Synthetic Metals 138 (2003) 223–227

www.elsevier.com/locate/synmet

Controlling the work function of indium tin oxide: differentiating dipolar from local surface effects

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Abstract

Indium tin oxide (ITO) reacts with tetra(*tert*-butoxy)tin to give surface bound alkoxytin species. Ligand exchange occurs in these surface bound species by reaction with substituted phenols. The speciation of surface phenoxides was measured in ultrahigh vacuum by X-ray photoelectron spectroscopy, as was the work function for the surface modified ITO. It is shown that the molecular dipole moment of the phenol correlates strongly with the measured ITO work function change; no such correlation exists between the acidity of the phenol and this measured change in work function. Results are consistent therefore with an electrostatic model and not with one involving electronegativities of the ligated phenoxide oxygens.

Keywords: ITO; Surface modification; Surface dipole

1. Introduction

Indium tin oxide (ITO) is a commonly used anode material for optoelectronic devices [1–3], and considerable effort has been expended to enhance hole injection from ITO into an organic overlayer. One general approach to facilite hole injection is based on a simple electrostatic model [4] which suggests that organizing a dipolar layer at the surface of the ITO electrode can affect its work function (ϕ) [5] and, ultimately, its carrier injection ability. In particular, this model predicts that a dipole organized with its negative end furthest from the surface of the ITO should increase the ITO work function [5,6]. Indeed, a large number of studies have used this model as a guide in attempts to use organics to introduce these surface dipoles [6–11]. However, many of these studies utilize *p*-substituted aromatic acids [8,10–14], and *p*-substitution with electron withdrawing groups increases both the putative surface dipole and also the acidity of the organic [15]; thus, results from such studies can be difficult to attribute unambiguously to dipole introduction, since surface protonation could also affect ϕ.

We have studied the surface chemistry of ITO [4,16] and we have found that several metal alkoxides can react with surface hydroxyl (OH) groups to give well defined surface-bound complexes of fixed stoichiometry [16–20]. These complexes can, in turn, be substituted in a systematic way using organics more acidic than the corresponding alcohols [17–20]. Through use of a series of both *p*- and *o*-substituted organics [17], it should be possible to clearly differentiate between the effects of surface dipole introduction and surface protonation: electron withdrawing groups substituted *ortho* to a potentially ligating atom of an organic will enhance the acidity of that organic, but will introduce a ligand dipole moment *opposite* to that imparted by similar substitution in the *p*-position [15] (Fig. 1).

2. Results and discussion

ITO/glass, even when cleaned using standard protocols, is still contaminated with surface carbon, as can be determined by X-ray photoelectron spectroscopy (XPS) in ultra-high vacuum (UHV). Argon ion bombardment removes such surface organic contamination, but this also removes any surface OH groups present on the ITO [4,16]. We have found that regeneration of these surface OH groups can be accomplished by cooling the ITO to 170 K, exposure to 3 L of H_2O, and then gentle warming [16]. Fourier transform reflection absorbtion infrared spectroscopy (FT-RAIRS) shows a peak

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doi:10.1016/S0379-6779(02)01290-0

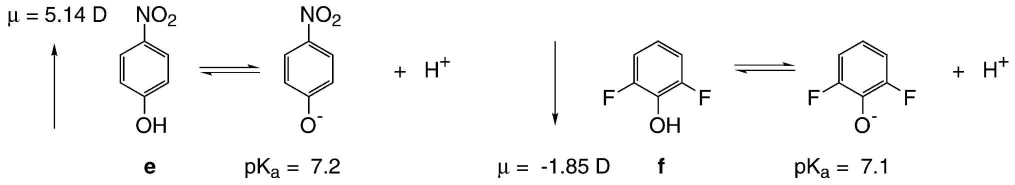


Fig. 1. Electron withdrawing groups substituted *ortho* to the phenoxide oxygen enhance the acidity of the phenol, but introduce a ligand dipole moment *opposite* to that imparted by similarly acidifying, electron withdrawing substitution in the *p*-position.

assigned to $\nu_{OH} = 3350\ cm^{-1}$, and XPS analysis showed an O(1s) peak with binding energy BE = 534.3 eV; both signals are attributed to ice. Warming the sample to 225 K led to desorption of multilayer H_2O. ITO-bound surface OH groups are characterized by O(1s) BE = 532.8 eV, and this signal grows concomitantly with an FT-RAIRS peak at $\nu_{OH} = 3644\ cm^{-1}$ through several cycles of low temperature water dose and thermal desorption, thus substantiating the XPS assignment to surface OH. XPS analysis shows that little change occurs in relative surface concentrations of Sn and In by Ar^+ bombardment or rehydroxylation; the peak shape for In was similarly unaffected. However, the Sn signal broadens with Ar^+ bombardment and it narrows again on rehydroxylation. We propose, therefore, that surface OH sites are bound primarily to Sn. Neither removal nor reintroduction of these OH groups significantly influences the ITO work function (ϕ) [4] (Figs. 2 and 3).

Surface OH groups are sites for chemisorption of organometallic complexes which can be used to introduce desired surface dipoles [17–19]. Organotin species are especially interesting for ITO surface modification since their use avoids the introduction of new metallic surface elements. Exposure of hydroxylated ITO to tetra(*tert*-butoxy)tin ($Sn(OBu^t)_4$, **1**) in UHV at 170 K gives a multilayer of the organometallic [17,19]. Temperature programmed desorption (TDS) and XPS analysis indicated loss of intact **1** up to 230 K. Above this temperature, there were no discrete thermal plateaus. We can differentiate indirectly between the

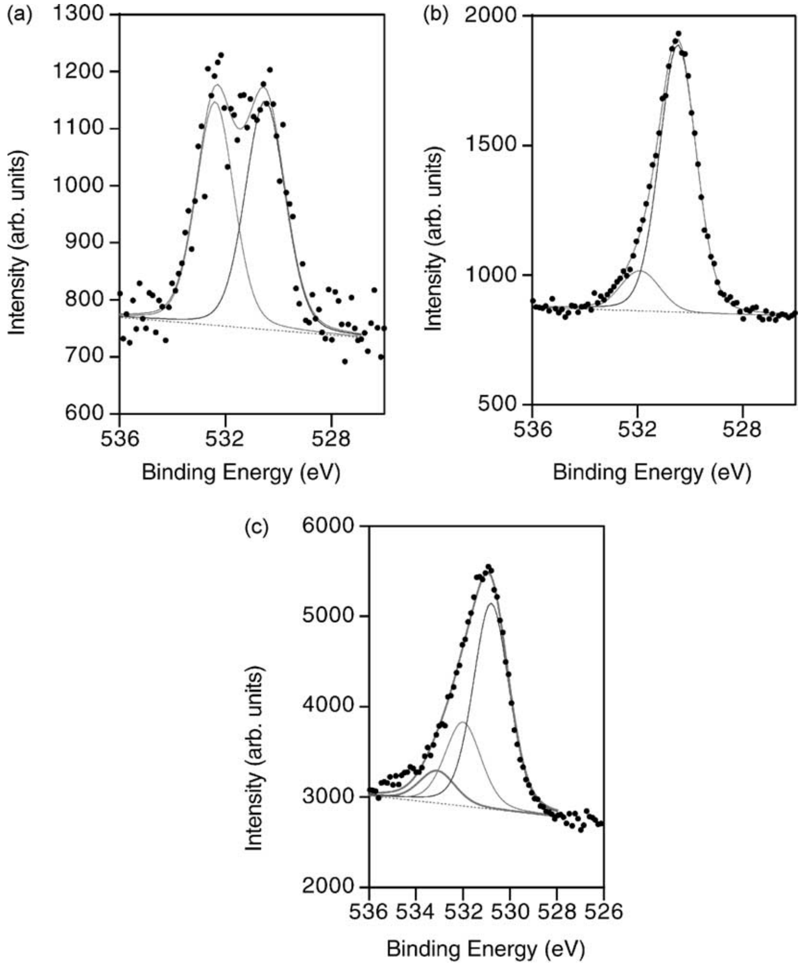


Fig. 2. O(1s) XPS analysis of ITO: (a) before Ar^+ bombardment; (b) after Ar^+ bombardment and dehydroxylation; (c) after water dose/desorb.

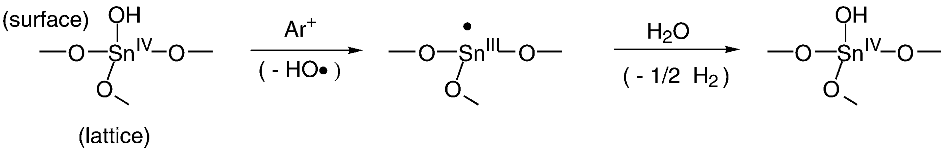


Fig. 3. Dehydroxylation and rehydroxylation of ITO may involve Sn(III) intermediates.

"inorganic" Sn of the ITO and the "organometallic" Sn of the surface complex since the "inorganic" Sn:In ratio is fixed at approximately 1:12. Thus, measuring the intensity of the In($3d_{5/2}$) peak can be used to calculate the fraction of the Sn($3d_{5/2}$) peak that is due to "inorganic" ITO Sn. Depending on surface complex coverage, the contribution of ITO-based Sn ranged from 10 to 50% of total Sn peak intensity. Surface complex stoichiometries are not coverage dependent. By measurement of relative Sn($3d_{5/2}$) and C(1s) peak intensities (correcting for experimentally derived sensitivities) we determined that at 230 K a 1:1 mixture of surface complexes (ITO)–$(O)_1$–$Sn(OBu^t)_3$ (**2**) and (ITO)–$(O)_2$–$Sn(OBu^t)_2$ (**3**) exists. At 380 K essentially a single surface species, (ITO)–$(O)_3$–$Sn(OBu^t)_1$ (**4**), is observed. Both the FT-RAIRS peak ($\nu_{OH} = 3644\ cm^{-1}$) and the XPS O(1s) signal (BE = 532.8 eV) due to surface OH groups nearly disappeared, even with only low exposure of ITO to **1** at 170 K, showing that chemisorption occurs easily by reaction between surface OH groups and the organometallic complex, even at this low temperature (Fig. 4).

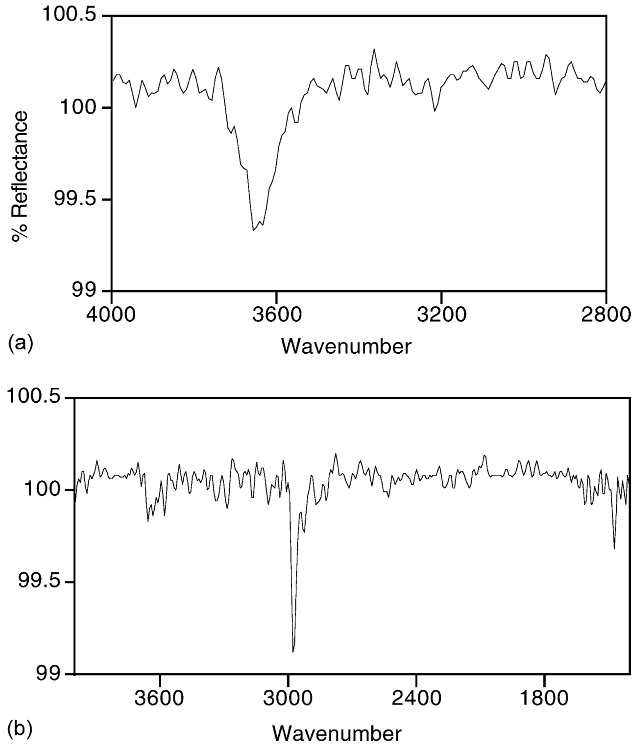


Fig. 4. FT-RAIRS spectrum of ITO (a) before and (b) after low exposure (<1 l) to **1** at 170 K. Note the relative intensities of the OH signal and the appearance of the peak at 2970 cm^{-1} characteristic of *tert*-butoxy groups of **1**.

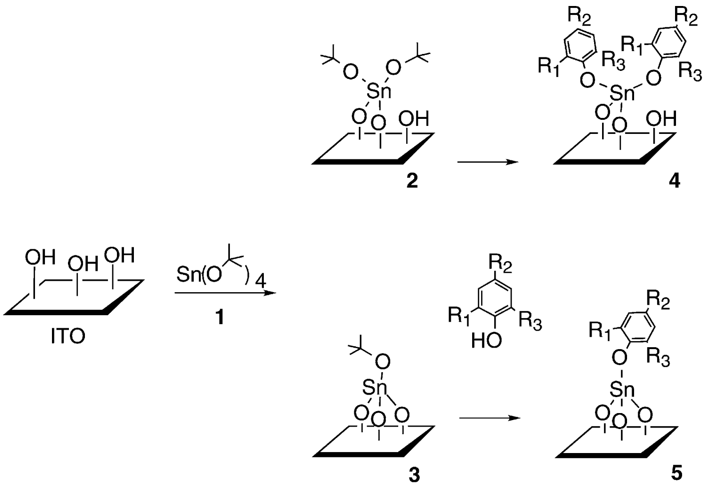
Surface tin alkoxides (**2/3**) were converted to a series of surface-bound tin phenoxides [17,19] by exposure to vapor of the corresponding phenol at 150 K. Substrates were then warmed to 293 K to desorb any multilayer phenol and to enable ligand exchange. Stoichiometries of surface tin phenoxides (**4/5**) were determined by XPS and were found to be similar to those for the starting tin alkoxides (Fig. 5).

Changes in ϕ for ITO on formation of the phenoxide complexes were measured by XPS by noting onset energies for secondary electron emission [17]. The work function was obtained from Eq. (1), in which the incident photon energy, the kinetic energies of electrons emitted from occupied states at the Fermi energy (E_{EF}), and the low kinetic energy onset of the secondary electron distribution (E_{onset}) are related [5]. It is assumed that E_{EF} is constant when the photon energy is fixed and the sample and spectrometer are in thermodynamic equilibrium, in electrical contact. Therefore, a change in ϕ can be determined by measuring the corresponding shift in the low kinetic energy onset of the secondary electrons.

$$\phi = h\nu - (E_{EF} - E_{onset}). \qquad (1)$$

Measured values for ϕ for a series of substituted surface tin phenoxides **4/5** were standardized against ϕ for the corresponding alkoxides **2/3**. This obviates effects of experimental variation in ITO surface complex loadings: both the magnitude of individual surface dipoles and the number of such sites per unit area affect ϕ [4–6] (Fig. 6).

We propose that *relative* dipole moments normal to an idealized ITO surface (μ_{avg}) which are derived from a series of surface-bound tin phenoxides can be related to gas phase calculated normal dipole moment components of the individual, free phenols. Examination of an idealized structure for a tetrahedrally-substituted surface tin complex shows that rotation about the Sn–O–C linkage can generate a family of rotamers. Each member of this family contributes to μ_{avg} according to its particular conformation. Assuming that surface dipoles induced by tin-surface bonding (Fig. 7), surface complex loadings, complex stoichiometries, and complex geometries for *all* series members are, on average, similar, a linear relationship would exist between calculated phenol dipole moments and changes in ϕ for ITO. In fact, measured data for ϕ for our series of tin phenoxide complexes, relative to ϕ for the corresponding alkoxides, do indeed vary linearly with gas-phase dipole moment calculations for the free phenols [17] (Fig. 8a).



a: $R_1 = R_2 = R_3 = H$; **b**: $R_1 = R_3 = H$, $R_2 = OCH_3$; **c**: $R_1 = R_3 = H$, $R_2 = F$;
d: $R_1 = R_3 = H$, $R_2 = CF_3$; **e**: $R_1 = R_3 = H$, $R_2 = NO_2$; **f**: $R_1 = R_3 = F$, $R_2 = H$;
g: $R_1 = OCH_3$; $R_2 = R_3 = H$; **h**: $R_1 = F$; $R_2 = R_3 = H$

Fig. 5. Synthesis of ITO surface-bound tin phenoxide complexes.

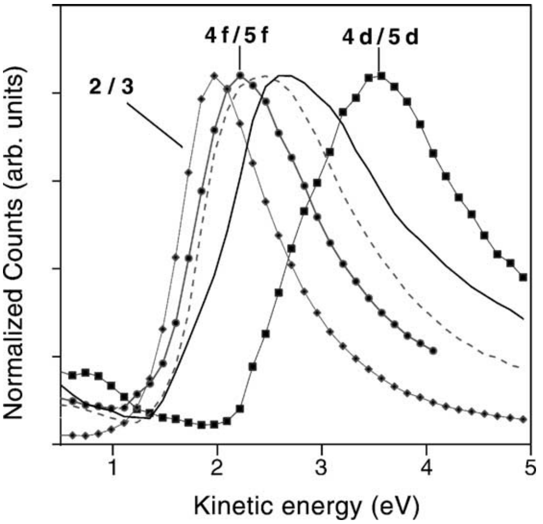


Fig. 6. XPS spectra showing photoemission onset for CF_3-substituted (**4d/5d**) and 2,6-diF-substituted (**4f/5f**) complexes, of comparable pK_a value for the phenols, but with *opposite* dipole contributions. Also shown are photoemission onset XPS spectra for **2/3**, dehydroxylated ITO (solid line) and rehydroxylated ITO (dashed line). Values for ϕ are determined from the baseline intercept of tangents drawn to these curves.

3. Conclusions

It is significant that work function data measured for surface modified ITO also correlate with relative free energy changes for simple deprotonation (versus the parent phenol) but only for *p*-substituted phenols [17,21]. Thus, simply using *p*-substituted materials it is *not* possible to distinguish between the effect of a putative surface dipole and simple proton transfer from the organic to the surface. However, data for *o*-substituted phenols can enable clear differentiation between these effects: *o*-substitution by electron withdrawing groups of a phenol increases the acidity of the organic, but produces a dipole moment *opposite* to that for comparable *p*-substitution. For example, note that *o*-substituted species **f**, **g**, and **h** have similar dipole components but vary greatly in their acidities; there is no correlation here between acidity and ϕ (Fig. 8b). In contrast, both *p*- and *o*-substituted phenols conform to the same trend relating changes in ϕ and ligand dipole moments. Thus, we can conclude that it is, in fact, dipolar properties of these surface-bound species, and not their propensities for proton transfer to a surface, that control the work function of the modified ITO.

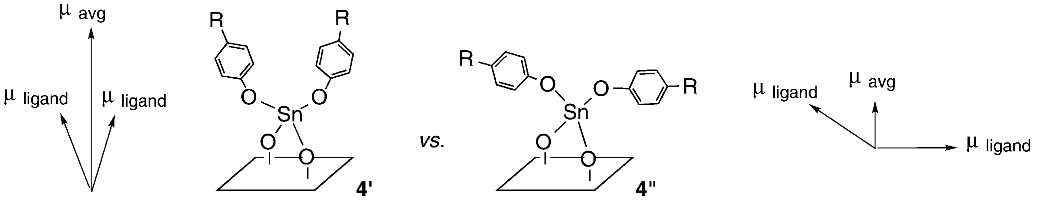


Fig. 7. The average normal component of the surface dipole (μ_{avg}) depends on the conformation of the phenoxy ligands (for example, rotation about Sn–O bonds of the phenoxide ligands). This is illustrated for two conformations of **4**: **4′** and **4″**. For **5**, rotation about the Sn–O bond of the phenoxide ligands does not change μ_{avg}.

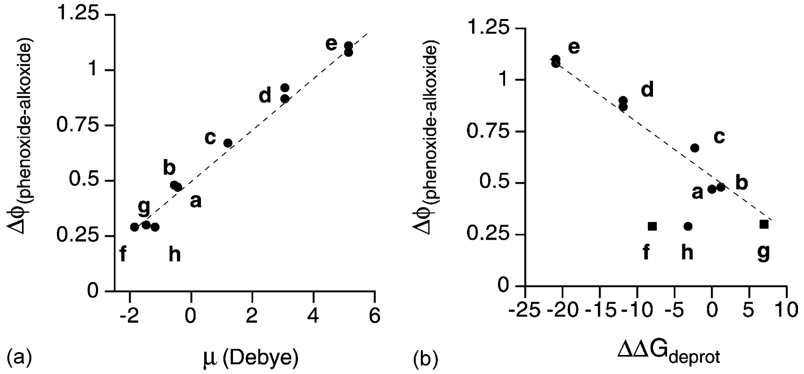


Fig. 8. (a) A good correlation exists between calculated gas phase dipole moments both for *para*- and *ortho*-substituted phenols and measured changes in ϕ for **4/5** bound to ITO electrodes. (b) A good correlation exists between deprotonation free energies vs. phenol for *para*-substituted phenols and measured changes in ϕ for **4/5** bound to ITO electrodes. Note the deviations measured (●) for *ortho*-substituted **h** and calculated (■) for **f** and **g**.

Acknowledgements

The authors thank the National Science Foundation. We also thank Professor Robert A. Pascal (Princeton University) for calculations of gas phase phenol dipole moment and phenol acidity data.

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