

Surface oxidation activates indium tin oxide for hole injection

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Oxygen plasma treatment of indium tin oxide (ITO) results in a change in work function and electron affinity by ~ 0.5 eV. This change correlates with the measured increase in injected current in simple “hole-only” organic devices with O-plasma treated ITO electrodes. Neither addition nor removal of surface hydroxyl functionality accounts for the observed work function and electron affinity changes. X-ray and ultraviolet photoelectron spectroscopies show a new type of oxygen species is formed. Oxidation of surface Sn-OH to surface Sn-O $\bullet$ units is proposed to account for the observed changes in O-plasma treated ITO; this proposal can explain a wide variety of previously described ITO surface activation results. © 2000 American Institute of Physics.

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I. INTRODUCTION

The relationship between the surface chemistry of indium tin oxide (ITO) and the injection of carriers into organic hole transport materials (HTMs) is of paramount importance for the development of organic light-emitting devices (OLEDs). Although a multitude of explanations has been put forth to account for the behavior of variously “activated” ITO-based OLEDs, none has yet rationalized these ostensibly disparate treatments into a single, cohesive, surface chemical model. We now report an experimental insight regarding charge injection at the interface between ITO and typical HTMs used in high efficiency OLEDs, and we show that many of the reported experimental observations of enhanced injection by chemically modified ITO can be explained on the basis of a single surface modification reaction.

Juxtaposing analysis of the chemistry and electronic structure of the ITO surface with direct interface transport measurements has been especially revealing. By direct measurement using ultraviolet and x-ray photoelectron spectroscopies (UPS; XPS), we have shown that oxygen plasma treatment (a common activation technique for ITO) generates a new type of oxygen species at the ITO surface. Furthermore, we have shown that factors such as the In:Sn or [In, Sn]:O ratios at the surface, the presence of metallic Sn or In,¹ or the degree of surface hydroxylation, each of which has been suggested to account for differences in the measured work function of ITO prepared under various conditions, can be excluded as the rationale for the large increase in work function measured upon mild ITO oxygen plasma treatment; rather, this increase is ascribed to an increased surface layer dipole due to the formation of this new oxygen species.

The prevalent architecture for OLEDs based on organic small molecule or polymer semiconductors comprises a transparent supporting platform, e.g., glass, covered with a thin film of transparent conducting oxide (usually ITO) that serves as one of the device electrodes.² Photons produced by recombination of carriers in the bulk of the device escape through the oxide film and the supporting platform. Commercially available thin film ITO has good conductivity and excellent transparency in the visible region of the spectrum (Applied Films, 20 Ω , 1500 Å). However, it is difficult to characterize ITO quantitatively, being a complex ternary compound containing 9–10 mol. % of tin oxide in indium oxide. Surface morphology and thin film composition vary with deposition and processing techniques, which lead to variations in thin film parameters and, consequently, device performance. Thus, it is difficult to standardize ITO as an efficient carrier injection contact. In particular, the work function of ITO films, which is one of the most relevant parameters for OLED applications, is not well characterized and is not particularly high. “As-received” films are reported to have work functions between 4.2 and 4.4 eV, barely greater than the work function of metals such as Al. Such films exhibit hole injection characteristics which are inferior to the electron injection characteristics of low work function metals,^{3,4} and resulting in high operating voltage and hole-limited, inefficient devices. Considerable effort has therefore been devoted to ITO processing to improve hole injection by making it, effectively, a “high work function, transparent metal.”

The magnitude of the injected current at an injection limited metal/semiconductor contact depends on the size of the interfacial Schottky barrier. Conceptually, minimizing the energy difference between the Fermi level of a metal and the highest occupied molecular orbital (HOMO) of an organic HTM optimizes hole injection. Typical HTMs like

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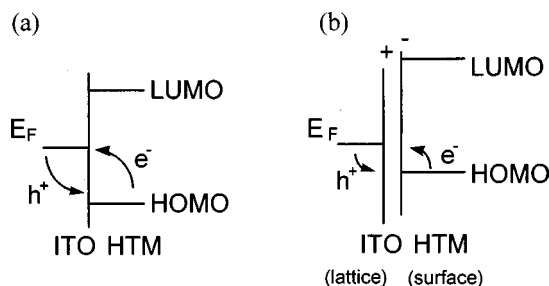


FIG. 1. Organizing a dipolar layer on the surface of ITO reduces the Schottky barrier to hole injection; (a) the barrier in the absence of the dipolar layer; (b) reduction in the barrier in the presence of the dipolar layer.

N,N'-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD) or α -NPD have ionization energies >5 eV;⁵ this results in excessive “hole barriers” at the ITO-HTM interfaces, on the order of 1 eV (Fig. 1). Two strategies have been described to alleviate this problem. The first consists of introducing a nanometer-thick interlayer (such as Cu(II) phthalocyanine),⁶ with a “hole energy level” intermediate between the ITO Fermi level and the HOMO of the HTM. This creates a “ladder-type” energy structure⁶ which has been shown to improve hole injection, but introduces an additional level of OLED fabrication complexity. The second, and more direct, strategy is to increase the ITO work function, itself, via mechanical and/or chemical surface treatment; in this context, an important model based on the organization of dipolar species at the ITO surface has been set forth: The work function of the ITO can be increased⁷ when this dipole is oriented as shown in Fig. 1.

II. EVALUATION OF O-PLASMA TREATED ITO

It has been amply documented that full, two-carrier OLEDs deposited on oxygen-plasma treated ITO substrates carry higher current densities at the same applied electric field than comparable devices deposited on untreated ITO.^{8–11} To focus on the origin of such decreased operating voltages, we constructed single-carrier (hole-only; ITO/1000 Å α -NPD/400 Å Al) devices on both untreated and oxygen-plasma treated (4 min, 150 mTorr O₂, ~ 50 mW/cm²) ITO substrates. Aluminum was chosen as the top contact because of its large injection barriers for both electrons and holes, estimated to be 1.4 and 1.7 eV, respectively, from UPS measurements of metal/ α -NPD interface properties.¹² Devices were grown, and work function and current–voltage (*I*–*V*) characteristics were measured in ultrahigh vacuum (UHV) (Fig. 2). Hole injection from O-plasma treated ITO was greatly enhanced compared with the “as-received” material, consistent with observed lowered OLED operating voltages.

Other research groups have claimed that improved hole injection from O-plasma treated ITO results from changes in relative surface concentrations of O, Sn, and In.^{8,9} We examined this material by XPS (AlK α 1486.6 eV) but we find that such atomic concentrations are not significantly altered by O-plasma treatment, or even by Ar⁺ bombardment (another common ITO surface cleaning procedure¹³): In:Sn remained consistent at $\sim 8 \pm 0.5$, for all surfaces studied (Table I). Closer inspection of XPS data showed, however, that sig-

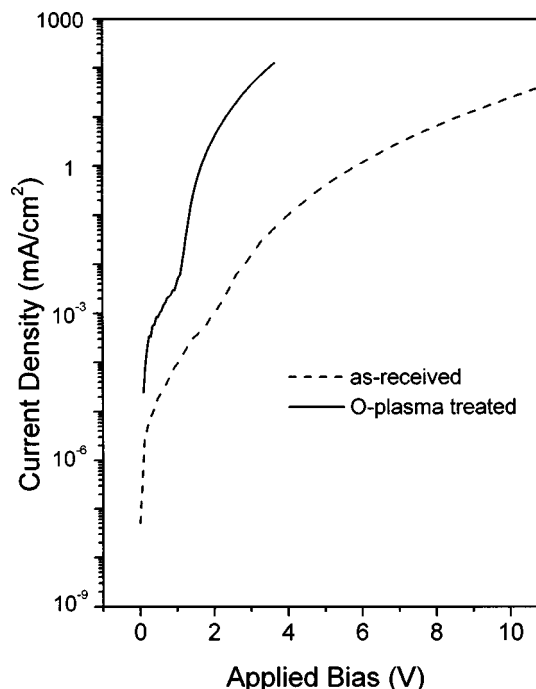


FIG. 2. *I*–*V* characteristics of hole-only ITO/ α -NPD/Al structures. Increased hole injection from O-plasma treated ITO (upper curve) vs “as-received” ITO (lower curve) is evident.

nificant changes accrue to the shape of the O(1s) core level as a result of either Ar⁺ or O plasma treatment (see Fig. 3). In particular, the O(1s) spectrum of untreated ITO shows two components: the main peak, corresponding to O bonded to Sn and/or In, and a higher binding energy component due to surface -OH sites. The assignment of the higher binding energy component to -OH groups has been confirmed using Fourier transform infrared (FTIR) analysis;¹⁴ the disappearance of this XPS shoulder on Ar⁺ bombardment (dehydroxylation) occurs concomitantly with loss of an IR band centered at 3379 cm^{−1} ($\nu_{\text{O-H}}$). Dosing with water (rehydroxylation) in UHV reestablishes both XPS and IR signals.¹⁴ Significantly, the O(1s) spectrum of O-plasma treated ITO indicates the presence of a new chemical species which is not found on “as-received” ITO, nor is formed by Ar⁺ bombardment induced dehydroxylation, or rehydroxylation: The low-binding energy edge of the O(1s) peak is broadened compared with these other ITO surfaces, indicating the formation of a chemically distinct oxygen species on the O-plasma treated surface.

Ultraviolet photoelectron spectra (UPS) were measured for “as-received,” O-plasma treated, Ar⁺-bombarded (30

TABLE I. Indium-to-tin ratios measured by XPS for variously treated ITO samples. The magnitude of uncertainty is due to nonuniformity of material grown by sputtering on glass.

ITO treatment	In:Sn
“As-received”	8.0 ± 0.5
Ar ⁺ bombarded	8.2 ± 0.5
Ar ⁺ bombarded; H ₂ O dosed	7.3 ± 1.0
O-plasma	8.1 ± 0.5

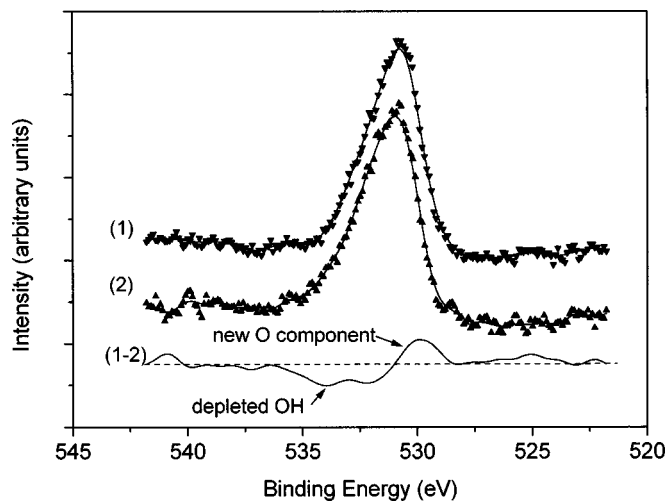


FIG. 3. O(1s) core-level XPS data (Al $K\alpha$ 1486.6 eV): uppermost spectrum (1), O-plasma treated; middle spectrum (2), "as-received;" lowest, difference spectrum highlighting the appearance of the new, low binding energy component and the corresponding depletion of OH (1-2).

min; $\approx 1 \mu\text{A}/\text{cm}^2$) and Ar^+ -bombarded/rehydroxylated ITO (three cycles of water condensation in UHV at low temperature followed by desorption at room temperature). In each case, the surface work function was determined using the position of the low-kinetic energy secondary electron cutoff (onset of photoemission) for each UPS spectrum. The work functions of "as-received," Ar^+ -bombarded and Ar^+ -bombarded/rehydroxylated ITO were all 4.2 ± 0.1 eV (Table II). Therefore, hydroxylation or dehydroxylation are not primary factors in determining the work function of ITO.

In contrast, an increase in the ITO work function (≈ 0.5 eV) is recorded for O-plasma treated ITO [see Fig. 4(a)], as has been noted previously,⁹ correspondingly, the hole injection barrier at oxygen-plasma treated ITO was ≈ 0.5 eV smaller than the barrier at untreated ITO (see Fig. 5). As in the case of XPS analyses, the valence density of states of untreated, Ar^+ -bombarded and Ar^+ -bombarded/rehydroxylated ITO were all similar (with features corresponding to those measured for In_2O_3),¹⁵ and a comparison of UPS spectra of α -NPD superdeposited on either Ar^+ -dehydroxylated or Ar^+ -dehydroxylated/rehydroxylated surfaces showed that the energy barrier for hole injection from ITO into α -NPD was independent of the surface hydroxyl content (see Fig. 5). However, the UPS spectrum of α -NPD superdeposited on O-plasma treated ITO indicated a reduced hole injection barrier, and the valence spectrum of this ITO showed a well-defined peak at ~ 8 eV below the

TABLE II. Work function measurements and barriers to hole injection, as determined by UPS, for a series of variously treated ITO-based OLEDs.

ITO treatment	ϕ (eV)	Injection barrier (eV)
"As-received"	4.1 ± 0.1	1.34 ± 0.05
Ar^+ bombarded	4.2 ± 0.1	1.17 ± 0.05
Ar^+ bombarded; H_2O dosed	4.2 ± 0.1	1.27 ± 0.05
O-plasma	4.7 ± 0.2	0.88 ± 0.10

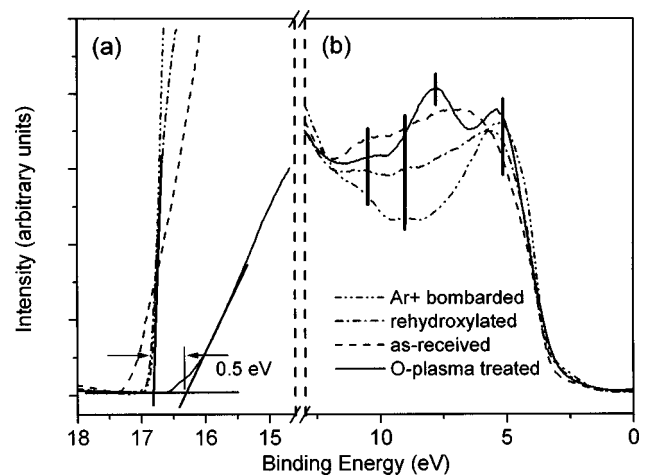


FIG. 4. (a) Photoemission onset region of ITO; (b) He(I) (21.2 eV) UPS spectra of ITO surfaces. The surface work functions are determined from the low kinetic energy onset of photoemission.

Fermi level, indicative of the introduction of a new, O(2p) derived state¹⁵ [Fig. 4(b)], which we propose to be related to a change in the ITO surface dipole layer.

III. MECHANISM OF WORK FUNCTION INCREASE

To test the surface dipole model (Fig. 1), we can determine the magnitude of the change in an ITO surface dipole layer that would give rise to the observed ≈ 0.5 eV increase in the ITO work function, and correlate this value with

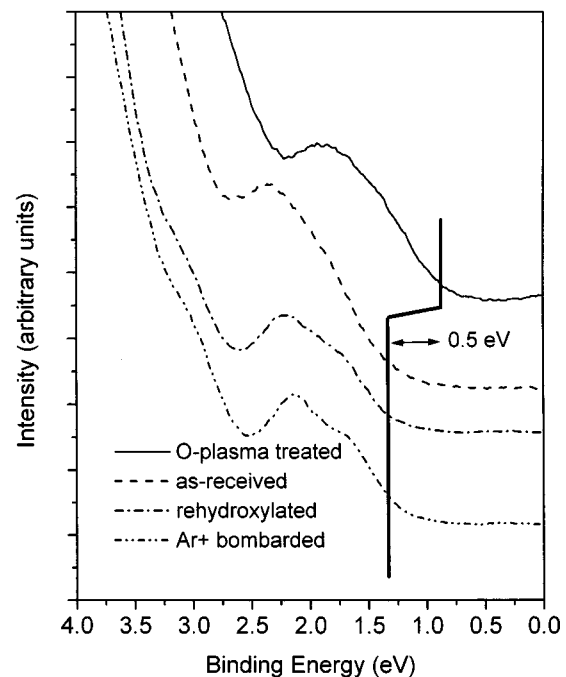


FIG. 5. UPS spectra showing the positions of the α -NPD HOMO relative to the Fermi level for 15 Å thick films of α -NPD deposited on variously treated ITO surfaces: uppermost, O-plasma; next, "as-received;" next, Ar^+ bombarded (dehydroxylated) and rehydroxylated; lowest, Ar^+ bombarded (dehydroxylated). The energy difference between the low-binding energy edge of the HOMO and the Fermi level represents the contact hole injection barrier.

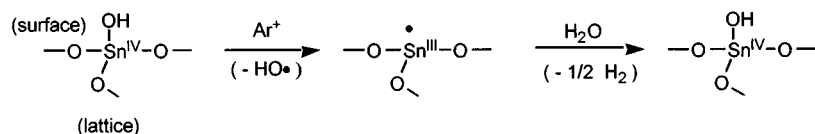
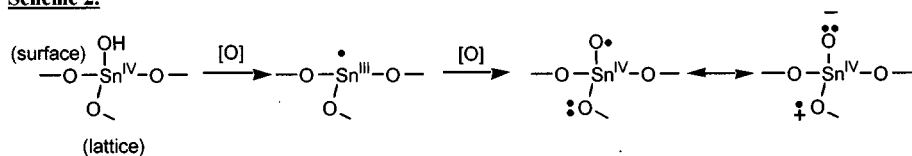
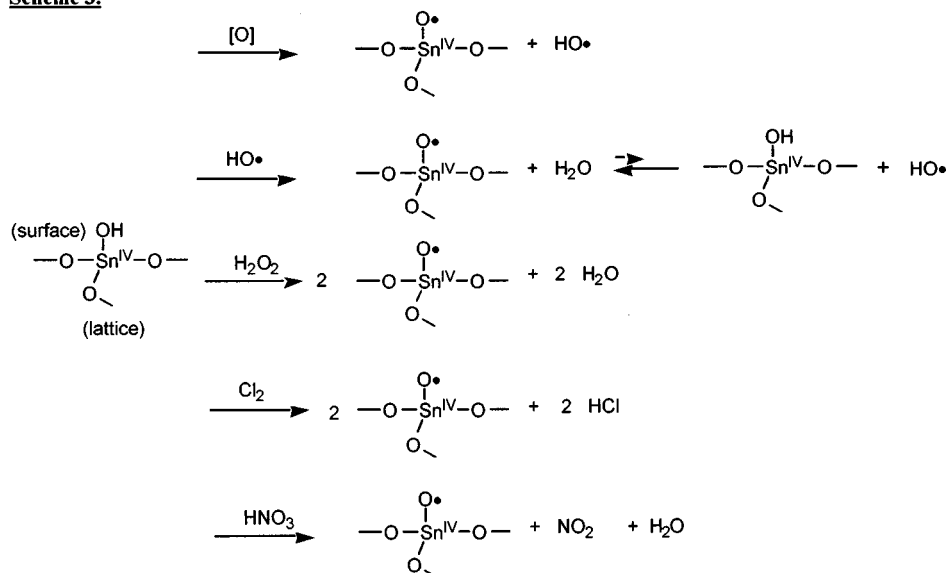
Scheme 1.**Scheme 2.****Scheme 3.**

FIG. 6. Chemical processes responsible for modifying the ITO surface. Scheme 1 represents the de/rehydroxylation processes. Scheme 2 is our model of the O-plasma treatment. Scheme 3 illustrates how reaction with various oxidation reagents will produce the same end product as O-plasma treatment.

changes in surface speciation for the electrode. Using Eq. (1), where μ is the dipole per unit area and q is the electronic charge, we set, as measured, $\Delta\phi = 0.5$ eV, and find the required surface dipole must change by 1.35 D (on the order of a change in dipole moment of 1–2 polar groups) per 100 Å² of surface area. It is intriguing that this concentration corresponds approximately to the hydroxyl group loading on the surface of “as-received” ITO, as measured by a combination of organometallic and electrochemical techniques,¹⁶ and suggests that a change in the chemical nature of surface -OH groups (consonant with our observed changes in UP and O(1s) XP spectra), could be responsible for the observed change in ITO work function imparted by O-plasma treatment.

$$\Delta\phi = 4\pi q\mu. \quad (1)$$

We suggest that Ar⁺ bombardment of ITO parallels that which is well known for TiO₂:^{17,18} Ar⁺ bombardment generates Ti^{III} (interalia) from Ti^{IV}; treatment with water reoxidizes Ti^{III} to Ti^{IV}, with concomitant surface hydroxylation. Tin(IV) compounds can be easily converted to Sn^{III} species, and vice versa, in the context of organic synthesis,¹⁹ and Sn–O• species are implicated as intermediates in the decomposition of Sn(IV) peroxides.²⁰ Thus, Ar⁺ bombardment of

ITO might remove surface hydroxyl groups bound to Sn^{IV} (interalia), generating Sn^{III} surface species; indeed, XPS analysis of Ar⁺-bombarded ITO shows the presence of a new, lower binding energy Sn species, but no obvious change in the In XPS.¹⁴ Reaction of these Sn^{III} surface sites with water would regenerate Sn^{IV}–OH, with evolution of H₂ (Fig. 6, Scheme 1). However as noted, neither dehydroxylation nor rehydroxylation leads to an increase in the work function for the ITO.

We further suggest that O-plasma treatment is, in a first step, analogous to Ar⁺ bombardment, and generates Sn^{III} surface species by dehydroxylation of Sn^{IV}–OH groups. However, in this instance these Sn^{III} species are formed in the presence of oxygen atoms,²¹ which would react immediately to give the “stannoxyl,” Sn^{IV}–O• (Fig. 6, Scheme 2).²⁰ Net, an equivalent of Sn^{IV}–OH is converted to Sn^{IV}–O• through -OH group oxidation chemistry. By virtue of the electron deficiency of the oxygen-based radical, this oxidation increases the ITO surface dipole layer (Fig. 6, Scheme 2). The magnitude of this effect should be directly proportional to the surface density of Sn^{IV}–OH groups of ITO which can be oxidized to Sn^{IV}–O• and to the change in dipole moment per group oxidized.

It is intriguing that many well-known methodologies which have been reported to increase the work function of ITO have as a common feature their ability to act as oxidation reagent systems. Apart from oxygen plasma treatment,⁸ these include reaction with: ozone under UV irradiation;⁸ hydrogen peroxide;²² aqua regia;⁹ or nitric acid.²³ We propose, therefore, that oxidation of surface $\text{Sn}^{\text{IV}}\text{-OH}$ accounts for the increase in ITO work function observed in all these cases. In these cases, ozone, peroxides, nitric acid or aqua regia (as a source of Cl_2) oxidize $\text{Sn}^{\text{IV}}\text{-OH}$ groups by direct attack to yield $\text{Sn}^{\text{IV}}\text{-O}^\bullet$; a byproduct of this step could consume a second equivalent of $\text{Sn}^{\text{IV}}\text{-OH}$ (Fig. 6, Scheme 3). Oxygen plasma might also directly oxidize Sn-OH in this manner. Because $\text{Sn}^{\text{IV}}\text{-O}^\bullet$ can be stabilized by "resonance" delocalization of unpaired spin density among lattice oxygens (Fig. 6, Scheme 2), it should be lower in energy relative to $\text{HO}^\bullet$; it would, therefore be expected that ITO activated as $\text{Sn}^{\text{IV}}\text{-O}^\bullet$ would be stable in the presence of water, as has been documented.^{9,22}

IV. SUMMARY

By direct measurement, we have shown that the change in ITO work function imparted by O-plasma treatment correlates strongly with the change in barrier for hole injection in a simple device. We have also shown that a new oxygen species is formed on ITO as a result of this O-plasma treatment, that the presence of this new species correlates with the change in ITO work function, and that such treatment has little, if any, effect on In/Sn or [In/Sn]/O ratios. Furthermore, we have demonstrated that addition or removal of ITO surface hydroxyl groups has no effect on the ITO work function. We propose that simple oxidation of $\text{Sn}^{\text{IV}}\text{-OH}$ to $\text{Sn}^{\text{IV}}\text{-O}^\bullet$ species can account for the spectroscopic changes measured for ITO treatment by O-plasma, as well as by a large number of other known processes. That simple oxidation of ITO might be adequate to effect beneficial changes in its electrode properties provides a rational guideline for the development of new processing methodologies to enhance ITO-based optoelectronic devices.

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- ¹⁶We have measured the surface hydroxyl group content of ITO on glass by a sequence involving protolytic reaction with tetra(tert-butoxy)zirconium, followed by reaction with (ferrocene)monocarboxylic acid, which gives surface bound (ferrocenecarboxylate)zirconium complexes. Since the stoichiometry of protolytic deposition of tetra(tert-butoxy)zirconium onto ITO proceeds with a ratio of one equivalent of Zr complex deposited per equivalent of surface hydroxyl group, determination of surface Zr is an indirect measure of surface OH group content. Quantification of the surface density of Zr ferrocenecarboxylate groups was accomplished independently by cyclic voltammetry and chronocoulometry; both techniques indicate on the order of 1×10^{-10} moles OH per cm^2 , or approximately 1 OH per 100 $\text{\AA}^2$ of ITO surface. The ITO used in this determination of ITO surface hydroxyl content (Donnelly Applied Films) has been shown by FTIR analysis to be less densely surface hydroxylated than that material used for the oxygen plasma studies described herein, which makes the measurement of 1 OH/100 $\text{\AA}^2$ a minimum estimate. See, S. K. Van der Kam, E. S. Gawalt, J. Schwartz, and A. B. Bocarsly, Langmuir **15**, 6598 (1999).
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