1808 *J. Am. Chem. Soc.* **2000,** *122,* 1808−1809

Surface Characterization and Modification of Indium Tin Oxide in Ultrahigh Vacuum

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Received August 11, 1999

Modern organic light emitting diode (OLED) architecture comprises a transparent supporting platform (for example, glass) covered with a thin film of transparent conducting oxide (usually indium tin oxide, ITO) that serves as the device anode.[1−4] The ITO is overlain first with an organic hole-transport layer (HTL) material, then an emissive, electron-transport layer, and finally, a low work function cathode. Photons produced by recombination of carriers escape through the oxide film and the supporting platform.[1,5] Commercially available thin film ITO has good conductivity and excellent transparency in the visible region, but it has been suggested that inefficiency of hole injection from ITO can lead to poor device characteristics in OLED applications.[1,6−10] Thus, considerable effort has been expended to modify the surface of ITO both to increase its work function[1,5,11−18] and to enhance its interaction, on the molecular level, with HTL materials.[7,19,20] We address the general issue of oxide surface modification through exploiting OH surface group reactivity;[21−28] such OH reactivity has been invoked for ITO,[7,29,30] but characterization of putative ITO surface OH sites and definite proof of their reactivity with derivatization reagents have been, heretofore, lacking. We now report the characterization of surface OH groups on ITO, and we show that these surface groups can be used to covalently bond well-defined surface modification reagents.

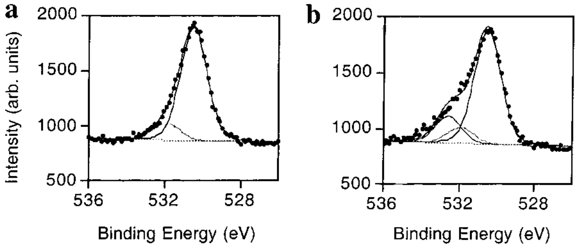

Figure 1. O(1s) XPS analysis of ITO. (a) After Ar$^+$ bombardment. (b) After 10 cycles of water dose (170 K)/desorb (225 K).

ITO/glass (Applied Films, 20 ohm/□, 1500 Å) was cleaned using standard protocols[7,12,16] but was still contaminated with surface carbon, as measured by X-ray photoelectron spectroscopy (XPS) in ultrahigh vacuum (UHV):[22,31] Vacuum-annealed ITO (500 K; 15 min; 10^{-10} Torr) showed a strong O(1s) peak at 530.5 eV (inorganic oxides), a second O(1s) peak at 532.4 eV, and a C(1s) peak at 284.0 eV; the latter two peaks indicate organic contamination. Argon ion bombardment (500 eV; 1.5×10^{-5} A; 15 min) removed surface organic oxygen and carbon, leaving a main O(1s) peak and a shoulder at 530.5 and 531.5 eV, respectively. Surface OH groups, observed by Fourier transform reflectance absorbance infrared spectroscopy (FT-RAIRS) at 3379 cm^{-1} (ν_{OH}) in the unannealed sample, were removed by Ar$^+$ bombardment. Regeneration of ITO surface OH groups was accomplished first by cooling the sample to 170 K and exposure to 3 L of H_2O, and then by gentle warming. FT-RAIRS at 170 K showed a broad band at $\nu_{\mathrm{OH}} = 3350$ cm^{-1}, and XPS showed an O(1s) peak at 534.3 eV (both corresponding to ice). Warming to 225 K led to desorption of multilayer H_2O. Surface OH groups were characterized[31] by O(1s) XPS as a high binding energy shoulder in the main O(1s) peak, at 532.8 eV, which grew concomitantly with FT-RAIRS absorbance at 3644 cm^{-1} through several cycles of low-temperature H_2O dose and thermal desorption (Figure 1).

XPS analysis showed that relative surface concentrations of Sn and In were essentially unchanged (In:Sn ≈ 12:1) by Ar$^+$ bombardment,[11,12,16] as was the peak shape for In, but the Sn signal had broadened. Before Ar$^+$ treatment, only a single Sn species was observed (binding energy [BE] for Sn[3d$_{5/2}$] = 486.7 eV); following Ar$^+$ treatment, two species were found (BE Sn[3d$_{5/2}$] = 486.7; 486.0 eV) by deconvolution using initial Sn line shape parameters. Intriguingly, the lower-binding energy species disappeared on water treatment (Figure 2), and the Sn(3d$_{5/2}$) spectrum reverted to that measured before Ar$^+$ treatment. Dehydroxylation of ITO apparently involves loss primarily of tin-bound surface hydroxyls which occurs with concomitant formal reduction of the metal to Sn(III) (Scheme 1); dehydroxylation−rehydroxylation of ITO seems, therefore, reminiscent of dehydroxylation−rehydroxylation of TiO_2.[32,33]

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[1] Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

[2] Campbell, I. H.; Davids, P. S.; Smith, D. L.; Barashkov, N. N.; Ferraris, J. P. *Applied Physics Lett.* **1998**, *72*, 1863.

[3] Antoniadis, H.; Miller, J. N.; Roitman, D. B.; Campbell, I. H. *IEEE Trans. Electron. Dev.* **1997**, *44*, 1289−1293.

[4] Burrows, P. E.; Gu, G.; Bulović, V.; Shen, Z.; Forrest, S. R.; Thompson, M. E. *Trans. Electron. Dev.* **1997**, *44*, 1188.

[5] Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 605−625.

[6] Kugler, T.; Lögdlund, M.; Salaneck, W. R. *IEEE J. Sel. Top. Quantum Electron.* **1998**, *4*, 14−23.

[7] Malinsky, J. E.; Jabbour, G. E.; Shaheen, S. E.; Anderson, J. D.; Richter, A. G.; Marks, T. J.; Armstrong, N. R.; Kippelen, B.; Dutta, P.; Peyghambarian, N. *Adv. Mater.* **1999**, *11*, 227−231.

[8] Forrest, S. R.; Burrows, P. E.; Thompson, M. E. *Laser Focus World*; PennWell Publishing Company, 1995; Vol. 31; pp 99−107.

[9] Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, 628−630.

[10] Burrows, P. E.; Bulović, V.; Forrest, S. R.; Sapochak, L. S.; McCarty, D. M.; Thompson, M. E. *Appl. Phys. Lett.* **1994**, *65*, 2922−2924.

[11] Wu, C. C.; Wu, C. I.; Sturm, J. C.; Kahn, A. *Applied Phys. Lett.* **1997**, *70*, 1348−1350.

[12] Kim, J. S.; Granström, M.; Friend, R. H.; Johansson, N.; Salanek, W. R.; Daik, R.; Feast, W. J.; Cacialli, F. *J. Appl. Phys.* **1998**, *84*, 6859−6870.

[13] Stössel, M.; Staudigel, J.; Steuber, F.; Simmerer, J.; Wittmann, G.; Kanitz, A.; Klausmann, H.; Rogler, W.; Roth, W.; Schumann, J.; Winnacker, A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1791−1793.

[14] Steuber, F.; Staudigel, J.; Stössel, M.; Simmerer, J.; Winnacker, A. *Appl. Phys. Lett.* **1999**, *74*, 3558−3560.

[15] Milliron, D. J.; Hill, I. G.; Kahn, A.; Schwartz, J. *J. Appl. Phys*. **2000**, in press

[16] Ishida, T.; Kobayashi, H.; Nakato, Y. *J. Appl. Phys.* **1993**, *73*, 4344.

[17] Osada, T.; Kugler, T.; Bröms, P.; Salaneck, W. R. *Synth. Metals* **1998**, *96*, 77−80.

[18] Nüesch, F.; Kamarás, K.; Zuppiroli, L. *Chem. Phys. Lett.* **1998**, *283*, 194−200.

[19] Nüesch, F.; Si-Ahmed, L.; François, B.; Zuppiroli, L. *Adv. Mater.* **1997**, *9*, 222−225.

[20] Ho, P. K. H.; Granström, M.; Friend, R. H.; Greenham, N. C. *Adv. Mater.* **1998**, *10*, 769.

[21] Miller, J. B.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 8239−8247.

[22] Miller, J. B.; Bernasek, S. L.; Schwartz, J. *J. Am. Chem. Soc.* **1995**, *117*, 4037−4041.

[23] Aronoff, Y. G.; Chen, B.; Lu, G.; Seto, C.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 259−262.

[24] Lu, G.; Purvis, K. L.; Schwartz, J.; Bernasek, S. *Langmuir* **1997**, *13*, 5791−5793.

[25] Lu, G.; Schwartz, J.; Bernasek, S. L. *Langmuir* **1998**, *14*, 1532−1534.

[26] Purvis, K. L.; Lu, G.; Schwartz, J.; Bernasek, S. L. *Langmuir* **1999**, *15*, 7092−7096.

[27] VanderKam, S. K.; Bocarsly, A. B.; Schwartz, J. *Chem. Mater.* **1998**, *10*, 685−687.

[28] VanderKam, S. K.; Gawalt, E. S.; Schwartz, J.; Bocarsly, A. B. *Langmuir* **1999**, *15*, 6598−6600.

[29] Herr, B.; R.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1157−1158.

[30] Chen, K.; Herr, B. R.; Singewald, E. T.; Mirkin, C. A. *Langmuir* **1992**, *8*, 2585−2587.

[31] Miller, J. B.; Bernasek, S. L.; Schwartz, J. *Langmuir* **1994**, *10*, 2629−2635.

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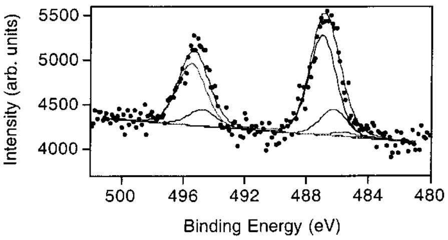
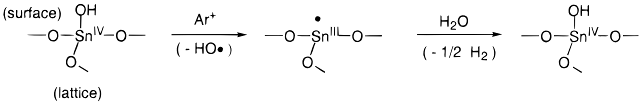
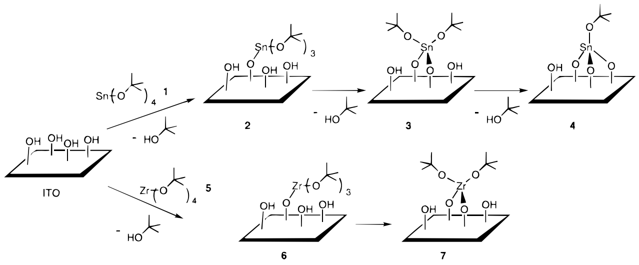


Figure 2. $Sn(3d_{5/2})$ XPS analysis of ITO after Ar^+ bombardment:. (The small peak at lowest binding energy is an Al Kα satellite.)

Scheme 1. Dehydroxylation and Rehydroxylation of ITO May Involve Sn(III) Intermediates



Scheme 2. Synthesis of Organotin and -zirconium Species on ITO in UHV



Organotin species are interesting for ITO surface modification; their use obviates introduction of new metallic surface elements. Reaction of tetra(*tert*-butoxy)tin (**1**) with hydroxylated ITO in UHV proceeded analogously to that with hydroxylated Al(110).[25] Exposure of ITO to **1** at 170 K deposited a multilayer on the substrate (FT-RAIRS: 2978 and 1180 cm^{-1}; XPS: C/Sn = 16; expected for **1**, C/Sn = 16). The $Sn(3d_{5/2})$ signal measured for this multilayer is due entirely to the Sn of complex **1** (organometallic Sn). No Sn signal from the ITO substrate (inorganic Sn) interfered: Even $In(3d_{5/2})$ photoemission from the substrate is completely attenuated by the organometallic multilayer, and the inorganic Sn content measured for the clean ITO surface is only ∼8.5% of the In (In:Sn ≈ 12:1). Temperature-programmed desorption (TDS) and XPS indicated loss of intact **1** up to 230 K; above this temperature there were no discrete thermal "plateaus" indicative of the presence of only single surface-tin species. However, XPS analysis of $Sn(3d_{5/2})$ and C(1s) data elucidated the thermal evolution of chemisorbed ITO surface-Sn alkoxides (the O[1s] XPS spectrum is complicated by the diversity of types of oxygen species present, which gives a broad, nearly featureless peak). We account for inorganic Sn by subtracting its contribution (∼8.5% of the measured $In[3d_{5/2}]$ peak, corrected for atomic sensitivities) from the total $Sn(3d_{5/2})$ signal (thus, inorganic Sn accounts for ∼1% of the total Sn signal measured for chemisorbed species). At 230 K, a ∼1:1 mixture of surface complexes $[ITO]-[O]_1-Sn(OBut)_3$ (**2**) and $[ITO]-[O]_2-Sn(OBut)_2$ (**3**) is present (XPS: $C/Sn_{organometallic} = 10.0 \pm 0.1$; for a 1:1 mixture of **2** and **3**, expected C/Sn = 10), at 285 K, an approximately equimolar mixture of $[ITO]-[O]_2-Sn(OBut)_2$ (**3**) and $[ITO]-[O]_3-Sn(OBut)_1$ (**4**) exists (XPS: $C/Sn_{organometallic} = 6.9 \pm 0.3$; for **3**: **4** ≈ 1:1, expected C/Sn = 6), but at 380 K, a single surface species, $[ITO]-[O]_3-Sn(OBut)_1$ (**4**) is observed (XPS: $C/Sn_{organometallic} = 4.2 \pm 0.1$; expected, C/Sn = 4; Scheme 2). A similar thermal profile was measured for reaction of tetra(*tert*-butoxy)zirconium (**5**) on hydroxylated ITO (Scheme 2), with slightly better thermal resolution of individual species. XPS data, including binding energies and composition ratios, are summarized in the Supporting Information. Both the FT-RAIRS peak at 3644 cm^{-1} and the XPS O(1s) signal due to surface OH groups nearly disappeared even following low exposure (<1L) of ITO to **1** at 170 K, showing that chemisorption occurs easily by reaction between surface OH groups and the organometallic (Figure 3).[34]

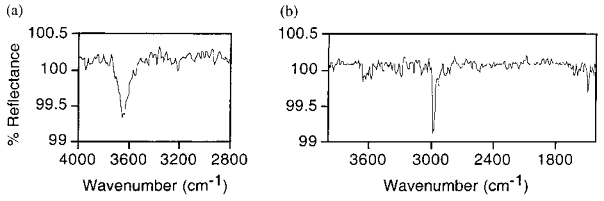


Figure 3. FT-RAIRS spectrum of ITO before and after low exposure (<1 L) to **1** at 170 K (note relative intensities of the OH signal): (a) hydroxylated ITO following ice desorption and before exposure to **1**; (b) hydroxylated ITO following exposure (<1 L) to **1** at 170 K.

Ligand groups in the coordination sphere of ITO surface bound Sn (or Zr) complexes react with organics of acidity greater than that of *tert*-butyl alcohol to give a variety of surface-modified ITO materials. Indeed, surface phenoxide[35] and carboxylate[36] derivatives of Sn have been prepared on other oxide surfaces by simple ligand exchange with phenols[35] and carboxylic acids.[37] Work on attaching functionalized HTL moieties to ITO via surface Sn complexes is now in progress.

Acknowledgment. The authors acknowledge support for this research given by the National Science Foundation and the New Jersey Center for Optoelectronic Materials.

Supporting Information Available: O(1s) XPS spectra of ITO before Ar^+ bombardment, following exposure to water at 170 K, and after five cycles of water dose (170 K)/desorb (225 K); Sn(3d) XPS spectra for pre- vs post-Ar^+-treated ITO; XPS data for surface tin complexes at 170 K and following heating to 230, 285, and 380 K; XPS data for surface zirconium complexes at 170, 315, and 440 K; Table summarizing these XPS data; and TDS profiles for the reaction of **1** and **5** with ITO are available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Smith, P. B.; Bernasek, S. L.; Schwartz, J.; McNulty, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 5654−6566.

(33) Sasaki, T. A.; Baba, Y.; Yamamoto, H.; Sasase, M.; Isobe, S. *Surf. Interface Anal.* **1993**, *20*, 682−686.

(34) A control experiment, in which **1** was deposited on dehydroxylated ITO at 150 K and then warmed to room temperature, showed no surface complex formation, by FT-RAIRS or XPS.

(35) VanderKam, S. K.; Lu, G.; Bernasek, S. L.; Schwartz, J. *J. Am. Chem. Soc.* **1997**, *119*, 11639−11642.

(36) Schwartz, J.; Bernasek, S. L.; Lu, G.; Keegan, J. P.; Purvis, K.; VanderKam, S. K. *J. Mol. Catal. A: Chem.* **1999**, *146*, 45−52.

(37) Purvis, K. L.; Lu, G.; Schwartz, J.; Bernasek, S. L. *Langmuir* **1998**, *14*, 3720−3722.