Effect of Time and Deposition Method on Quality of Phosphonic Acid Modifier Self-assembled Monolayers on Indium Zinc Oxide

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ABSTRACT

Phosphonic acid (PA) self-assembled monolayers (SAMs) are utilized at critical interfaces between transparent conductive oxides (TCO) and organic active layers in organic photovoltaic devices (OPVs). The effects of PA deposition method and time on the formation of close-packed, high-quality monolayers is investigated here for SAMs fabricated by solution deposition, micro-contact printing, and spray coating. The solution deposition isotherm for pentafluorinated benzylphosphonic acid (F₅BnPA) on indium-doped zinc oxide (IZO) is studied using polarization modulation-infrared reflection-absorption spectroscopy (PM-IRRAS) at room temperature as a model PA/IZO system. Fast surface adsorption occurs within the first min; however, well-oriented high-quality SAMs are reached only after ~48 h, presumably through a continual process of molecular adsorption/desorption and monolayer filling accompanied by molecular reorientation. Two other rapid, soak-free deposition techniques, micro-contact printing and spray coating, are also explored. SAM quality is compared for deposition of phenyl phosphonic acid (PPA), F₁₃-octylphosphonic acid (F₁₃OPA), and pentafluorinated benzyl phosphonic acid (F₅BnPA) by solution deposition, micro-contact printing and spray coating using PM-IRRAS. In contrast to micro-contact printing and spray coating techniques, 48-168 h solution deposition at both room temperature and 70 °C result in contamination- and surface etch-free close-packed monolayers with good reproducibility. SAMs fabricated by micro-contact printing and spray coating are much less well ordered.

KEYWORDS: Self-assembly; phosphonic acid deposition methods; indium zinc oxide (IZO); organic photovoltaic (OPV)

INTRODUCTION

Organic/metal oxide interfaces affect the performance of many kinds of organic electronic devices including organic photovoltaics (OPVs)¹⁻⁴, organic light-emitting diodes (OLEDs)^{5,6} and field-effect transistors (FETs).⁷⁻¹¹ Small-acid self-assembled monolayers (SAMs) are widely used as modifiers at organic/metal oxide interfaces to control interface properties such as heterogeneity,^{1-3,12,13} work function,² surface wetting¹⁴ and charge-transfer rates.¹⁵ For many applications and oxides, phosphonic acids (PAs) are the most desirable linkers among possible candidates¹⁶ and have been used commonly for oxide surface modification, because they form close-packed and stable monolayers.^{2,4,17-25} Considerable recent work has been published on PA modification of transparent conductive oxide (TCO) surface properties to improve wettability, alter work function, and enhance device performance²⁶ for use as the bottom contacts in organic photovoltaic devices. Several studies have focused on determination of PA molecular orientation, which is believed to play an important role in work function and charge-transfer rate control.¹⁵ While this detailed fundamental understanding of the molecular orientation for PA monolayers now exists, a similar analysis focusing on the final quality of the resulting monolayer on TCO surfaces has not yet emerged. Monolayer formation mechanisms have been discussed for other types of systems over the past two decades;^{25,27-29} these are relevant and useful for understanding PA monolayer formation on TCO surfaces. As a classic model system, alkanethiol deposition on gold surfaces was studied by Poirer and Pylant.²⁹ A phase transition from loosely-packed layers with alkanethiols lying down to denser layers with alkanethiols standing up by molecular filling and realignment was observed directly using constant-current scanning tunneling microscopy. Island formation was observed in both phases.

PAs on Al₂O₃ are also relevant systems. Atomic force microscopy (AFM) and ellipsometry data for PA-modified Al₂O₃ surfaces were reported by Hauffman et al.^{30,31} In situ

AFM shows fast island formation at the beginning of deposition followed by gap filling. The islands then grow further before the monolayer fully covers the surface. Rapid molecular uptake occurs in the first 10 min before the monolayer slowly reaches surface saturation. Vega et al. reported a detailed study of PA SAM formation on silicon oxide surfaces deposited by the tethering by aggregation and growth (T-BAG) method.³² A high temperature was used to trigger a physisorption-to-chemisorption transition in a water free environment.

These previous studies indicate monolayer formation by a general “fast adsorption/slow equilibration” process associated with molecules becoming increasingly upright with monolayer filling until film saturation is attained. However, no detailed research on how PA modifier deposition processes affect monolayer quality and formation has been reported on TCO surfaces. Thus, in this work, the time course of SAM formation on indium zinc oxide (IZO), a model TCO,³³ is investigated using PM-IRRAS for solution modification by pentafluorinated benzylphosphonic acid (F₅BnPA). Films formed by this approach are then compared to those formed by two soak-free methods, micro-contact printing³⁴ and spray coating,³⁵ for phenyl phosphonic acid (PPA), F₁₃-octylphosphonic acid (F₁₃OPA) and pentafluorinated benzylphosphonic acid (F₅BnPA) modifiers. These soak-free techniques do not require long solution contact times, and therefore, save not only time but also decrease any effects of solvent on the TCO surface. PM-IRRAS is the technique of choice for this work because of its high surface sensitivity and molecular specificity.³⁶⁻³⁹

EXPERIMENTAL

Materials. PPA,^{19,40} F₁₃OPA¹⁹ and F₅BnPA⁴¹ were synthesized and purified as described previously. Absolute ethanol (Aaper Alcohol and Chemical Company, Shelbyville, KY) and

HPLC-grade acetonitrile (>99.8%, EMD Chemicals) were used as received. Water was purified to a resistivity of >18 M Ω with <6 ppb total organic carbon content with a Millipore Q-UV system. FTIR-grade KBr was purchased from Alfa Aesar. (Ward Hill, MA) Liquinox Critical Cleaning Liquid Detergent was purchased from Alconox (White Plains, NY) and diluted to 1% (v/v) with Milli-Q water before use.

Reflective substrates of 100 nm Au-on-glass microscope slides from Evaporated Metal Films (Ithaca, NY) were used to support PM-IRRAS measurements. These substrates possess roughness of 1.5-2.0 nm root-mean-squared (RMS) by atomic force microscopy (AFM). Conformal,³⁶ 10 nm-thick IZO films were sputtered onto these substrates from a 3 in, 70:30 (wt %) In₂O₃:ZnO target under a base pressure of 10⁻⁶ Torr at a deposition pressure of 4.5 mTorr. During an 8.5 s deposition, the O₂ flow was maintained at 0.5 sccm, and the Ar flow at 13.4 sccm, with a DC sputtering power of 100 W. Prior to use, the IZO substrates were detergent-cleaned before sonication in acetone and absolute ethanol for 5 min each, with drying under a gentle flow of N₂ after each step. Substrates were then placed into a Harrick model PDC-32G plasma cleaner (Harrick Plasma, Ithaca, NY) and exposed to a 400 mTorr O₂ plasma using 10.5 W RF power for 10 min.

SAM Deposition. For SAM formation by a solution soak, pre-cleaned substrates were placed immediately into a 10 mM PA in ethanol solution for either 48 h or 168 h at room temperature. Upon removal, SAMs were thoroughly rinsed with ethanol and then sonicated for 5 min in ethanol and blown dry with a gentle flow of N₂. For films formed using solution deposition at 70 °C with a 48 h deposition time, substrates were soaked in a 10 mM PA in ethanol preheated to 70 °C, rinsed with ethanol, dried under N₂, and annealed at 140 °C in an oven for 2 h followed by

sonication in 5% (v/v) triethylamine in ethanol for 30 min, a final rinse in ethanol, and dried in a N₂ stream.

Films formed by micro-contact printing have been described in detail elsewhere³⁴. Briefly, a poly(dimethylsiloxane) (PDMS) stamp was fabricated from a silicon wafer. The PDMS stamp was rinsed with ethanol and dried under a gentle flow of N₂. A 10 mM PA in ethanol solution was swabbed onto the stamp, which was immediately pressed onto the pre-cleaned IZO surface and held down by a 35-40 g weight for 10 min. The surface modified in this way was immediately transferred to a pre-heated hot plate and annealed at 140 °C for 5 min followed by an ethanol rinse and drying in a N₂ stream. Surfaces were then sonicated in 5% (v/v) triethylamine solution in ethanol for 30 min before a final ethanol rinse and N₂ drying.

As described by Bulusu et al.,³⁵ spray coating modification of IZO surfaces with PPA, F₅BnPA and F₁₃OPA was performed with an Iwata HP-SB Plus air brush immediately after plasma treatment. A 10 mM PA in ethanol solution was fed through a cup attached to the spray nozzle and entrained in a stream of N₂. 1 mL of solution is used in one spray action. In order to ensure that the solution was converted to small droplets that impinge on the surface at high velocity, the gas pressure and average solution flow rate are maintained at 25 psi and 0.03 mL/s, respectively. Two sets of 60 s spray actions were applied to pre-heated samples on a 150 °C hot plate. Surfaces were kept on the hot plate at 150 °C after spraying for 2 min before a thorough ethanol rinse. Surfaces were then sonicated in 5% (v/v) triethylamine in ethanol for 30 min before a final ethanol rinse and N₂ drying.

PM-IRRAS. Spectra were acquired on a Nicolet Nexus 670-FTIR spectrometer coupled to a tabletop optical module. Polarization modulation was accomplished with a Hinds Instruments

(Hillsboro, OR) PM-90 with a ZnSe 50 kHz optical head and a synchronous sampling demodulator (GWC Instruments, Madison, WI). The optical signal was detected with a type A MCT detector (Thermo Electron Scientific Instrument Corp., Beverly, MA). Samples were placed at an 80° incident angle. Spectra are an average of 4096 scans with 4 cm⁻¹ resolution and maximum dephasing at 1600 cm⁻¹. Reference spectra were acquired on samples that were identically cleaned and prepared without modifiers. PM-IRRAS spectral conversion to real absorbance units has been described in detail in previous publications.³⁶

To determine average molecular orientation within a F₅BnPA monolayer of known surface coverage, the experimental IR reflectance-absorbance spectrum must be compared to a spectrum that is calculated for an isotropic film of comparable thickness. This calculation requires values for the optical constants n and k at the spectral frequencies of interest. Based on the observation of similar frequencies, the spectrum of the F₅BnPA⁻ salt was chosen as an appropriate model for the surface-bound F₅BnPA molecules. Thus, the transmission IR spectrum of the F₅BnPA⁻ salt gives a direct measure of the imaginary part of the refractive index, $k(\nu)$, at the frequencies of interest with the corresponding $n(\nu)$ values calculated by a Kramers-Kronig (KK) transformation.⁴²⁻⁴⁵ The spectrum for an isotropic layer of the F₅BnPA⁻ salt equivalent to monolayer thickness is then calculated with a three-phase model.^{42,43} Starting with this calculated spectrum, the analysis of the PM-IRRAS data for a F₅BnPA surface layer of fixed coverage starts from the assumption that F₅BnPA on the surface exists as the F₅BnPA⁻ salt and that any differences in intensities between the PM-IRRA spectrum and the calculated spectrum indicate a preferred orientation of the surface-bound molecules. From these relative intensity changes, the average orientation of surface-confined molecules is determined as described in the next section.

RESULTS AND DISCUSSION

Time Dependence of SAM Formation

Solution deposition of small PA SAMs on oxide surfaces has been used extensively, because it is a straightforward processing method and results in uniform monolayers. In order to understand the monolayer formation process at a molecular level for PA SAMs on IZO substrates, the time evolution of the SAM vibrational behavior is monitored using PM-IRRAS. F₅BnPA is chosen here as a model PA molecule due to its high molar absorptivity and good PM-IRRAS spectral quality over a large range of surface coverage. Detailed vibrational assignments for the F₅BnPA SAM are thoroughly discussed elsewhere.³⁷

As two of the most intense PM-IRRAS bands in the spectra, two aromatic ring modes, the ν_{19a} at 1529 cm⁻¹ and the ν_{19b} at 1507 cm⁻¹, are chosen to monitor surface coverage as a function of deposition time. Figure 1 shows a series of spectra in the region of the two ν_{19} bands acquired during SAM formation between 1 s and 48 h soak times. Time-dependent spectral changes are observed that include absorbance changes and peak frequency shifts in both ν_{19} modes. As shown in Figure 1, the absorbance values of both the ν_{19a} and ν_{19b} modes systematically increase during the SAM formation process. This absorbance increase could be the result of an increase in surface coverage, or a change in orientation during SAM formation according to surface selection rules,^{43,46,47} or both. Combined with other evidence that is presented below, this dramatic increase in absorbance is most likely dominated by an increase in surface coverage during SAM formation.

For oriented surface molecules in an external-reflection geometry, electric field amplitude exists only normal to the surface at infrared frequencies.^{43,46,47} Thus, the integrated absorbance for a vibrational band is proportional to the square of the electric field amplitude at the surface,

the magnitude of the transition dipole moment (μ), and the tilt angle θ of μ from the surface normal.⁴⁸

$$A \propto (\mu \cdot \cos \theta)^2 \quad [1]$$

As shown by Hansen⁴² and McIntyre,⁴³ due to this anisotropic electric field at the surface, the integrated absorbance of a vibrational mode with a transition moment oriented along the surface normal will be three times that of the integrated absorbance of the same vibrational band measured from an isotropic collection of identical molecules in a thin film of equivalent thickness and molecular density. This latter value is extracted from the simulated spectrum as $A_{\text{simulated}}$. Therefore, the tilt angle for a particular transition dipole moment can be calculated from:

$$\cos \theta = \frac{A_{\text{film}}}{3 \cdot A_{\text{simulated}}} \quad [2]$$

where A_{film} is the integrated absorbance of the F₅BnPA band in the PM-IRRA spectrum, with both A_{film} and $A_{\text{simulated}}$ appropriately corrected for molecular density (that includes surface coverage for the surface film) as described previously.^{36,37}

The time-dependent change in integrated absorbance values of the ν_{19a} and ν_{19b} bands during SAM formation by solution deposition are plotted in Figure 2. These values are acquired from spectra taken on independently prepared samples left in solution for the times indicated before being removed for spectral acquisition. A very rapid increase in the integrated absorbance of the ν_{19a} band is observed in the first 10 s of F₅BnPA solution exposure before a plateau is reached. Beyond this time, a slow monolayer equilibration process occurs over the following 24 h as evidenced by a further slight increase in absorbance. The integrated absorbance of the ν_{19b}

band increases in a manner similar to that for the ν_{19a} band in that it shows that the major portion of the monolayer is formed in the first 10 s followed by a 24-48 h slow equilibration to reach monolayer saturation. These two adsorption isotherms indicate that the process of F₅BnPA monolayer formation on IZO is fast and energetically favorable.

The spectra in Figure 1 also show frequency shifts for both the ν_{19a} and ν_{19b} bands during formation of the F₅BnPA monolayer. A shift to higher frequencies of the ν_{19a} band is readily observed, but a careful analysis of the ν_{19b} band shows a similar frequency increase, albeit smaller in magnitude. The time evolution of the peak frequencies for these bands is plotted in Figure 3. These frequency increases are attributed to the effects of increasing molecular packing in the surface monolayer as it forms. This phenomenon has been well-studied for aromatic systems both experimentally and theoretically, and it has been shown that, in general, due to an increase in intermolecular restoring force experienced by close-packed, solid-phase aromatic molecules compared to more loosely-packed liquid phase molecules, the aromatic ring modes increase in frequency.⁴⁹⁻⁵⁶ Indeed, such increases in frequency of ring modes have been observed for other aromatic SAMs studied in this laboratory.⁵⁷ Similar increases in ring mode frequencies can be observed by imposing increased pressure to the system leading to a similar increase in molecular density as occurs in a SAM. In the case of a SAM, the vibrational motions of the “solid-like” F₅BnPA surface modifiers in the monolayer are hindered by close-packed, neighboring modifier molecules as the surface coverage increases, leading to higher frequencies.

As shown in Figure 3, the frequency of the ν_{19a} band reaches a plateau after 6 h of solution deposition while the frequency of the ν_{19b} band stabilizes at 24 h after reaching a maximum frequency after 6 h. These trends generally track the adsorption isotherms plotted from the absorbance, and hence support our initial assertion above that the absorbance increase is

dominated by a surface coverage increase instead of an orientation change. Nonetheless, there are some slight differences between the absorbance changes (Figure 2) and the frequency shifts (Figure 3) in the first 6 h of solution deposition that may indicate changes in orientation of the modifiers.

Careful consideration of the spectra in Figure 1 shows that, throughout monolayer formation, the absorbance of the ν_{19a} band grows faster than that for the ν_{19b} band. The ν_{19a} and ν_{19b} modes have transition dipole moments that are orthogonal in the phenyl ring plane. As discussed previously,^{36,37} the orientation of ν_{19a} transition dipole moment is along the C_6H_5-C axis, which is perpendicular to the ν_{19b} mode. The relative orientations of the ν_{19a} and ν_{19b} modes in the plane of the fluorinated phenyl ring are shown in Figure 1. Surface selection rules dictate that the absorbance associated with a transition dipole moment on a metallic substrate is proportional to its projection on the p-polarized electric field that is aligned along the surface normal. Due to a lack of quantitative surface coverage values during SAM formation, molecular orientation in terms of ring plane tilt and twist cannot be precisely calculated as has been done previously.^{36,37} However, the ratio of absorbance values of the ν_{19a} to ν_{19b} bands can provide qualitative insight about the evolution of average molecular orientation during the 48 h solution deposition process.

Figure 4 shows the absorbance ratio of the ν_{19a} to ν_{19b} bands with time during monolayer formation. The dramatic increase of this ratio within the first 10 s, when a large percentage of the monolayer forms, indicates that the ring axis rapidly becomes more upright as the monolayer assembles due to an increase in close packing of molecules. Poirier et al. were the first to study the similar process of SAM formation from alkanethiols on Au (111) by STM.²⁹ This work showed that monolayer formation starts by adsorption of small molecular aggregates in which

the molecules lie down on the surface at low coverage until the surface is almost completely occupied. At this point, which happens early in the adsorption isotherm, the molecules then begin to reorient to a more vertical orientation in order to accommodate greater surface coverage within the monolayer film. During this transition, more upright modifiers will start to form islands that eventually coalesce as the surface approaches its saturation coverage. A similar process is likely occurring here, although given the constraints imposed by binding of the phosphonic acid group, the range of accessible orientations of the ring is probably not as broad as the range of orientations accessible to alkanethiols on metals.

Another noticeable change during the 48 h monolayer formation process is a decrease of the absorbance ratio of the ν_{19a} to ν_{19b} bands after ~30 min of deposition (see Figure 4), suggesting that ν_{19b} is becoming oriented along the surface normal. This ratio decrease may reveal a ring twist around the C_6H_5-C bond in order to find a local energy minimum within the monolayer as it fills in. The ultimate average molecular orientation of F₅BnPA in a saturated monolayer after solution deposition has the ring axis, along which the transition dipole moment of ν_{19a} lies, at a tilt angle of ~40° with respect to the surface normal.³⁷ A schematic showing the estimated molecular orientation evolution during F₅BnPA monolayer formation is shown in Figure 5.

Comparison of SAMs Formed with Different Deposition Methods

With an understanding in hand of the adsorption process for PAs on IZO surfaces, an efficient, convenient, and contamination free method of PA-modified IZO surface fabrication would be desirable. As found previously by Vega et al., annealing is critical for PA adsorption on Al₂O₃ surfaces, because in certain cases, the activated process of transitioning the

physisorption state to the chemisorption state requires heating to 140 °C.³² In order to optimize monolayer quality, both heating of the modification solution and a post-modification annealing step are used in addition to the methodology previously outlined for room temperature modification. The quality of the resulting monolayers is subsequently evaluated with vibrational spectroscopy. Additionally, two soak-free methods, micro-contact printing and spray coating, are of interest because they require less processing time, thereby possibly minimizing solvent etching effects on the oxide surface. Given interest in the use of fast, soak-free techniques in organic electronics manufacturing, it is important to fully characterize the quality of PA monolayers formed by these methods as well. Here, we assess film quality of PA SAMs fabricated with different deposition techniques using PM-IRRAS. PPA, F₅BnPA and F₁₃OPA are chosen as molecular models to compare film quality across five deposition techniques: 1 week solution deposition at room temperature, 48 h solution deposition at room temperature, 48 h solution deposition at 70 °C, spray coating, and micro-contact printing.

Figures 6a-e show PM-IRRA spectra of PPA-modified IZO surfaces prepared with the five deposition methods noted above. Similar major peaks observed in these spectra are the $\nu(\text{C}_6\text{H}_5\text{-P})$ at 1150 cm^{-1} and the less intense ν_{19a} , ν_{19b} and ν_{8a} ring modes at 1498, 1452, and 1608 cm^{-1} , respectively. As reported previously,³⁶ both near edge X-ray absorption fine structure spectroscopy (NEXAFS) and PM-IRRAS demonstrate that PPA forms ordered monolayers on IZO dominated by tridentate surface binding with a phenyl ring tilt of $\sim 13^\circ$ from the surface normal. Comparing the $\nu(\text{C}_6\text{H}_5\text{-P})$ band across the samples prepared with the different deposition techniques, one sees that the spray coated and micro-contact printed samples show a relatively broad, largely symmetric feature, while in the spectra from the samples prepared with the other three methods, this band is sharp and narrower with a broad, higher frequency shoulder of

differing relative intensity at $\sim 1180\text{ cm}^{-1}$. Given the sensitivity of the $\nu(\text{C}_6\text{H}_5\text{-P})$ band to PA binding type,³⁶ the larger width of this band in the spectra from the spray coated and micro-contact printed samples suggests a broader distribution of binding modes for PPA on the IZO in these samples. The shoulder at $\sim 1180\text{ cm}^{-1}$ is assigned to the associated $\nu(\text{P-O-metal})$ mode.³⁶ Its lower relative intensity versus the 1180 cm^{-1} peak for the sample prepared by room temperature soaking for 48 h (Figure 6c) compared to that prepared by a 1 week room temperature (Figure 6e) or 48 h hot soak (Figure 6d) suggests less P-O-metal bonding.

The sharp band at 1265 cm^{-1} in the spectrum from the spray coated sample (Figure 6a) is unique among these samples. However, this band has also been observed for other PA-modified IZO surfaces after solution deposition followed by long-term oxidation in air. A similar sharp peak at 1265 cm^{-1} has been reported by Kryszinski and coworkers⁵⁸ and been assigned to the presence of a stretching vibration from C-O-Au ester-like bonds.⁵⁹ Its presence here suggests partial etching of the IZO thin film during spray coating³⁵ that exposes the underlying Au surface, leading to its oxidation. The mechanism of this surface etching and reconstruction chemistry is presumably similar to that of thiol-modified Au surfaces. During thiol modification, Au (111) surface defects and reconstruction were observed using scanning tunneling microscopy (STM).⁶⁰⁻⁶² Moreover, gold was also found by atomic absorption spectroscopy in the thiol deposition solution after substrate immersion, confirming Au corrosion through formation and later dissolution of thiolate-Au species.⁶² Similar to thiolate formation on Au surfaces, we hypothesize that metal extraction in the form of metal phosphonates is likely here. More evidence for IZO surface etching through this mechanism is discussed below. Also noticeable in the spectrum from the spray coated sample (Figure 6a) are two broad features centered at 1260

and 1520 cm^{-1} ; these are only observed from the spray-coated sample. These new features are discussed below.

A unique asymmetric and broad band at 1250 cm^{-1} is observed in the spectrum from the micro-contact printed sample (Figure 6b) that is assigned to the $\nu(\text{P}=\text{O})$ mode from free $\text{P}=\text{O}$ groups of molecules with bidentate binding^{63,64}. Thus, in total, the PM-IRRA spectra from PPA-modified IZO surfaces show that the soak-free techniques produce less uniformly bound PPA compared to solution deposition techniques. Evidence for surface etching and new spectroscopic features are observed in the spray-coated sample.

PM-IRRA spectra of F_5BnPA -modified IZO surfaces fabricated with these different deposition techniques are shown in Figures 6f-j. In general, the absorbance values for bands in the spectra of the samples fabricated by solution deposition are larger than those of the micro-contact printed and spray coated samples, indicating higher modifier surface coverage, consistent with previous research from this laboratory⁵⁷. Significantly, the absorbance values in the spectra from the micro-contact printed and spray coated samples are comparable to or less than those in samples prepared by solution deposition with soak times of 1 s. Based on the kinetics of monolayer formation discussed above, these low absorbance values suggest that micro-contact printing and spray coating are less efficient at high-quality monolayer assembly. Broad features centered at 1260 and 1520 cm^{-1} , similar to those observed for PPA, are also evident in the spectrum of the F_5BnPA -modified surface prepared by spray coating.

Figures 6k-o show PM-IRRA spectra from F_{13}OPA -modified surfaces prepared with the different deposition methods. These spectra look similar, suggesting similar surface coverage, molecular binding, and orientation. The only difference is the presence of the broad features at 1280 and 1520 cm^{-1} in the spray-coated sample (Figure 6k).

Collectively, this series of spectra from PA-modified surfaces suggests that soak-free techniques do not produce SAMs with uniform binding or close packing. This outcome may be the result of short deposition times or overall less surface contact between the PA and the substrate before compact and energetically favored structure are formed. Evidence for IZO etching is also observed here in the micro-contact printed samples and has been observed previously for samples prepared from spray coating on IZO.³⁵ In contrast, the PM-IRRA spectra of samples prepared with the three solution deposition techniques show similar spectroscopic features, suggesting that 48 h is a sufficient formation period and annealing is unnecessary to induce the transition from physisorbed to chemisorbed state on IZO.

Among the five deposition methods, micro-contact printing produces the least reproducible SAMs. As shown in Figure 7, spectra of three independently-prepared films from PPA, F₅BnPA, and F₁₃OPA show obvious differences. In Figures 7a-c, three spectra of PPA-modified surfaces clearly exhibit shape and intensity differences in the $\nu(\text{C}_6\text{H}_5\text{-P})$ band at $\sim 1150\text{ cm}^{-1}$, indicating poor reproducibility and uniformity of PPA binding. Moreover, in the spectra shown by the purple and red lines for PPA, the presence of a broad, asymmetric band between 1200 and 1270 cm^{-1} suggests the appearance of free P=O bonds due to bidentate binding^{63,64}. The spectrum shown by the blue line in the same figure shows a band at these frequencies far more intense than can be attributed to bidentate binding alone. This feature is taken here to be indicative of some monolayer degradation or IZO surface etching, with a strong sharp band expected at 1265 cm^{-1} that overlaps a weaker band, consistent with some bidentate binding.

Micro-contact printed F₁₃OPA-modified surfaces (Figures 7g-i) appear to be more reproducible compared with SAMs of the other two PA modifiers. Nonetheless, the bands due to the $\delta(\text{pd-CF}_2)$ modes with transition dipole moments perpendicular to the chain axis do show a

range of absorbance values indicative of significant variability in the quality of films printed at different times. In summary, the variability of PM-IRRA spectra from samples prepared by micro-contact printing clearly suggests that this is a less reliable method for fabricating well-ordered PA-modified TCO surfaces than solution deposition.

Compared with micro-contact printing, spray coating results in PA-modified surfaces exhibiting less sample-to-sample variability, although the surface coverage is not optimized and degradation by surface etching and contamination are problematic.³⁵ Significantly, several new features appear in the spectra from PA-modified surfaces fabricated by spray coating. Figure 8 shows a series of spectra from PPA, F₅BnPA, and F₁₃OPA-modified surfaces. Broad bands at ~1520 and 1280 cm⁻¹ appear in all of these spectra which are ascribed to vibrations of amorphous carbon, based on both experimental observations⁶⁵⁻⁶⁷ and calculations,⁶⁶ that forms presumably from thermal degradation of the phosphonic acids during the spray coating protocol used. It is noted that the spectra shown in Figure 8 are referenced to spectra from samples prepared by the identical spray coating method but in the absence of the PA. Thus, these broad features only occur or are enhanced with PA modification, suggesting that they result from some PA-catalyzed substrate degradation process or by the formation of P-O-Au bond on the Au substrate beneath the IZO layer.

Soak-free modification methods are of interest because of their potential application in the fabrication of printable devices. In order to improve film and substrate uniformity, multiple factors such as sample exposure time, substrate temperature, solvent volatility and substrate and “stamp material”-surface contact should be optimized. Nonetheless, the current state-of-the-art is such that despite the above evidence of significant film quality differences, soak free methods produce PA films that perform in devices similarly to those fabricated with solution deposition

methods^{34,35,68-71} due to the fact that the PA monolayer quality was not the main factor limiting device performance in these studies. However, as other performance-limiting factors are systematically improved or eliminated in such devices that utilize PA monolayers, the quality of the PA monolayer may ultimately become limiting. Under these circumstances, the choice of deposition method will thereby become critical to the overall performance of the device.

CONCLUSIONS

Solution deposition kinetics for F₅BnPA modification of IZO surfaces indicate that the majority of the monolayer occurs in the first 10 s of exposure with equilibrium reached in ~48 h. In contrast to PA/Al₂O₃ systems, F₅BnPA adsorption on IZO surface is energetically favorable and occurs rapidly at room temperature, thereby not requiring post annealing to induce the physisorption to chemisorption transition.

PM-IRRAS analysis has also been performed on PA-modified IZO surfaces using 48 h solution deposition at room temperature, 48 h solution deposition at 70 °C with post annealing, 1 week solution deposition at room temperature, micro-contact printing and spray coating for three modifiers, PPA, F₅BnPA, and F₁₃OPA. The results indicate that: 1) 48 h is sufficient time for high-quality SAM formation using a solution deposition process; elevated temperatures during deposition or by and post annealing are not necessary; 2) soak-free techniques, including micro-contact printing and spray coating, do not typically produce fully covered, uniform monolayers; 3) micro-contact printing is a modification strategy that results in greater sample-to-sample variability; also, evidence for surface etching of the IZO was observed using these fabrication methods; and 4) spray coating results in the greatest formation of a hydrous gold oxide layer in our stratified sample assembly consistent with the greatest amount of IZO etching. This is most

likely the result of the very high temperatures to which the samples are exposed during this process and not anything inherent to the spray coating process itself. Nonetheless, these observations do indicate that caution should be exercised in the use of temperatures much above 70 °C for extended periods when modifying TCOs with PAs to minimize significant degradation of the TCO surface, with its concomitant effects on further steps of device assembly or in device performance.

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FIGURE CAPTIONS

- Figure 1. PM-IRRA spectra from F₅BnPA-modified IZO surfaces prepared by solution deposition with exposure times from 1 s to 48 h at room temperature.
- Figure 2. Absorbance values of the ν_{19a} (blue circles) and ν_{19b} (maroon squares) bands for F₅BnPA with deposition time for a) full 48 h and b) first 60 s. Error bars represent standard deviations from three independently-prepared surfaces.
- Figure 3. a) ν_{19a} and b) ν_{19b} peak frequencies for F₅BnPA as a function of deposition time. Error bars represent standard deviations from three independently-prepared surfaces.
- Figure 4. Ratio of absorbance values of the $\nu_{19a}:\nu_{19b}$ bands for F₅BnPA with deposition time for a) full 48 h and b) first 60 min.
- Figure 5. Proposed evolution of F₅BnPA orientation at room temperature during solution deposition. a) Initial orientation; b) upward reorientation within the first 10 s of solution deposition due to increased surface coverage, and c) possible ring twist to reach a local energy minimum in a close-packed monolayer.
- Figure 6. PM-IRRA spectra from PA-modified IZO surfaces for a)-e) PPA, f)-j) F₅BnPA, and k)-o) F₁₃OPA fabricated by a), f), k) spray coating; b), g), l) micro-contact printing; c), h), m) 48 h solution deposition at room temperature; d), i), n) 48 h solution deposition at 70 °C, and e), j), o) 1 week solution deposition at room temperature.

Figure 7. PM-IRRA spectra from three independently-prepared monolayers fabricated by micro-contact printing for a)-c) PPA, d)-f) F₅BnPA, g)-i) F₁₃OPA.

Figure 8. PM-IRRA spectra from three independently-prepared monolayers fabricated by spray coating for a) PPA, b) F₅BnPA, and c) F₁₃OPA.

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 8