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Probing the polymer-electrode interface using neutron reflection

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We demonstrate that neutron reflection (NR) can be used to characterize polymer films deposited on indium tin oxide (ITO). When the chloro precursor to poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEHPPV) was spin-coated onto ITO NR revealed that between the ITO and the uniform polymer layer was a 20 Å thick low contact zone. We found that the conversion of the chloro precursor to MEHPPV at 180 °C under vacuum gave a uniform film of MEHPPV with the layer of low contact between the polymer and ITO remaining. Finally, the NR profile suggests that the blueshift in the MEHPPV absorption spectrum on ITO when compared to quartz is due to polymer morphology and not incomplete conversion. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1567825]

Light-emitting materials in organic light-emitting diodes (OLEDs) fall into three main classes: molecular materials, and solution processed polymers and dendrimers. For soluble conjugated polymers it has become clear that polymer morphology strongly affects the device properties.[1–6] Processing solvent, polymer concentration, spin-coating speed, and annealing can all affect morphology and, hence change, the photoluminescence properties, charge injection and transport, device performance, and surface morphology of the materials. While most of the polymer morphology studies have been in the context of OLEDs it is also important for other device applications such as photovoltaics.[7] Neutron reflection (NR) is a powerful technique that can characterize the physical properties of polymer films directly. We have recently reported that NR can be used to reveal the structure property relationships of precursor polymers and conjugated polymers.[8] However, the study was on silicon wafers while for device applications the polymer is often deposited onto an electrode such as indium tin oxide (ITO). The composition of the substrate and its interface with the polymer layer can directly affect the morphology of the polymer. We were therefore interested to see whether we could use NR to study polymer films deposited onto electrode materials. In this letter we demonstrate that ITO is a suitable substrate for NR studies and in combination with partially deuterated polymers provides a powerful technique for film characterization.

A NR profile is a measure of the specular reflectivity as a function of momentum transfer Q [$Q = (4\pi \sin\theta)/\lambda$, where θ is the grazing angle of incidence and l is the wavelength of the neutron]. The NR profile is determined by the scattering length density profile normal to the surface and, in the case of a polymer film, this is directly related to the actual density profile.[9] NR measurements were carried out on the dedicated reflectometer, $D17$, at the Institut Laue–Langevin, Grenoble.[10] The NR measurements were done under a dynamic vacuum. The ITO was from Merck Display Technologies (Part No. 255 645 XE) and consisted of (in order) soda lime glass, a silicon dioxide barrier layer, and a 1000 Å layer of ITO. For this work we studied films of the chloro precursor with a perdeuterated 2-ethylhexyl group **1** and its thermal conversion to poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] **2** (Fig. 1) to allow direct comparison with our earlier NR work on silicon substrates. The weight average molecular weight, $\bar{M}_w$, of **1** used in this study was determined by gel-permeation chromatography (against polystyrene standards in tetrahydrofuran) and found to be $>3\times10^6$ before disaggregation.[11] For the NR experiments **1** was spin-coated onto 2 in. square ITO substrates with the polymer concentration ≈10 mg/ml in tetrahydrofu-
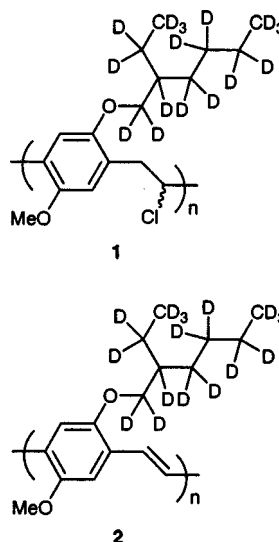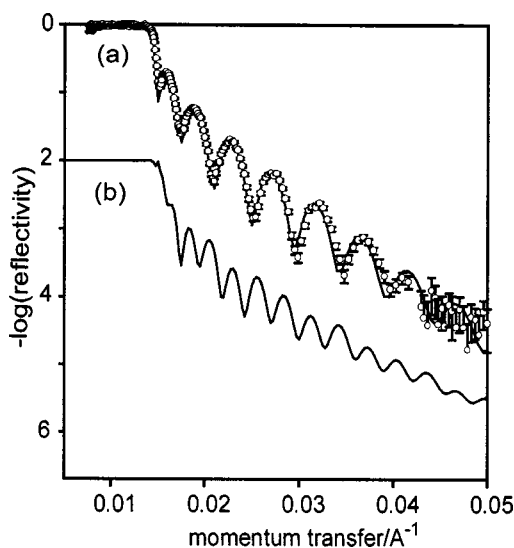

FIG. 1. Polymer structures.

FIG. 2. (a) Reflectivity profile of ITO on glass showing the data points and fit (solid line). (b) Reflectivity profile calculated for a layer of **2** deposited on ITO.
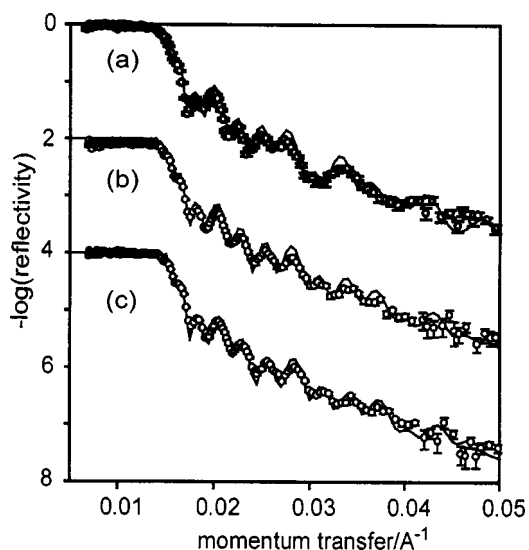

FIG. 3. (a) Reflectivity profile and fit (solid line) for **1** on ITO. (b) Reflectivity profile and fit (solid line) for **2** on ITO at 180 °C. (c) Reflectivity profile and fit (solid line) for **2** on ITO at room temperature.

ran at 2000 rpm for 60 s. The ITO substrates were cleaned with tetrahydrofuran. NR profiles were collected for ITO, **1**, and **2** at 180 °C and room temperature. **1** was converted to **2** *in situ* at 180 °C for 40 min under vacuum before the measurement at 180 °C. We followed the conversion by UV-visible spectroscopy on ITO and quartz, and infrared spectroscopy on a KBr disk.

The NR profile for the ITO on glass is shown in Fig. 2(a). For a uniform film the NR profile consists of a series of fringes whose spacing is directly related to the thickness of the film. The density of the film can be calculated from either the amplitude of the fringes or from the critical angle of the total reflection. For the latter the scattering length density (SLD) must be greater than that of the substrate and the film thickness must typically be larger than a few tens of a nanometer, depending on the substrate. The observed reflectivity profiles are fitted with profiles calculated by the optical matrix method.[12,13] Interestingly, fitting the reflectivity profile of the ITO film requires it to be comprised of two layers of different densities. The exact details of the denser layer are difficult to establish with accuracy but its presence is essential because the amplitude of the fringes would be otherwise too small. We have modeled this dense layer, which is next to the glass, as approximately 80 Å thick with a SLD of 5.0×10^{-6} Å^{-2}. The remainder of the ITO film, 1120 ± 20 Å, is less dense with a SLD of 4.0×10^{-6} Å^{-2}. The total thickness of 1200 Å compares well with the specified ITO film thickness. The difference in SLD indicates that the two layers in the ITO film have different chemical compositions. The scattering length of indium and tin are 2.08×10^{-6} Å^{-2} and 4.87×10^{-6} Å^{-2}, respectively, indicating that the thin layer near the glass has a higher tin content. The mean roughness of the composite layer was approximately 35 Å.

Our previous work on silicon substrates showed that **1** had a SLD of $4.0 - 5.0 \times 10^{-6}$ Å^{-2}.[8] With the SLD of the polymer and thick ITO layer being similar it was therefore expected that the NR profile would simply be of a film that was thicker by the thickness of the polymer layer. The result

should then be that the periodicity of the fringes in the reflectivity profile would merely decrease, as illustrated in Fig. 2(b). The actual NR profiles of **1** and **2** are shown in Fig. 3 and are more complex than expected for the introduction of a single polymer layer of SLD about 4.5×10^{-6} Å^{-2}. The NR profiles of **1** and **2** could only be fitted by the introduction of a layer of very low SLD intervening between the polymer film and the ITO. The extra layer was found to be about 20 Å thick and had a scattering length density of $0.0 - 2.0 \times 10^{-6}$ Å^{-2}, that is, the layer between the ITO and the polymer is mostly empty space (vacuum or air). Although we cannot give a definite explanation for the presence of this layer (for example, it could result from failure of the polymer to wet the ITO, loss of an intervening layer of spreading solvent on evaporation under vacuum, or support of a fairly rigid polymer layer on ITO asperities), the result clearly shows that there are only a relatively low number of contacts between polymer and ITO. What is more, this layer is largely maintained even after thermal conversion under vacuum of **1** to **2**. This unexpected result has important ramifications for the development of polymer-based devices. The presence of a low contact region between a conjugated polymer and the electrode will inhibit charge injection and if this layer contains air then this would directly contribute to poor device lifetime. It is important to note that only the presence of the deuterated 2-ethylhexyl groups makes this layer visible to NR.

From the NR profile of **1** shown in Fig. 3(a) the SLD of **1** was determined to be $4.3 \pm 0.15 \times 10^{-6}$ Å^{-2} and the film thickness 750 ± 20 Å. **1** was converted to **2** at 180 °C under vacuum and the NR profile of **2** at 180 °C is shown in Fig. 3(b). The film of **2** at 180 °C was found to have a thickness of 710 ± 20 Å and a SLD of $4.4 \pm 0.15 \times 10^{-6}$ Å^{-2}. The $\approx 5\%$ decrease in film thickness corresponds primarily to the elimination of hydrogen chloride from the film plus some densification. On cooling to room temperature the film of **2** decreased in thickness to 690 ± 20 Å and the SLD increased slightly to $4.5 \pm 0.15 \times 10^{-6}$ Å^{-2}. The increase in SLD corresponds to an increase in film density of around 5% relative
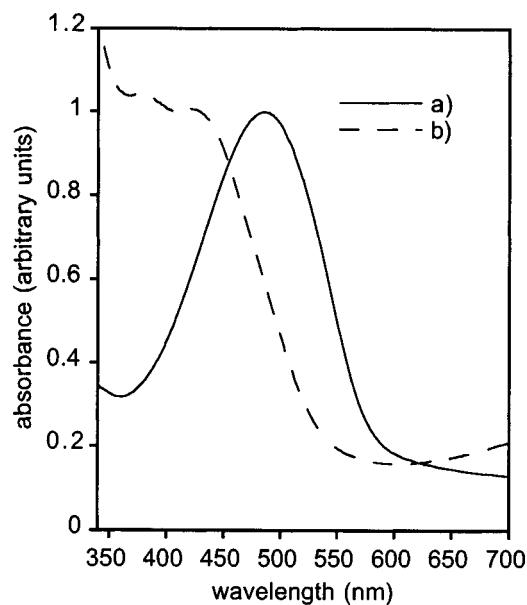
FIG. 4. UV-visible spectra of **2** prepared from **1** on quartz (a) and ITO (b).

to the original film which is similar to that observed when the measurements were carried out on silicon substrates.[8] Comparison of the total amount of the material in the film before and after conversion shows that about 4% of the original material is lost completely. This corresponds to the expected loss of the hydrogen chloride and shows that the polymer film is only conjugated polymer. That is, there can be no significant amounts of indium chloride or hydrogen chloride in the polymer. There are small changes in the low contact zone but these are too small to account for the missing hydrogen chloride. It is important to note that the presence of the low contact layer and the changes to the polymer film appear to be independent of the treatment of the formed film. For example, if **1** is annealed prior to conversion then the material lost, polymer densification, and low contact region all follow similar trends as when **1** is converted directly.

Finally, the NR profiles also gave information about the morphology of **2**. The conversion process of **1** to **2** was followed by UV-visible spectra (on ITO and quartz) and infrared (KBr disk) spectroscopy. The UV-visible spectrum on quartz and infrared spectrum showed that the conversion process had gone to completion. However, the absorption spectrum of **2** on ITO was blueshifted compared to the

sample on quartz (Fig. 4). Incomplete conversion, doping, and twisting of the polymer backbone can all give rise to a blueshift in the absorption spectra.[14] There was no evidence for the film being doped and the NR profile clearly shows that the film has fully converted. To achieve a similar blueshift in the absorption spectrum would require on average more than 25% of the polymer to be unreacted.[15] This is inconsistent with the NR profiles and infrared spectrum and strongly suggests that the difference in absorption spectrum between ITO and quartz is due to different film morphologies. If the air polymer interface is important for controlling film morphology then when air (or vacuum) is at both interfaces of the polymer layer then the influence of these interfaces may predominate.

In conclusion we have used neutron reflection to show that a simple deposition of a polymer onto an ITO layer on glass can lead to a stable layer of significant thickness (≈ 20 Å) preventing good contact between the polymer and the ITO.

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