The Reaction between Tetrakis(diethylamino)tin and Indium Tin Oxide

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Received April 2, 2001. In Final Form: June 12, 2001

Indium tin oxide (ITO) is a common anodic material for modern optoelectronics,1–4 and it has been proposed5 that organizing a dipole at the ITO surface can change the work function of that material, directly affecting its hole injection propensity in a device. Surface adsorption of organics can create this surface dipole; systematic variation of these organics could provide a means to control injection propensity in a device. Surface adsorption of thiols do not bind strongly to ITO.8 Our approach to surface organizing a dipole at the ITO surface can change the work function of that material, directly affecting its hole injection propensity in a device. The reaction of these organics could provide a means to control injection propensity in a device. Surface adsorption of thiols do not bind strongly to ITO.8

We have also found that these surface tin amides can react with acetylenes to give the corresponding surface bound acetylidy derivatives, but slowly. The elementary reaction is given in eq 1.

**Experimental Section**

**General.** Our UHV chamber is equipped with a Mattson Research Series Fourier transform infrared spectrometer (FTIR), a quadrupole mass spectrometer (QMS), and an XPS spectrometer. ITO on glass (Colorado Concept Coatings, 15 Ω, 1500 Å) was cleaned by sonication in detergent and then rinsing successively with water, hot trichloroethylene, acetone, and methanol. Slides thus treated were stored under vacuum and then bombarded with Ar+ ions after transfer into UHV to remove residual organics. XPS analysis of the cleaned ITO showed the Sn/In ratio to be ca. 6%. The In signal serves as an internal standard for determination of surface tin complex stoichiometries, which is described below. The preparation of a surface tin acetylide by metathesis of tin acetylides in solution from tin amides17 or phenols (pK\textsubscript{a} ≈ 5)16 or phenols (pK\textsubscript{a} ≈ 10)14 are more acidic than the tert-butyl alcohol “leaving group” (pK\textsubscript{a} ≈ 18)14 and kinetic barriers to proton transfer between the oxygens of reagent and ligand are low.11 By these precedents, metathesis should be possible with arythiols (pK\textsubscript{a} ≈ 6),15 but surface modification with weakly acidic carboxylic acids may not succeed. For example, the preparation of a surface tin acetylide by metathesis between an acetylene (pK\textsubscript{a} ≈ 25)16 and a surface tin acetylide would not be anticipated. However, the preparation of tin acetylides in solution from tin amides19–21 (for the amine “leaving group,” pK\textsubscript{a} ≈ 36),22 is well-known, and the reaction between tetrakis(diethylamino)tin (1) and silica, followed by treatment with an acetylene at elevated temperature, has been reported23,24 to yield surface bound tin monocarbonyl. Unfortunately, although qualitative X-ray photoelectron spectroscopic (XPS) data were obtained, which do show the presence of C and Sn on the silica surface, no direct evidence was offered for the chemical reaction between 1 and silica, nor was the stoichiometry of any resulting surface bound materials reported. It was therefore important, as a starting point, to elucidate details of the chemistry of 1 with an hydroxylated surface, since metathesis would give surface bound products of comparable stoichiometry. We report herein details of the reaction between 1 and hydroxylated ITO, both under “normal” laboratory conditions and in ultrahigh vacuum (UHV). We find that surface bound tin amides are indeed formed and that the composition of these amides evolves with increasing temperature of the surface. We have also found that these surface tin amides can react with acetylenes to give the corresponding surface bound acetylidy derivatives, but slowly.

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raphy and mass spectrometry (GC) after 1 h. Gas chromatography was performed on a HP 6890N instrument equipped with a HP 5973 mass selective detector. A solution of trimethylsilylacetylene (3.6 mmol, 0.354 g) in diisopropylamine (5 mL) was stirred under nitrogen at 0 °C. A second solution of 4-iodo-(trifluoromethyl)benzene (3.0 mmol, 0.816 g), palladium dichloride (0.06 mmol, 0.0106 g), triphenylphosphine (0.42 mmol, 0.221 g), and copper(I) iodide (0.15 mmol, 0.029 g) in diisopropylamine (4 mL) was added after 1 h. The mixture was concentrated by rotary evaporation. The residue was dissolved in methanol (2.5 mL) containing pulverized KOH (0.4 mmol, 0.026 g). GC analysis indicated removal of the silyl protecting group within 30 min. The reaction mixture was diluted with water (4.8 mL), extracted with ether, and the organic phase was washed with water and brine. The dried (MgSO4) ether was removed by distillation under nitrogen to give 0.236 g of the product (1.4 mmol, 70%) as a clear liquid.1H NMR (300 MHz, CDCl₃): δ 7.58 (s, 4 H), 3.18 (s, 1 H).

IR (neat): 3306, 1624, 1612, 1408, 1326, 1171, 1129, 1067, 1017, 843 cm⁻¹.

**Table 1. X-ray Photoelectron Spectral Analysis of the Reaction between ITO and 1**

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>complex obsd.</th>
<th>atomic species</th>
<th>binding energy (eV)</th>
<th>atomic ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>multilayer of Sn(NEt₂)₄, 1</td>
<td>Sn(3d₅/₂)</td>
<td>487.5</td>
<td>C/Sn = 16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C(1s)</td>
<td>285.3, 286.0</td>
<td>C/N = 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N(1s)</td>
<td>399.1</td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>mixture of 2 and 3 (1:4)</td>
<td>Sn(3d₅/₂)</td>
<td>487.5</td>
<td>C/Sn = 9.3, C/N = 4.2, N/Sn = 2.1</td>
</tr>
<tr>
<td>[ITO]⁻[O]⁻Sn(NEt₂)₂, 2</td>
<td>C(1s)</td>
<td>286.7, 287.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N(1s)</td>
<td>400.6</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>mixture of 3 and 4 (1:1.5)</td>
<td>Sn(3d₅/₂)</td>
<td>486.9</td>
<td>C/Sn = 5.9, C/N = 4.0, N/Sn = 1.4</td>
</tr>
<tr>
<td>[ITO]⁻[O]⁻Sn(NEt₂)₂, 3</td>
<td>C(1s)</td>
<td>284.6, 285.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N(1s)</td>
<td>399.1</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>mixture of 3 and 4 (1:9)</td>
<td>Sn(3d₅/₂)</td>
<td>486.6</td>
<td>C/Sn = 4.6, C/N = 4.0, N/Sn = 1.1</td>
</tr>
</tbody>
</table>

- **Notes**
  - a Calibrated against In(3d₅/₂).
  - b Experimental sensitivity factors determined from atomic ratios in the defined species Sn(NEt₂)₄ (1).

a nitrogen-filled glovebox using a Midac Illuminator FTIR spectrometer equipped with a Surface Optics specular reflectance accessory.

**1-Ethynyl-4-(trifluoromethyl)benzene.** A solution of 4-iodo-(trifluoromethyl)benzene (3.0 mmol, 0.816 g), palladium dichloride (0.06 mmol, 0.0106 g), triphenylphosphine (0.42 mmol, 0.221 g), and copper(I) iodide (0.15 mmol, 0.029 g) in diisopropylamine (5 mL) was stirred under nitrogen at 0 °C. A second solution of trimethylsilylacetylene (3.6 mmol, 0.354 g) in diisopropylamine (2 mL) was added by syringe. The reaction was warmed to room temperature and stirred vigorously. Additional diisopropylamine (4 mL) was added after 1 h. Gas chromatography and mass spectrometry (GC–MS) analysis showed the coupling reaction to be complete after a total of 2.5 h. The reaction mixture was concentrated by rotary evaporation. The residue was suspended in hexanes (15 mL), filtered through Celite, and concentrated again by rotary evaporation. The resulting brown liquid was distilled to give 0.479 g (2 mmol, 66%) of 1-(trimethylsilyl)ethynyl-4-(trifluoromethyl)benzene as a colorless oil (1H NMR [300 MHz, CDCl₃]: δ 7.50 [s, 4 H], 0.25 [s, 9 H]), which was then dissolved in methanol (2.5 mL) containing pulverized KOH (0.4 mmol, 0.026 g). GC–MS analysis indicated removal of the silyl protecting group within 30 min. The reaction mixture was diluted with water (4.8 mL), extracted with ether, and dried (MgSO₄). The ether was removed by distillation under nitrogen to give 0.236 g of the product (1.4 mmol, 70%) as a clear liquid.1H NMR (300 MHz, CDCl₃): δ 7.58 (s, 4 H), 3.18 (s, 1 H).

**Figure 1.** Infrared spectra of 1 on ITO: (a) multilayer of 1 prepared in UHV; (b) film of 1 evaporated on ITO at –78 °C at 10⁻⁴ Torr.
Results and Discussion

The reaction between ITO and 1 was studied in UHV to determine the stoichiometry of surface complex formation at low temperature and to elucidate the thermal evolution9 of such surface tin amide species. Deposition of 1 was accomplished from the vapor phase onto the hydroxylated ITO surface at 185 K. XPS analysis showed complete attenuation of the In(3d5/2) and O(1s) core level signals, indicative of formation of a multilayer of 1 (see Table 1). Under these conditions, the Sn(3d5/2) signal measured is due entirely to 1, and C(1s)/Sn(3d5/2) and N(1s)/Sn(3d5/2) sensitivity factor ratios can be determined experimentally according to the stoichiometry of 1. The FT-RAIRS spectrum of multilayer 1 (recorded at 150 K) showed prominent peaks for νC–H at 2952 and 2927 cm⁻¹ and two weaker, broader peaks centered at 2867 and 2819 cm⁻¹ (Figure 1a); this pattern is similar to that recorded for a film of 1 evaporated onto conventionally prepared ITO at −78 °C and 10⁻⁴ Torr (2962, 2925, 2861, and 2831 cm⁻¹; Figure 1b). Thermal desorption of excess 1 was accomplished at 293 K over 15 min, and the composition of the chemisorbed tin amide was determined by XPS to be a mixture of tris-amide [ITO]-[O]1-Sn(NEt2)3, 2, and bis-amide [ITO]-[O]1-Sn(NEt2)2, 3 (C/Sn) 9.3, N/Sn) 2.1, 2:3 = 1:4, Table 1). Whereas O(1s) signals for lattice oxygens of ITO were again apparent, the signal for surface OH was substantially lost, showing that this functionality was consumed on formation of 2/3. The FT-RAIRS spectrum of 2/3 (recorded at 150 K) showed a prominent peak for νC–H at 2970 cm⁻¹ and two weaker, broader peaks centered at 2915 and 2876 cm⁻¹ (Figure 2). Heating the substrate to 380 K for 10 min caused further surface OH group reaction, to yield a 1.5:1 mixture of 3 and monoamide species [ITO]-[O]1-Sn(NEt2), 4 (C/Sn = 5.9, N/Sn = 2.1, 2.3 = 1:4, Table 1). Heating the initial mixture of 2 and 3 to 293 K for 10 h or to 450 K for 10 min gave 3 and 4 (C/Sn = 4.6, 2:3 = 1:9, Table 1). This stepwise reactivity of surface tin amides with OH groups on ITO (Scheme 1) closely parallels that of their surface Sn alkoxide analogues on this surface10 and on others of low hydroxyl group content.27 The C(1s) and N(1s) binding energies of component complexes were determined by deconvolution

of the corresponding XP spectra of mixtures (Figures 3 and 4). Deconvolution of C(1s) binding energy data for 1 was done with the assumption that the intensities for the two types of carbon signals in the ethyl group, N-CH$_2$-CH$_3$ and N-CH$_2$CH$_3$, were equal; binding energy differences obtained for these carbons were the same (0.7 eV) as those reported for ethylamine. Carbon(1s) binding energies for 3 and 4 were similarly obtained from deconvolution of the XP spectra measured for material heated to both 380 and 450 K, taking into account relative amounts of 3 and 4 present at these temperatures (Table 1) as determined from integration of total C(1s), N(1s), and Sn(3d$_{5/2}$) signals. Binding energies for 2 were obtained analogously from data for material warmed to 293 K.

Nitrogen(1s) binding energies for individual amide complex components were also determined based on deconvolution of spectra weighted according to relative amounts of amide complexes present (Figure 4), though error in assignment for N(1s) binding energies is likely to be higher than that for C(1s) (for C(1s) error is ±0.2 eV), given the 4-fold higher signal-to-noise ratios measured for the latter element. Fitting N(1s) peaks of 2 and 3 using binding energies of 1 and 4 served as an independent validation of peak position assignments made based on integration ratios; both deconvolution procedures gave similar peak position values, within experimental error.

Figure 3. C(1s) XP spectra for surface tin amide species: (a) multilayer of 1; (b) substrate heated to 293 K, showing a mixture of 2 (higher binding energy peaks) and 3 (1:4); (c) substrate heated to 380 K, showing a mixture of 3 (higher binding energy peaks) and 4 (1:1.5); (d) substrate heated to 450 K, showing a mixture of 3 and 4 (1:9).

In a parallel series of experiments, samples of ITO/glass were cleaned and dried under conventional conditions and were placed in a simple reactor connected to reservoirs of \(1\) and a particular phenylacetylene. This tube could be evacuated and either heated with external heating tape or cooled by externally applied dry ice. A multilayer of \(1\) was deposited on the ITO substrate at \(-78^\circ C\) by evaporation from a reservoir held at \(55^\circ C\) at \(\sim 10^{-4}\) Torr (IR: \(\nu_{C-H} = 2962, 2925,\) and \(2831\) cm\(^{-1}\); Figure 3a). Excess \(1\) was removed in vacuo at room temperature to give \(2/3\), by analogy with material produced by similar thermal processing in UHV.

Acetylides are interesting targets for possible surface dipole introduction in the context of device behavior modification through work function change. Because the Sn–acetylide bond is linear,\(^{17,29}\) binding a substituted acetylide moiety to ITO might optimize the effective dipole moment normal to the surface\(^{5,6,30,31}\) imparted by surface molecular coordination. (In contrast, because the Sn–S–C bond is bent,\(^{17,32,33}\) conformational variation in surface thiolate geometries might give rise to net surface dipole normal components that are far smaller than those expected based on the dipole moment of the free ligands.)

Samples of \(2/3\) were exposed to vapor of each of a series of reactants to study the reaction pathways and product distributions.

![Figure 4](image.jpg)

**Figure 4.** N(1s) XP spectra for surface tin amide species: (a) substrate heated to 293 K, showing a mixture of \(2\) (higher binding energy peaks) and \(3\) (1:4); (b) substrate heated to 380 K, showing a mixture of \(3\) (higher binding energy peaks) and \(4\) (1:1.5); (c) substrate heated to 450 K, showing a mixture of \(3\) and \(4\) (1:9).

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of substituted phenylacetylenes (p-X-C6H4C≡CH; X = H, F, CF3, OCH3, and NO2), with substrate cooling to form multilayers. The multilayers were then desorbed in vacuo, at room temperature, to yield the surface acetylides (for 1-ethynyl-4-nitrobenzene, the reservoir was warmed for initial deposition, as was the substrate for multilayer desorption). Conversion of 2/3 to the corresponding acetylides (5/6) was slow at 10⁻⁴ Torr, perhaps because of a relatively high kinetic barrier to proton transfer from the carbon acid to the amide ligand in a weakly bound tin–acetylene complex intermediate (8, Scheme 2). Exchange was, however, complete at this reaction pressure. Product tin acetylides were identified by DRIFT,
noting the introduction of peaks characteristic of the various acetylenes and the disappearance of $\nu_{C-H}$ signals both for 2/3 and for the terminal C–H bond of the free acetylenes (Figure 5). In control experiments, it was found that no surface acetylenic materials remained on the ITO surface in the absence of 2/3, following simple evacuation.

Attempts were made to measure the stoichiometry of tin acetylide formation by metathesis in UHV, but they were hampered by slow ligand exchange rates, which are likely to be exacerbated by low residence times, expected for weak complexation of the acetylene to tin, and at operating background pressures $\leq 10^{-7}$ Torr. Nonetheless, partial metathesis could be observed for reasonable exposure times and pressures. For example, a sample of 3/4 (1:9) prepared from 1 by heating to 450 K was cooled to 190 K and exposed to 1-ethynyl-4-nitrobenzene for 20 min at $2 \times 10^{-7}$ Torr, which gave a multilayer of the acetylene on the substrate (Table 2). Thermal desorption of excess acetylene was accomplished at 293 K over a period of 10 min. Following two further cycles of dose/desorption, XPS analysis (Figure 6) showed that metathesis to the corresponding surface tin acetylides, 6d/7d, was about one-third to one-half complete, based on comparative nitro group N(1s) and O(1s) data (Table 2); we have noted similar requirements for multiple dose/desorption cycles to ensure complete metathesis even using kinetically more reactive systems, such as carboxylic acids or phenols.13,36

Conclusions

Synthesizing a surface tin amide complex on ITO enables strong bonding of substituted ary lacetylenes to the ITO as surface tin acetylides. Since previous work has shown that acetylenic group substitution in a thiol can lead to large changes in the work function of gold,6 it is now important to determine how acetylide coordination can affect the work function of an ITO electrode to which it is indirectly bonded. Accordingly, ultraviolet photoelectron spectroscopic measurements are now in progress, and organic light-emitting devices are being constructed in UHV so that device-characteristic determinations can be made using these materials.

Acknowledgment. The authors thank the National Science Foundation and the New Jersey Center for Optoelectronic Materials for their support of this research.

Supporting Information Available: The N(1s) XPS spectrum of the multilayer of tetrakis(diethylamino)tin (1); the Sn(3d$_{5/2}$) XPS spectra of [ITO]-[O]$_1$–Sn(NEt$_2$)$_x$ 2, [ITO]-[O]$_1$–Sn(NET$_2$)$_x$, 3, and [ITO]-[O]$_1$–Sn(NET$_2$)$_x$, 4; and the IR spectra (3800–800 cm$^{-1}$) of multilayer 5b/6b, 5c/6c, 5d/6d, and 5e/6e. These materials are available free of charge via the Internet at http://pubs.acs.org.

LA010495L