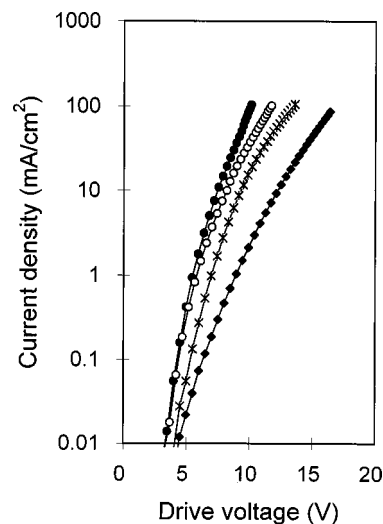


FIG. 1. Current–voltage characteristics of four EL devices with various surface treatments of the ITO: (◆) as-cleaned, (○) O-GDT, (●) UV-ozone, and (×) with a 15 nm CuPc layer between the ITO and NPB. Some of the curvature at high currents may be due to resistance changes at these high powers.

h. The work functions associated with the cell modifications shown in Fig. 1 were measured by UPS. Since the Fermi level is fixed, the change in work function is determined solely by changes in the position of the low energy secondary cutoff. This is shown in Fig. 2 for the identical treatments that produced the cell characteristics shown in Fig. 1. A movement of the secondary cutoff to higher (lower) kinetic energy represents an increase (decrease) in the work function equal to the observed shift. The spectra in Fig. 2 show that the O-GDT and UV-ozone treatments produce work function increases of  $\approx 0.25$  and  $\approx 0.65$  eV, respectively. The absolute values of the work functions are 4.36 and 4.23 eV for the two controls, 4.58 eV for the O-GDT, and 4.96 eV for the UV-ozone treated samples. The O-GDT results are in

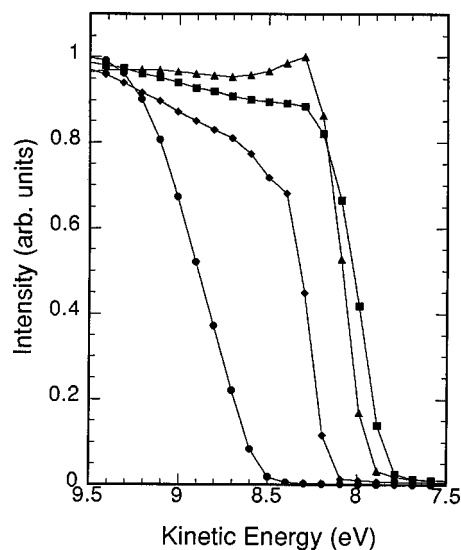


FIG. 2. The low energy, secondary cutoff of the ITO, UPS spectra with various treatments: (■) and (▲) as-cleaned, controls, (◆) O-GDT, and (●) UV-ozone treated.

general agreement with previously reported results.<sup>9</sup> In measuring different samples produced in the same treatment, a variation of approximately  $\pm 0.1$  eV was common. This represents a true spatial inhomogeneity in the surface potential as the instrumental reproducibility is more on the order of  $\pm 0.01$  eV. Much of the improvement in drive voltage may well be due to this increase in work function that is expected to lower the barrier to hole injection.

XPS is helpful in elucidating the changes in surface chemistry, which may be responsible for the increased work function. As mentioned above, the XPS spectra must be interpreted with some care because of the significant presence of impurities. This is particularly true with O-GDT treatment. Aluminum oxide contamination is quite common in this process when aluminum electrodes are used. Fortunately, this is not a problem with the UV-ozone and some meaningful, quantitative conclusions can be drawn in this case. In order to assess the stoichiometry of the surface, we consider the value of  $[O]/(1.5[In] + 2[Sn])$ , where  $[X]$  is the concentration of species  $X$  as determined from the XPS measurement. This would equal one for a perfectly stoichiometric material, so the deviation from unity is a measure of the oxygen excess or deficiency. In the "as-cleaned" material, this value is 0.91 as compared to 0.96 after UV-ozone treatment. This significant surface oxygen enhancement occurs along with a loss in carbon caused by the partial removal of the surface contamination layer. The  $[Sn]/[In]$  ratio is virtually constant, decreasing insignificantly from 0.115 to 0.112. The Sn and In peak binding energies are also unaffected by the treatment, but the Sn shows a slight line narrowing because of a lessening of the high binding energy asymmetry. Sn in ITO is postulated to exist in three possible chemical states determined by thermal history and interstitial oxygen concentration.<sup>18</sup> The electrically active Sn atoms are thought to be bound to three lattice O atoms and donate one electron to the conduction band. The other two types of Sn are bound in electrically inactive complexes involving interstitial oxygen and neighboring Sn atoms. A shift in the equilibrium towards the oxygen containing species would lessen the concentration of ionized Sn donors and cause a loss of intensity of the highest binding energy component. Experimentally, this would be manifested as a line narrowing caused by the loss of high binding energy asymmetry. In addition, the observed drop in surface conductivity is due to the decrease in electrically active, ionized donors. The lower conductivity in the near surface region may enhance the potential drop under bias and thus favor charge injection.

The characteristics of cells employing the CuPc buffer layer are somewhat unexpected. In Fig. 1, this cell shows a device performance intermediate between that of untreated and treated ITO. The surprising result is observed when the CuPc is deposited onto treated and untreated ITO substrates. In this case, Fig. 3, the treatment history has no effect of the  $I$ - $V$  characteristics. This is contrary to what is found when PEDOT is used as an interlayer in polymer, light emitting diodes.<sup>7</sup> In the present case, the implication is that the injection process is limited by the CuPc/NPB interface rather than that of CuPc and ITO. Indeed, there have been reports of ohmic hole currents in thin CuPc films.<sup>19</sup>

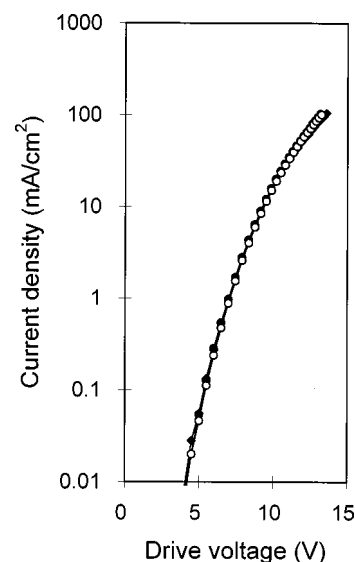


FIG. 3. Current-voltage characteristics of EL devices with the same treatments shown in Fig. 1 except for the presence of a 15 nm CuPc between the ITO and NPB: (■) as-cleaned, (○) oxygen-plasma treated, and (●) UV-ozone treated.

## B. *In situ* prepared films

In this series of experiments, we took advantage of the capabilities of performing high temperature, vacuum annealing and *in situ* O-GDT in an aluminum free environment. UV-ozone treatment was also done, but this required removal from the ultrahigh vacuum. The work function was again determined by UPS, but the surface composition was determined from Auger spectroscopy instead of XPS. Once the sample is cleaned of surface contamination, there is a very good correlation between composition and work function. In Fig. 4 the variation in both the work function and the surface oxygen deficiency are plotted as a function of the surface treatment. The oxygen deficiency is expressed here as the percent of oxygen that would have to be added to make the material stoichiometric as  $In_2O_3$  and  $SnO_2$ . The "as-received" ITO was a very low work function material with a relatively low, surface oxygen deficiency. The relatively high oxygen concentration is due to surface contamination. High temperature annealing removes much of the adventitious contamination layer as evidenced by the decrease in both carbon and oxygen. This raises the work function to a value more characteristic of clean ITO. The first O-GDT treatment further removes the adventitious carbon while slightly increasing the oxygen concentration. Once this relatively clean surface is achieved, the work function is largely determined by the surface oxygen composition, rising as the surface becomes oxygen rich and falling as the surface becomes more oxygen depleted. The rise in work function with oxygen results from an outward facing, negative dipole, an almost universally observed effect in oxygen adsorption on metals.<sup>17</sup>

The observed behavior is exactly what would be expected based on the rather extensive knowledge of bulk ITO.<sup>18</sup> The four valent Sn is an *n*-type dopant in the three valent In lattice, donating one electron to the conduction

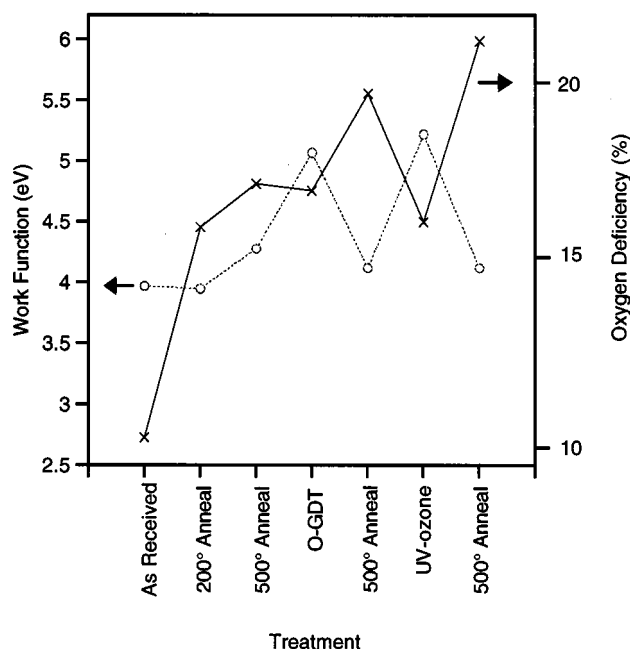


FIG. 4. Variations in the UPS measure work function (○) and surface oxygen deficiency (×) for various surface treatments on a particular sample. The sample remained in ultrahigh vacuum until the UV-ozone treatment.

band, which is primarily In 5s like. At the high doping levels common in ITO, around 10%, this is the dominant mechanism for producing free charge carriers. This electrically active Sn species is deactivated by complexing with interstitial oxygen. High temperature annealing allows interstitial oxygen to diffuse out of the crystal to produce high conductivity material. Indeed, one method of preparing highly conducting ITO involves the sputtering in an oxygen rich atmosphere producing a highly resistive film. This material is then made conducting by annealing in a reducing ambient. This process can lower the resistivity by more than 2 orders of magnitude.<sup>18</sup> Surface treatments, such as O-GDT or UV-

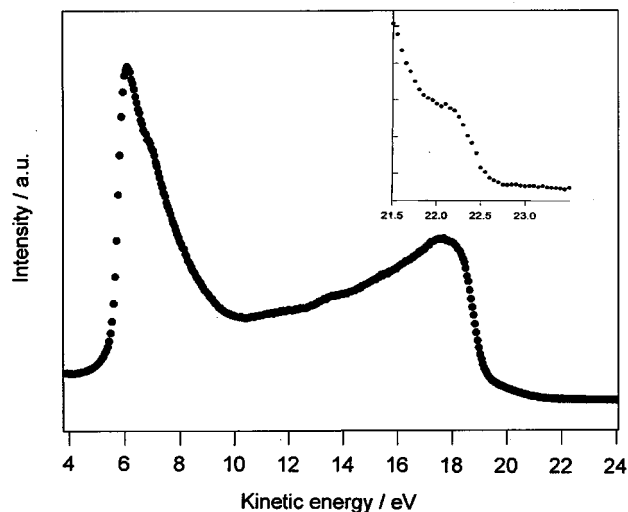


FIG. 5. A survey, He I, UPS spectra of ITO after UV-ozone treatment and 500 °C annealing. Insert shows an expanded view of the Fermi edge.

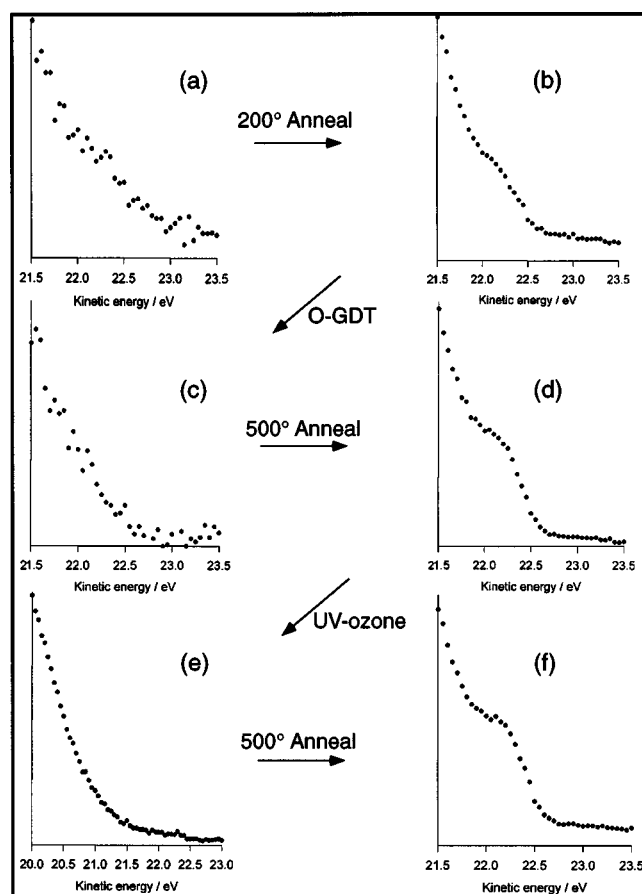


FIG. 6. Changes in the Fermi edge region of the He I, UPS spectra with various, sequential surface treatments: (a) chemically cleaned; (b) 200 °C vacuum anneal; (c) O-GDT; (d) 500 °C vacuum anneal; (e) UV-ozone; and (f) 500 °C vacuum anneal.

ozone, allow us to have oxygen deficient, highly conducting, bulk materials in which only the near surface region is modified to increase the work function. This engineering of the work function aligns the energy levels appropriately for efficient charge injection into the organic hole-transport layers of the device.

The effect of temperature on the free carrier density of ITO can be directly seen in the UPS spectra. A typical He I survey spectrum for ITO after UV-ozone treatment followed by a 500 °C anneal is shown in Fig. 5. The spectrum implies some revealing characteristics of ITO's electronic structure. In a normal, degenerate semiconductor, one would expect to see emission from the filled valence band, which would be followed by a gap and then emission from the conduction band, populated by the *n*-type donor states. Such spectra have been observed for degenerately doped Si.<sup>20,21</sup> However, in the present case, there is no indication of a gap between emission at the Fermi level and the onset of the oxygen, 2*p*-like valence band features at about 19 eV. In fact, the emission intensity increases between the Fermi edge and the valence band. From optical data, there is an indirect gap of about 2.6 eV, which should be observable.<sup>22</sup> The simplest interpretation for the absence of such a gap is that the doping level is so high that impurity bands completely fill the gap. This complication aside, the variation of intensity at



the Fermi edge lends strong support for the above-presented interpretation of the conductivity with temperature. From optical data, the free carrier density for the material represented by Fig. 5 is estimated to be about  $2 \times 10^{20} \text{ cm}^{-3}$ .<sup>22</sup> This is about two orders of magnitude lower than in a typical metal and makes the Fermi edge difficult to observe, even for what is considered highly conducting ITO. In Fig. 6, we follow the evolution of the Fermi edge intensity as the various treatments are applied. With oxidative treatments, interstitial oxygen diffuses into the ITO forming electrically inactive complexes with Sn, which remove electrons from the conduction band. This process depletes the density of occupied states at the Fermi energy causing a loss in measured, photoemission intensity. The spectrum shown in Fig. 6(a) was so depleted of free charge, that sample charging occurred in measuring the UPS spectra. With high temperature annealing, the interstitial oxygen again diffuses to the surface, leaving the Sn dopants in the electrically active state and increasing the free carrier density at the Fermi level. The variations in Fermi edge intensity correlate very well with the behavior of the oxygen deficiency and work function shown in Fig. 4.

#### IV. CONCLUSIONS

The hole injecting properties of ITO in EL devices can be dramatically enhanced by oxidative treatments such as O-GDT or UV-ozone. Popular models of charge injection have associated these enhancements with a lowering of the barrier to hole injection as a result of the observed increases in work function. We have used the surface characterization spectroscopies of UPS and XPS to investigate the composition and electronic structure of the ITO surface as a function of these treatments and high temperature, vacuum annealing. The conclusions are totally consistent with the well understood, bulk properties of ITO. The oxidative treatments do incorporate more oxygen into the lattice making it more stoichiometric. The core levels of the dopant Sn atoms narrow as electrically inactive complexes are formed between the Sn and interstitial oxygen. The attending depletion of free, conduction electrons is reflected in a decrease in intensity at the Fermi level in the UPS spectrum and an increase in surface resistivity. The work function is increased due to a dipole resulting from a surface rich in negatively charged oxygen. With high temperature, 500 °C, annealing, these processes are reversed: the materials become more oxygen depleted, the Sn 3d core levels again become asymmetric, photoemission intensity at the Fermi level drops dramatically, and sur-

face conductivity increases as does the work function. The work function correlates very well with the oxygen deficiency determined by XPS. These processes appear to be reversible, at least in the near surface region probed by the photoemission spectroscopies. The ability of modifying only the near surface region of the ITO allows us to maintain the high, bulk conductivity necessary for device efficiency and yet increase the work function to enhance the hole injection properties of the anode.

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