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Influence of indium-tin oxide surface structure on the ordering and coverage of carboxylic acid and thiol monolayers

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Abstract

This paper analyses the variability of self-assembled monolayers (SAMs) formation on ITO depending on the substrate surface features. In particular, we report on the formation of carboxylic acid- and thiol-based SAMs on two lots of commercially prepared indium-tin oxide (ITO) thin films. Contact angle measurements, electrochemical experiments, and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy showed that the quality of monolayers formed differed substantially between the two ITO batches. Only one of the two ITO substrates was capable of forming well-organized thiol- and carboxylic acid-based SAMs. In order to rationalize these observations, atomic force microscopy and x-ray diffraction analyses were carried out, and SAMs were prepared on ITO substrates fabricated by sputtering in our laboratories. An attempt was made to influence the film microstructure and surface morphology by varying substrate temperatures during ITO deposition. Good-quality thiol and carboxylic acid SAMs were obtained on one of the ITO substrates prepared in-house. While our characterization could not single out conclusively one specific parameter in ITO surface structure that could be responsible for good SAMs formation, we could point out homogeneous surface morphology as a relevant factor for the quality of the SAMs. Evidence was also found for ITO crystallographic orientation to be a parameter influencing SAMs organization.

M This article includes supplementary information in the online edition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Indium-tin oxide (ITO) has been utilized in many different technological applications, including organic-light

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emitting diodes (OLEDs) [1], optical devices (liquid crystal displays) [2], electroluminescent devices [3], sensors [4], DNA detection [5], solar applications [6], electrodes [7]. Many of these applications require a self-assembled monolayer (SAM) to form on ITO substrates. ITO surface roughness is often a concern, as it can prevent the formation of a well-packed

and ordered SAM [8]. Moreover, ITO properties depend crucially on the film preparation and are often difficult to reproduce [9,10]. Here we present a study aimed at correlating properties of ITO substrates with the quality of SAMs formed on their surface.

SAMs have been formed on ITO starting from organosilanes, carboxylic acids, phosphonic acids and thiols [8-15]. It is interesting to note that while the type of bond formed between silanes, carboxylic acids and phosphonic acids on ITO seems to be understood (condensation with surface hydroxyls), the interaction between thiols and ITO surface has not been clarified yet. Nevertheless, SAMs formed with thiols, carboxylic acids and silanes have been shown to be ordered in many instances [8, 16]. This is an intriguing result, given the known surface roughness of ITO, and the variability of ITO surface properties [8,9]. In our experience, monolayers formed using the same procedure on ITO purchased under the same product number from the same company showed amazing variability in terms of ordering and packing. Still, even though SAMs on ITO have been extensively characterized, we could not find studies in the literature that correlate differences in monolayer packing and organization with differences in the properties of the ITO substrate. Understanding such a correlation seems to be crucial: it could explain the variability that can be observed when preparing monolayers using the same protocol on different types of ITO, and it would help to determine which type of ITO to use for specific applications. To shed some light on this problem, in this paper we report on the influence of morphology, roughness, and crystallinity of different commercial and locally prepared ITO samples in relation to their ability to form well-organized SAMs. We compare the results obtained with different techniques (contact angle measurements, electrochemistry, NEXAFS spectroscopy), in order to obtain a detailed picture of the ordering and coverage of thiol- and carboxylic acid-based SAMs on ITO.

2. Materials and methods

2.1. ITO substrate preparation and characterization

Commercial ITO samples⁶ were purchased from Delta Technologies, Limited. Two different batches of samples were purchased, with the same product number (CG-51IN-S115). The nominal film thickness provided by the company was \approx 170 nm. Home-made ITO films having a thickness of \approx 120 nm were prepared by RF magnetron sputtering on glass substrates (SF-10, Schott Glass). The 2.54 cm diameter ITO target (90 wt% In₂O₃/10 wt% SnO₂, Superconductor Materials, Inc.) was sputtered at 4 W cm⁻² in a 4 mTorr argon atmosphere. The substrate was positioned at a distance of 6 cm below the target. Films were deposited at varying substrate temperatures (25, 85, 170 and 350°C) in an attempt to influence film morphology and crystallographic texturing. After deposition, the films were annealed at 440 °C for 60 min in a reducing atmosphere ($p_{oxygen} \approx 10^{-17}$ atm) in

order to achieve full crystallinity and improve conductivity. Film resistivity was investigated by a standard four-point probe technique. Film crystallinity was evaluated by x-ray diffraction (XRD) using a Bruker AXS D-5000 equipped with an area detector.

2.2. Hexadecanethiol (C16-SH) and carboxylic acids (C16-COOH and C18-COOH) monolayer preparation

ITO slides were cleaned with UV-Ozoneolysis (UVO) for 5 min (UVO-cleaner UVO-60, model number 42, Jelight Company, Inc) and immediately immersed in a neat solution of *n*-hexadecanethiol (C16-SH, supplied by Sigma-Aldrich) or a 10 mM ethanolic solution of palmitic (C16-COOH) or stearic (C18-COOH) acid (both supplied by Sigma-Aldrich). The samples remained in solution overnight and were subsequently rinsed with copious amounts of EtOH and blow-dried with nitrogen gas. The specimens were then kept in sealed containers and analysed within two days from the time of preparation.

2.3. Contact angle measurements

Contact angle experiments were performed using a Ramé-Hart contact angle goniometer (model 100–00) equipped with a CCD camera and analysed with the Ramé-Hart software. Advancing contact angles were measured by carefully depositing $8 \mu l$ of deionized (DI) water on the sample surface, whereas receding angles were measured after removing $4 \mu l$ of water from the deposited drop. These operations were repeated at least three times on two different samples, and the results were averaged.

2.4. Electrochemistry

The electrochemical measurements were performed on an EG&G Princeton Applied Research instrument (Potentiostat Model 273A). The electrochemical setup consisted of a three-electrode cell consisting of $Ag_{(s)}/AgCl$ as the reference electrode and a Pt wire as the counter electrode. The area of the working electrode was $\approx 1 \text{ cm}^2$. Cyclic voltammetry experiments were performed in 10 mM TRIS buffer (supplied by Fischer), using a scan rate of 50 mV s⁻¹.

2.5. Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy

NEXAFS spectroscopy experiments were carried out at the NIST/Dow Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS-BNL) using a partial electron yield (PEY) intensity detector (grid bias of -150 V) and a charge compensation of $25 \,\mu$ A. NEXAFS spectra were collected in the PEY mode (i.e. Auger electrons) at several incident angles (θ , angle between the sample normal and the electric vector of the x-ray beam), ranging from 20° to 90° (see scheme 1 and text), with photon energies varying from 240 to 400 eV and a variable resolution and integration time; the highest resolution, 0.1 eV and 1 s⁻¹ integration time were used in the region closer to the C-edge, from 280 to 300 eV. All NEXAFS spectra were normalized to the incident photon flux by dividing the raw PEY NEXAFS signal by

⁶ Identification of a commercial product is made only to facilitate reproducibility and to adequately describe procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the procedure.



Scheme 1. Relation between polarization vector p of the x-ray beam and orientation of the monolayer deposited on the ITO sample. The cartoon shows two different geometries, with incident photon angle of $(a) 30^{\circ}$ and $(b) 90^{\circ}$. In (b), the direction of C–H an C–C stretchings are shown, thus indicating that in the normal incidence configuration, C–H stretchings are parallel to p, if the monolayer stands perpendicular off the sample surface.

the monochromator transmission function that was determined from an in situ gold coated 90% transmission grid placed in the path of the x-rays [17]. Moreover, NEXAFS spectra shown in figures 3, 4 and 7 were further normalized in order to compare the relative intensities of the different peaks: the spectra were pre-edge subtracted and then post-edge normalized to unity in order to achieve a common height of the carbon-edge jump (pre-edge was fitted using 5 points centred at 280 eV and post-edge at 320 eV) [18]. From NEXAFS spectra, average tilt angle of the SAMs has been evaluated using the method described in the Supporting Information.

2.6. Atomic force microscopy (AFM)

Samples for AFM were sonicated for 20 min in EtOH and dried under a N_2 stream immediately prior to the analysis. Atomic force micrographs were obtained on a Digital Instruments Nanoscope IIIa in tapping mode using Al-coated tips (BS-Tap300, Budget Sensors). Images shown in this paper were flattened (2nd order flattening). Root-mean square (RMS) roughness was calculated in the selected regions shown in the figures using the AFM software.

3. Results and Discussion

Two samples of commercial ITO (named ITO-1 and ITO-2), both supplied by Delta Technologies (listed under the same product number CG-51IN-S115), were used to prepare SAMs of alkanethiols (C16-SH, i.e. hexadecanethiol) and carboxylic acids (C16-COOH and C18-COOH, i.e. palmitic and stearic acid, respectively). The packing and the ordering of the monolayers, and the amount of molecules adsorbed on both substrates were analysed by carrying out contact angle, cyclic voltammetry and NEXAFS experiments.



Figure 1. Advancing (solid black) and receding (diagonal pattern) contact angles measured using DI water on ITO-1 and ITO-2 covered with carboxylic acid- and thiol-based SAMs.

3.1. Contact angle

Advancing and receding contact angles using DI water were measured on ITO-1 and ITO-2 before and after the formation of thiol and carboxylic acid monolayers. Contact angle measurement represents a powerful and simple tool to determine the degree of packing of the monolayers formed on the surface. While in an ideal case, where the surface is physically smooth, chemically homogeneous, rigid and inert with respect to the liquid employed, only one contact angle should be measured [19], in reality, one measures socalled advancing and receding contact angles. The difference between the advancing and the receding contact angles is referred to as the contact angle hysteresis; it reflects a measure of the sample roughness and heterogeneity of the surface, packing of the monolayer formed [20], and any possible rearrangement of the surface due to the interaction with the probing liquid [19].

We first measured the contact angle on ITO-1 and ITO-2 immediately after the UVO treatment. The advancing contact angle was $<10^{\circ}$, thus indicating that ITO surface was very hydrophilic. Measuring the contact angle a few minutes after the UVO treatment resulted in higher values (15–20° after ten minutes), indicating that sample contamination from impurities present in air occurred rather rapidly. After a few hours of exposure to air, contact angles ranging between 75° and 80° were found. These results underline the importance of UVO-cleaning the ITO films right before the monolayer preparation and also suggest that SAMs should be deposited immediately after the UVO treatment.

Advancing and receding contact angles measured on ITO-1 and ITO-2 covered with different types of monolayers are shown in figure 1. The results represent averages over contact angles measured on two different samples, using at least three droplets per sample. On all samples, a contact angle hysteresis of $15^{\circ}-20^{\circ}$ was found, indicating that the surface was quite inhomogeneous. None of the SAMs prepared showed a contact angle higher than 90° , a value that one would expect to detect



Figure 2. Charging currents measured in 10 mM Tris, scan rate= 50 mV s^{-1} . The potential was measured versus Ag/AgCl reference electrode. (*a*) Currents measured before and after preparation of carboxylic acid monolayers: on bare ITO (solid black line), ITO/EtOH (dashed black), ITO-1/C18-COOH (solid light grey line), ITO-1/C16-COOH (dashed light grey line), ITO-2/C18-COOH (solid grey line), ITO-2/C16-COOH (dashed grey line). (*b*) Currents measured before and after preparation of thiol monolayers: on bare ITO (solid black line), ITO-1/C16-SH (solid light grey line), ITO-2/C16-SH (solid grey line).

for a well-packed aliphatic SAM [8]. The highest contact angles ($\approx 70^{\circ}$) were observed on the carboxylic- and thiolbased SAMs on ITO-1. This value is indicative of a partially covered surface. The different chain length used for carboxylic monolayers did not seem to affect the contact angle measured. Low contact angles were obtained on ITO-2 for all the SAMs prepared indicating that on this substrate SAMs covered the surface very sparsely, and were not well-packed. Thus, contact angle measurements revealed that only one type of commercial ITO supported somewhat packed SAMs.

3.2. Electrochemistry

Electrochemistry is often used as a convenient tool for determining the presence of SAMs on the surfaces of conductive materials. The changes in charging current were measured before and after SAM formation on ITO. The charging current (i_{charg}) is due to the electrical doublelayer formed at the interface between the electrode and the solution [21]; if a hydrophobic SAM is present on the electrode, the charging current should decrease due to the decrease in dielectric constant [14]. The results obtained for the measurements of the charging current (i_{charg}) on ITO-1 and ITO-2 before and after the formation of the carboxylic acid and thiol monolayers are shown in figures 2(a)and (b), respectively. In each graph, i_{charg} measured after the preparation of the SAMs is compared with icharg measured on bare ITO after UVO treatment, or ITO soaked in EtOH overnight (ITO/EtOH), depending on which solvent was used to prepare the monolayers. No difference was observed

between icharg measured on ITO-1 and ITO-2 in the absence of SAMs, thus only one curve for both samples is shown in each graph. The presence of EtOH did not affect icharg measured on ITO (figure 2(a)). When carboxylic acid SAMs were prepared on both ITO-1 and ITO-2, a decrease in i_{charg} was observed compared with bare ITO or ITO/EtOH (figure 2(a)). The difference between i_{charg} measured in the presence of C16-COOH or C18-COOH was negligible, but, in general, a larger decrease was observed for both carboxylic acids on ITO-1. This observation indicates that the SAMs formed on ITO-1 were more compact, or covered the ITO substrate more homogeneously, than those formed on ITO-2. This result thus confirms the trends obtained with contact angle measurements (figure 1). Similar information can be obtained from figure 2(b): compared with bare ITO, i_{charg} decreased more when C16-SH monolayer was deposited onto ITO-1 than on ITO-2, thus confirming again the results collected with contact angle experiments (figure 1).

3.3. NEXAFS

NEXAFS spectroscopy represents one of the most powerful techniques to determine the molecular organization of organic SAMs on virtually any type of substrate. As a result of the interaction of x-rays with the sample, core electrons are excited from a ground state (K or L shell) to an unoccupied antibonding molecular orbital (σ^* or π^*) when x-rays at the right energy hit the sample (e.g. \approx 290 eV for C, \approx 400 eV for N) [22]. The different spectral features observed correspond to the excitation of different types of bonds (e.g. 1s $\rightarrow \sigma^*$ transitions for C–H bonds occur at \approx 287 eV, whereas for C–C bonds at \approx 294 eV) [23, 24]. Thus, NEXAFS spectroscopy is very sensitive to the local environment of the excited atoms. Moreover, the peak intensities in the NEXAFS spectra depend on the orientation of the antibonding orbitals and the polarization direction of the x-ray beam: transitions that involve orbitals that are parallel to the electrical field of the x-ray beam absorb the radiation more strongly than those that are not parallel. Thus, if the molecules in the SAM formed on the surface are ordered (hence, they point roughly into one direction), it is possible to selectively excite different types of bond by changing the orientation of the sample relative to the beam [25]. This is shown in scheme 1: if the SAM- forming molecules are positioned perpendicularly to the surface, just like illustrated in the cartoon, increasing the incident beam angle (going from (a) to (b)) leads to an increase of the $1s \rightarrow$ $\sigma *$ for C–H and a concurrent decrease of the 1s $\rightarrow \sigma *_{C-C}$ signal

We used NEXAFS spectroscopy to analyse the ordering of the previously described thiol-, carboxylic acid SAMs on ITO-1 and ITO-2. The formation of ordered thiol and carboxylic acid SAMs on ITO was already studied using NEXAFS spectroscopy by Yan *et al* [8]. In their paper, the authors showed that both C15-SH and C17-SH monolayers prepared from either a neat solution or from vapors and C16-COOH and C18-COOH monolayers formed from an ethanolic solution (molarity non specified) were ordered. Our results will demonstrate that the ordering of the monolayers is strongly dependent on the type of ITO used for the experiment.

Figure 3 depicts NEXAFS spectra collected at 30° and 90° of C16-SH monolayer prepared on ITO-1 and ITO-2. The



Figure 3. Normalized PEY NEXAFS intensity of C16-SH monolayer on ITO-1 and ITO-2, recorded for photon incidence angles of 30° (dotted line) and 90° (dashed line). Insets — differential spectra (90° – 30°).

spectra were normalized according to the procedures described in the 'Materials and methods' section. Three main peaks are observed on these spectra: (1) a small peak at ≈ 285 eV, whose intensity does not change much when the photon incidence angle is varied. This peak has been attributed to either hybrid metal/alkane orbitals [26] or to carbonaceous impurities possessing C=C bonds present on the surface [27, 28]. (2) A peak located at ≈ 287.5 eV, which is attributed to transitions into Rydberg states [29], and can be more easily understood as the excitation of C–H bonds in saturated alkane chains [30]. (3) A peak located at ≈ 293 eV, which is related to the excitation of C–C bonds in saturated alkane chains [30].

The differences in ordering observed on the two samples are striking. Specifically, on ITO-1 a very consistent and strong increase in the PEY intensity of the peak located at \approx 287.5 eV and a parallel decrease of the larger peak located at \approx 293 eV is observed upon increasing the angle of incidence of the x-rays (θ). This trend was not as well defined on ITO-2. The differences between the two samples are highlighted better when the NEXAFS spectra collected at $\theta = 30^{\circ}$ are subtracted from those recorded at $\theta = 90^{\circ}$ (insets in figure 3). The difference in the intensity of the 1s $\rightarrow \sigma_{C-H}$ and 1s $\rightarrow \sigma_{C-C}$ peaks for the spectra measured at $\theta = 90^{\circ}$ compared with the spectra measured at $\theta = 30^{\circ}$ were much more pronounced on ITO-1 than on ITO-2. These results imply that the SAMs prepared on ITO-1 are well-organized and oriented closer to the surface normal, whereas the molecules in SAMs prepared on ITO-2 are presumably not well-organized; the alkyl chains of C16-SH are predominantly randomly oriented.

A similar trend is observed when carboxylic acid-based SAMs are deposited on the two ITO substrates. NEXAFS spectra collected at $\theta = 30^{\circ}$ and 90° of C18-COOH monolayer on ITO-1 are shown in figure 4. These spectra exhibit peaks similar to those observed in figure 3, and also a new feature located at \approx 288.6 eV. The latter signal arises due to the 1s \rightarrow π^* excitation of the C=O bonds present in the carboxylate groups [31]. The differential (90°–30°) spectrum relative to ITO-1 (cf left inset to figure 4) shows that the C–H and the C–C peaks increase and decrease, respectively, with increasing the incident angle of the x-ray beam. This indicates that the molecules in the carboxylic acid SAM on ITO-1 are ordered and oriented. The spectra relative to C18-COOH monolayer formed on ITO-2 are very different from those observed when C18-COOH SAMs were formed on ITO-1: the component at $\approx 287 \text{ eV}$ does not change in intensity at all when the angle is changed; also, the changes observed in the peak at $\approx 293 \text{ eV}$ are almost negligible. These observations are further confirmed by the differential spectrum shown in the inset. No major differences could be observed between the spectra collected at $\theta = 90^{\circ}$ and $\theta = 30^{\circ}$. Evidently, little or no chain organization was achieved when the C18-COOH SAM was formed on ITO-2.

In order to test the robustness of the ordering of carboxylic acid and thiol SAMs, we tested different alkane chain lengths and concentrations of the precursors in solution. While a good ordering was observed on C16-SH SAM formed on ITO-1 (see figure 3), no ordering was ever observed on either ITO-1 or ITO-2 when C16-COOH SAMs were prepared using the same conditions used for C18-COOH SAMs (data not shown). Only longer carboxylic acids could form ordered SAMs. A possible reason for this observation could be that thiol-based SAMs were deposited from neat solutions, whereas the carboxylic monolayers were deposited from 10 mM solutions. When the thiol concentration was decreased (from neat to 100 mM), no ordering was observed on either ITO-1 or ITO-2 (data not shown). Evidently, the very high concentration thiol solutions produced a well-packed monolayer that helped the chain alignment for shorter molecules. This behaviour is in contrast to typical conditions utilized in the formation of mercapto-based SAMs on gold substrates, where one works with concentration of the solute that is only 1-2 mM.

Quantitative information about the relative amount of molecules adsorbed for each SAM on the two ITO films and about tilt angles of the monolayers formed on ITO-1 can be



Figure 4. Normalized PEY NEXAFS intensity of C18-COOH monolayer on ITO-1 and ITO-2, recorded for photon incidence angles of 30° (dotted line) and 90° (dashed line). Insets are differential spectra (90° - 30°).



Figure 5. AFM images of ITO-1 (a) and ITO-2 (b). The z-scale is 20 nm for both samples. (c) XRD spectra of ITO-1 and ITO-2.

extracted from NEXAFS spectra. This will be discussed at the end of the next section.

3.4. Comparison with SAMs prepared on home-made ITO

Our previous experiments showed how relevant the ITO substrate was in determining the quality of the SAM formed. In order to shed more light on the role of the substrate in forming dense, well-organized SAMs, we needed to establish which ITO structural and compositional characteristics were important for the achievement of a good-quality SAM. The overall aim was to use this information for designing an optimal ITO surface for SAM adsorption.

The first and most direct difference that we could detect between the two commercial ITO-1 and ITO-2 films was their microstructure. Experiments using AFM revealed that while ITO-1 exhibited a regular granular morphology, ITO-2 showed larger features that disrupted the surface homogeneity (figures 5(a) and (b)). Some variation in crystallographic texturing was also observed (cf XRD spectra shown in figure 5(c)). ITO-1 exhibited more grains with $\langle 400 \rangle$ orientation normal to the sample surface than ITO-2 (in a randomly oriented sample, the $\langle 222 \rangle$ reflection is about 3 times higher than the $\langle 400 \rangle$ [32]). Although many authors (see for example [33, 34]) have studied how to obtain different crystallographic orientation on ITO by changing deposition conditions (e.g. substrate temperature, sputtering rate, O₂ pressure), we could not find any studies in the literature concerning the influence of such different crystallographic orientations on monolayer formation. Some studies of simple molecules (such as CO, CO₂, water, NH₂) adsorption on SnO were described in a review paper [35], and showed, for example, that there are differences in degree of water dissociation on SnO (110) and (101) single crystals. Considering that SnO is known to preferentially segregate on the surface of ITO [36], some of the results described in [35] may apply to the study of ITO too, and may thus indicate that different reactivity towards monolayer formation should be expected on samples showing different preferential crystallographic orientation. The thickness, sheet resistance, resistivity and RMS roughness for ITO-1 and ITO-2 are reported in table 1. Apparently, even though ITO-2 showed a more uneven structure, its RMS was lower than that measured on ITO-1. Considering that ITO-1 was the sample that exhibited the best SAM formation, this result seemed to suggest that a low RMS value was not

Table 1. Deposition temperatures, thickness, sheet resistance, resistivity and RMS roughness (calculated on $4 \mu m^2$ areas) of commercial and home-made ITO samples.

Samples	Deposition temperature (°C)	Thickness (nm)	Sheet resistance ($\Omegasq^{-1})$	Resistivity $\times ~10^4~(\Omega~\text{cm})$	RMS roughness (nm)
ITO-1	Unknown	170	11.1	1.89	3.4
ITO-2	Unknown	170	12	2.04	2.7
SF10-RT	25	120	21.7	2.60	2.5
SF10-85	85	120	16.7	2.00	2.0
SF10-170	170	120	19.7	2.36	1.6
SF10-350	350	120	15	1.80	17.2



Figure 6. AFM images of SF10-RT (*a*), SF10-85 (*b*), SF10-170 (*c*) and SF10-350 (*d*). The *z*-scale is 20 nm for images (*a*), (*b*) and (*c*), and 100 nm for image (*d*). (*e*): XRD spectra of SF10-RT, SF10-85, SF10-170 and SF10-350.

directly correlated to the quality of SAMs on the substrate. Differences in conductivity did not seem to be relevant in this regard either, considering that the two samples showed the same sheet resistance and thickness. Thus, from our data, it looked like the homogenous granular structure and the preferential crystallographic orientation of ITO-1 might have been responsible for good-quality SAM formation.

In an attempt to reproduce this type of morphology, we prepared sputtered ITO films at different deposition temperatures. The deposition temperature is known to influence the morphology and surface composition of ITO [10]. This parameter and the film resistivity of each sample are summarized in table 1; for comparison, the resistivities of ITO-1 and ITO-2 are also reported. Samples prepared at 85 °C and 350 °C had resistivities within 5% of the commercial samples, while the ITO films prepared at 25 °C and 170 °C showed 30% and 20% higher resistivities, respectively. AFM images of the prepared samples are shown in figure 6. None of them reproduced the same morphology detected on ITO-1. The sample prepared at the highest temperature (SF10-350) crystallized during deposition and exhibited a significantly rougher surface (RMS = 17 nm). At lower temperatures, the

ITO films replicated the linear ridges of the underlying SF10 substrate. These linear streaks began to fade at 170 °C. Grain size also increased for the 170 and 350 °C. The XRD spectra of the home-made samples are reported in figure 6(e). None of them showed the crystal orientation observed in sample ITO-1 (on all the spectra showed in figure 6(e), peak 222 was higher than 400).

We prepared thiol- and carboxylic acid-based SAMs on the four home-made samples, to see if we could establish a correlation between the quality of monolayers formed and the structural and morphological information collected before. We tested the molecular ordering in the SAMs deposited on the home-made ITO substrates by NEXAFS. Both thiol- and carboxylic acid-based SAMs were ordered only on one of the samples, SF10-170 (cf figure 7). Only on this sample did the C-H peak intensity at \approx 287.9 eV increase and the C-C peak at \approx 293.7 eV decrease with increasing the incident angle of the x-ray beam. This is evidenced by the inset plots to figure 7. Given the differences in sample morphology observed on the home-made SF10 samples, we suggest that the better quality of SAMs formed on this sample should be ascribed to its regular surface structure, which showed lower roughness,



Figure 7. Normalized PEY NEXAFS intensity of C16-SH and C18-COOH monolayer on SF10-170, recorded for photon incidence angles of 30° (dotted line) and 90° (dashed line). Insets are differential spectra ($90^{\circ}-30^{\circ}$).

increased grain size, and a more homogenous microstructure. As previously reported [10], differences in surface morphology can correspond to differences in surface composition (i.e. ratio of In/Sn/O at the surface), which could also be also responsible for differences in the quality of the SAM prepared.

A quantitative comparison of the overall quality of the SAMs formed on commercial ITO samples and on the locally prepared ITO films can be obtained using NEXAFS spectroscopy. In particular, it is possible to determine both the relative amount of molecules present on each substrate for each SAM, and the tilt angle of the ordered SAMs. The relative SAM coverage on the different ITO films can be extracted from the raw NEXAFS data by comparing the edge-jump, i.e. the difference between the pre- and post-edges defined loosely at 280 eV and 320 eV, respectively, measured for each sample. The magnitude of the edge-jump provides a convenient relative measure of the molecular density in the SAMs, assuming only SAM alkane chains are present on the surface. An example of the raw NEXAFS spectra for SAMs formed on the commercial samples is shown in figure 8. From the data it is evident that ITO-1 substrates exhibit higher molecular coverages relative to the ITO-2 specimens, for both C16-SH and C18-COOH SAMs prepared under identical deposition conditions. In order to compare all the SAMs formed on each ITO substrate, we measured the height of the edge-jump and normalized this value per number of C atoms. We then normalized all the values to the SAM that gave the highest coverage (i.e. C16-SH on ITO-1). The results are shown in figure 9. On all the substrates, the coverage obtained for thiol SAMs was higher than that obtained for carboxylic acid SAMs, in agreement with the higher concentration used to form the thiol SAMS. The coverage obtained on the locally sputtered ITO films was comparable to that obtained on ITO-2. This indicates that the amount of molecules adsorbed was not directly related to the organization of the SAM obtained, since the same coverage was observed on SF10-170 and on ITO-2, but only on the former could organized SAMs be formed.

Using the procedure described in the Supporting Information, we extracted the values of the tilt angles of



Figure 8. PEY NEXAFS intensity (shifted to the same PEY intensity at the pre-edge, at 280 eV) recorded for photon incidence angle of 55° of C16-SH monolayer on ITO-1 (black solid line) and on ITO-2 (grey solid line), and of C18-COOH monolayer on ITO-1 (black dashed line) and on ITO-2 (grey dashed line).

molecules in SAMs by comparing the experimental C-H and C-C peak intensities (from the NEXAFS spectra) at different photon incidence angles with those calculated using the 'tilted chain model' [26]. The tilt angles obtained for the ordered thiol and carboxylic monolayers formed on ITO-1 and SF10-170 are summarized in table 2. These values refer to the angle measured between the alkyl chain in the SAM and the normal to the ITO surface, thus a lower tilt angle indicates that the SAM is oriented more perpendicularly to the surface. The tilt angles have been reported as calculated from both the C-H peak and the C-C peak. If the model used to evaluate the tilt angles applied perfectly to our real system, these two values should be the same. It is evident that this is not the case: in general, the values obtained from the C-H peak were higher than those obtained from the C-C peak, and this must be related to the non-perfect agreement between the tilted chain model and the real SAMs on ITO. It can be noted that the tilt angles obtained on the locally prepared SF10-170 and those obtained



Figure 9. Relative coverage of thiol (solid black) and carboxylic acid (diagonal pattern) SAMs on ITO-1, ITO-2, SF10-25, SF10-85, SF10-170, SF10-250. Each SAM coverage was first normalized per number of C atoms and then to the C16-SH SAM formed on ITO-1 (which was assigned a formal '100%' coverage value).

Table 2. Tilt angles calculated from NEXAFS spectra as described in the supplementary information section.

Samples	Monolayer	Tilt angle (CH) (°) $^{(a)}$	Tilt angle (CC) (°) $^{(a)}$
ITO-1	C16-SH	58 ± 5	41 ± 5
ITO-1	C18-COOH	72 ± 5	45 ± 5
SF10-170	C16-SH	61 ± 5	45 ± 5
SF10-170	C18-COOH	61 ± 5	53 ± 5

^aThe tilt angle is defined as the angle formed between the alkyl chain of the SAMs and the normal to the ITO surface.

on the commercial ITO-1 are comparable, within the error bars associated to each angle. The same observation holds for the comparison between carboxylic acid- and thiol-based SAMs. This indicates that even though fewer C18-COOH molecules are present on ITO surface than C16-SH (e.g. cf figure 9), the chains are oriented in similar directions for both SAMs. The tilt angles obtained for both carboxylic and thiol SAMs are higher than those reported in the literature for alkylthiol SAMs on clean gold ($\approx 35^\circ$) [28]. We believe this observation can be explained by considering a rather large lateral inhomogeneity of the SAMs (as deduced from the contact angle data) and the fact that NEXAFS data are collected from an area of ≈ 0.5 mm².

4. Conclusions

The difficulty in reproducibility of thin film formation on ITO is well known. Although many authors have analysed the influence of deposition conditions of ITO on its surface features, not many studies can be found that try to link such variability in surface features with monolayer formation on ITO. We have addressed the issue by studying thiol and carboxylic acid SAMs with 16 or 18 carbon atom alkyl chains. SAMs were deposited on samples coming from two batches of commercial samples (named ITO-1 and ITO-2), supplied by the same company under the same

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product number. SAMs were also prepared on ITO samples prepared in-house at varying deposition temperatures. To determine molecular ordering and packing, the deposited monolayers were analysed by contact angle, charging current measurements, and NEXAFS spectroscopy. Contact angle and cyclic voltammetry experiments showed that only on ITO-1 could somewhat packed thiol and carboxylic acid monolayers be formed. Moreover, NEXAFS spectroscopy proved that well-ordered SAMs were observed for thiols and carboxylic acids on ITO-1 and the ITO film prepared in-house at 170 °C (SF10-170), even though a lower coverage for both thiol and carboxylic acid based SAM was obtained on SF10-170 compared with ITO-1. Tilt angles of $\approx 45^{\circ}$ and $\approx 55^{\circ}$ were obtained for SAMs formed on ITO-1 and SF10-170, respectively, indicating that the molecules in the SAMs stood more perpendicularly on the surface of the commercial ITO film. In order to understand which factors govern the quality of the SAM formed on ITO, we characterized the ITO films with AFM and XRD. Microstructural homogeneity appeared to be important for both ITO-1 and SF10-170. On ITO-1, a preferential crystallographic orientation was observed, which was not present on ITO-2. Surface roughness turned out to be the most difficult parameter to correlate with adlayer order: between the two commercial samples, best monolayers were formed on ITO-1, which was on average 0.6 nm rougher than ITO-2, whereas when samples were prepared locally in controlled conditions, the most ordered monolayers were formed on SF10-170, which was the smoothest sample. We cannot single out only one of these parameters as the most influential on monolayer formation, but we can see that a systematic variation in preparative procedures can be used to reproduce conditions conducive to formation of wellordered SAMs on ITO. This finding provides a basis for a systematic study of the influence of surface properties of ITO such as crystallographic orientation, grain size, composition, roughness, on thin film preparation, which is still an open question in the vast literature on ITO.

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Supplementary information

A detailed description of the tilt-angle calculation based on the NEXAFS spectra and a figure that gives an example of the procedure are available in the online version of this paper at http://stacks.iop.org/jphysd/40/4212

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