

Toward Well-Defined Metal–Polymer Interfaces: Temperature-Controlled Suppression of Subsurface Diffusion and Reaction at the Calcium/Poly(3-Hexylthiophene) Interface

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Abstract: The thickness of the reaction zone at the interface between calcium and regioregular poly(3-hexylthiophene), which is one of the best performing metal/polymer combinations in photovoltaic devices, depends critically on the temperature of the polymer during the initial phase of metal deposition. It is shown that deposition at 130 K reduces the thickness of the reaction zone, an effect that also persists after warming to room temperature.

Interfaces between metal electrodes and semiconducting polymers (or molecular organic films) occur in all organic electronic and optoelectronic devices.¹ Their performance depends critically on the chemical composition and electronic structure of the electrode interface, since charge injection rates and other decisive parameters are directly influenced by wave function overlap, chemical bonding, band alignment, and electronic barriers at this metal/semiconducting interface.² Low work-function materials such as Al or alkaline earth metals are commonly used as materials for electron injection electrodes. Metal/polymer interfaces can be produced by vacuum-based vapor deposition of a metal on a polymer.³ Due to the low thermal energy of the metal atoms ($\ll 1$ eV), this process provides far milder conditions than, for example, sputter deposition, where metal ions and electrons with much higher energies ($\gg 1$ eV) are involved. These charged, high-energy particles can easily induce chemical reactions in the near-surface region of the polymer.⁴ However, even gentle vapor deposition produces a chemically and structurally complex interface: metal atoms can diffuse into the polymer, form clusters on or below the surface, and undergo chemical reactions with the polymer.^{5–9} Especially the very reactive alkaline earth metals exhibit a strong thermodynamic driving force for interfacial (or subsurface) diffusion and reaction.^{7–9} Since these processes will indirectly affect the properties of the organic electronic devices, it is desirable to suppress or reduce them. This goal requires a detailed mechanistic understanding of the interface formation process, which would enable potential control of the chemical, geometric and electronic structure of the metal/organic interface.

In this communication, we focus on the interface between calcium and regioregular poly(3-hexylthiophene) (rr-P3HT). Ca/rr-P3HT is one of the best performing electrode/polymer combinations in solar cell applications¹⁰ and has proven to be a suitable model system for the fundamental understanding of the interface

formation between reactive, low work function metals and semiconducting polymers.^{8,9} In particular, we show that low-temperature deposition can significantly and *permanently*, i.e., even after heating to room temperature, reduce the thickness of the reaction zone between metal and polymer. Previous studies have shown that Ca reacts with the thiophene units of the polymer, forming calcium sulfide (CaS). When Ca is deposited at 300 K and with a low flux of typically 0.4 ML/min,¹¹ the reaction zone extends ultimately ~ 3 nm into the polymer but does not grow any further irrespective of a continued dosage of Ca. Such a subsurface reaction with limited diffusion is typical for deposition of reactive metals on polymers.^{7–14} A detailed investigation of the energetics and dynamics of the interface formation revealed that this interfacial diffusion and

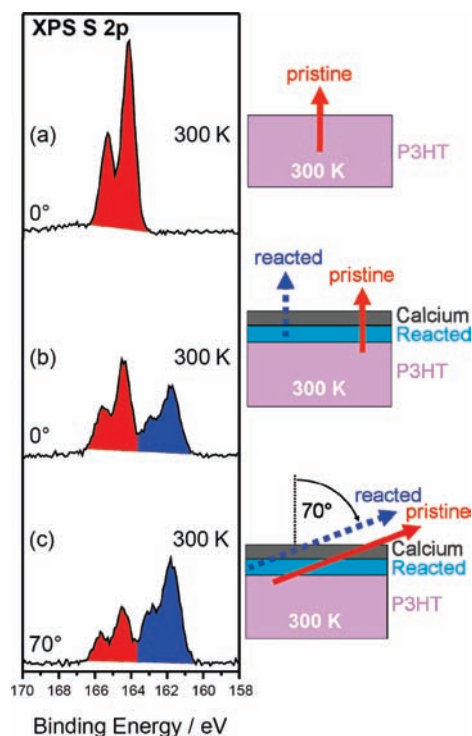


Figure 1. S 2p X-ray photoelectron spectra ($h\nu = 1486.6$ eV) of (a) pristine rr-P3HT and (b, c) after dosing 12 ML Ca on rr-P3HT at 300 K. The red-shaded signal area (left) is attributed to unreacted (pristine) rr-P3HT, and the blue-shaded area (right) to rr-P3HT that has reacted with Ca atoms. The photoelectron detection angle relative to the surface normal was 0° for spectra (a, b) and 70° for spectrum (c). The information depth is ~ 14 nm at 0° and ~ 5 nm at 70°. The spectra are normalized to the same integral intensity to account for the angle-dependent damping by the Ca overlayer (which affects both signal components to the same degree).

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reaction of Ca proceed initially at a faster rate than the growth of Ca particles on the surface of the polymer, but as the reaction front moves deeper, the relative rate (probability) of forming Ca clusters on the surface increases (attributed to the longer diffusion depth slowing down the subsurface reaction).^{7,8} Once Ca clusters form, additional Ca adds predominantly to these clusters rather than diffusing into and reacting with the polymer. This model is also in agreement with previous experimental and Monte Carlo simulation studies of noble metal diffusion in polymers.⁵

On the basis of this mechanism, we predict that a sharp, well-defined metal/polymer interface will be obtained, if interfacial diffusion and reaction are suppressed during the *initial* stages of metal adsorption, for example by deposition at low polymer temperature. It should not be necessary to meet the conditions for reduced diffusion (such as low temperature) at later stages of the deposition or during usage of the interface in devices. In this communication, we show that this goal can be achieved for the Ca/rr-P3HT interface by cooling the polymer to 130 K during metal deposition. After warming up to 300 K, the resulting metal/polymer interface remains significantly sharper compared to the case when Ca was deposited at 300 K, even though the temperature is now sufficient for rapid diffusion of the metal atoms.

For monitoring the reaction between Ca and rr-P3HT, we recorded X-ray photoelectron (XP) spectra of the sulfur 2p core level, which show well-separated signals for unreacted and reacted rr-P3HT. The S 2p XP spectrum of the clean, unreacted polymer (a thin rr-P3HT film spin-coated onto an Al foil; see Supporting Information (SI)) is shown in Figure 1a. The sulfur in the unperturbed thiophene units gives rise to a spin-orbit split signal with components at 164.1 eV (S 2p_{3/2}) and 165.3 eV (S 2p_{1/2}). Ca is then vapor deposited onto the rr-P3HT surface at 0.4 ML/min up to a total dose of 12 ML. With the coverage-dependent sticking probability taken into account,⁸ this dose leads to a coverage of 10.5 ML, which is sufficient for the formation of a complete Ca film on the surface of the polymer. The latter is also confirmed by low-energy ion scattering (LEIS) spectroscopy (see SI, Figure S1). Figure 1b shows the S 2p spectrum after Ca deposition onto the rr-P3HT film at 300 K. The signal of pristine rr-P3HT (red shading) now appears at 164.4 eV (S 2p_{3/2}), i.e., shifted by +0.3 eV relative to the position before Ca deposition. This shift is due to band bending and occurs similarly in all spectra with Ca deposition; it is a purely electronic effect and has previously been discussed.^{8,9} More importantly, the S 2p spectrum in Figure 1b features a new component at 161.7 eV, i.e., -2.7 eV relative to the signal of pristine P3HT (blue shading). According to previous studies, this component results from small calcium sulfide (CaS) clusters which are formed by reaction between Ca and thiophene in the near-surface region.^{8,9} Spectrum 1c refers to the same sample as spectrum 1b, but the photoelectrons were here detected at an angle of 70° relative to the surface normal. Due to the limited inelastic mean free path of the photoelectrons, this leads to an increased surface sensitivity; i.e., the information depth¹⁵ of the experiment is reduced from ~14 nm (for detection along the surface normal) to ~5 nm. The relative signal intensities for reacted versus unreacted thiophene and their angular dependences allow us to estimate the depth of the reaction zone to be 2.5 ± 0.3 nm (see the SI for details). This result is consistent with our previous studies.^{8,9}

To suppress the reaction between Ca and rr-P3HT and to produce a sharp, well-defined metal-polymer interface, we vapor deposited Ca onto the polymer cooled to 130 K, applying the same Ca dose of 12 ML as above. The resulting S 2p spectrum is shown in Figure 2b. The signal of reacted sulfur around 162.3 eV (blue) is now very small and appears only slightly larger in the more surface

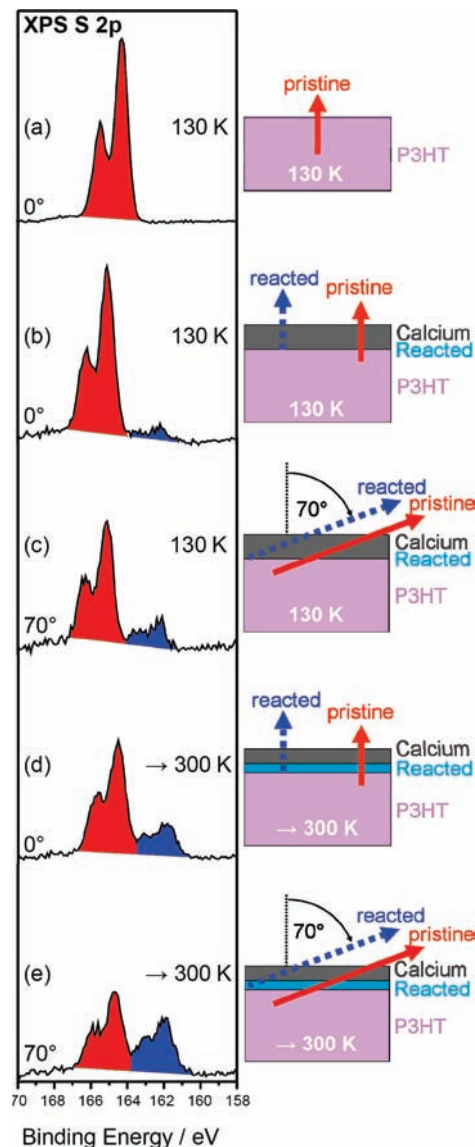


Figure 2. S 2p X-ray photoelectron spectra ($h\nu = 1486.6$ eV) for low-temperature Ca deposition onto rr-P3HT. (a) Pristine rr-P3HT; (b, c) after dosing 12 ML Ca on rr-P3HT at 130 K; (d, e) after warming to 300 K. The red-shaded signal area is attributed to unreacted (pristine) rr-P3HT, and the blue-shaded area to rr-P3HT that has reacted with Ca atoms. The photoelectron detection angle relative to the surface normal was 0° for spectra (a, b, d) and 70° for spectra (c, e). The spectra are normalized to the same integral intensity to account for the angle-dependent damping by the Ca overlayer.

sensitive 70° detection geometry (Figure 2c), indicating that the reaction zone is very shallow: 0.3 ± 0.1 nm. Apparently, subsurface diffusion and reaction are efficiently suppressed. This is also confirmed by the Ca 2p spectra (SI, Figure S2), which show a higher amount of metallic and much less reacted Ca compared to Ca deposition at 300 K.

At this point, the question arises whether the sharp Ca/P3HT interface persists after warming up to 300 K (for approximately 1 h). The answer is provided by the S 2p spectrum in Figure 2d, which shows that the intensity of the component related to reacted sulfur is considerably smaller than that after room temperature deposition of the same amount of Ca (cf. Figure 1b). We conclude that deposition at 130 K permanently reduces interfacial (or subsurface) diffusion of Ca and thus its reaction with the polymer. The 70° spectrum 2e confirms this conclusion, especially by direct

comparison with spectrum 1c for deposition at 300 K. The estimated depth of the reaction zone is now only $\sim 1.2 \pm 0.1$ nm compared to ~ 2.5 nm for room-temperature deposition. The reaction zone did not grow further, even after keeping the sample at 300 K for 12 h.

This observation has two important implications. First, it supports the previously reported model⁸ that subsurface diffusion of Ca atoms occurs predominantly before Ca clusters have formed on the surface. It is also in agreement with previous Monte Carlo simulations, which show that the degree of diffusion can be influenced by the deposition rate of the metal, since it is known that a high deposition rate favors cluster formation and thus reduces the time frame in which interfacial diffusion and reaction can compete with cluster formation.⁵ Second, from a practical point of view, our findings demonstrate that metal deposition at low temperatures is a convenient approach to control subsurface diffusion and reaction and to produce relatively sharp metal–polymer interfaces, if desired.

Comparison of the spectra 2b and 2d shows that some subsurface diffusion of Ca and reaction with the polymer occur upon warming up the Ca/rr-P3HT interface from 130 to 300 K. Most likely, low-temperature deposition of Ca leads initially to the formation of metastable, dendritic Ca structures with a large fraction of low-coordinated Ca atoms, as is typical for metal deposition at low temperatures.¹⁶ These low-coordinated atoms are bound much more weakly to the metal than normal surface or interface atoms and, as the temperature increases, can detach easily and diffuse into the polymer, where they react. This suggests that there may be an optimum substrate temperature during deposition: sufficiently low to suppress diffusion of the Ca atoms into the polymer, but still allowing for a certain degree of sintering of the Ca structures, such that formation of low-coordinated metal atoms is avoided. Alternatively, the reaction observed upon warming may result from single Ca atoms which diffused into the polymer at 130 K but cannot react at this temperature because of an activation barrier for reaction.^{8,9} Finally, the reaction may instead be due to polymer motion that allows thiophenes to touch the Ca solid, which may abstract S to form S adatoms. The reacted amount corresponds to $\sim 6 \times 10^{14}$ S atoms/cm², similar to the saturation packing density of S adatoms on metal surfaces, so this may be an unavoidable amount of reaction.

In summary, we have shown that deposition of Ca on rr-P3HT at 130 K results in a “sharper” interface with a less extended reaction zone between metal and polymer compared to deposition at 300 K under otherwise identical conditions. Most importantly, these differences in the interface structure and composition persist

to a large extent after warming up the Ca/rr-P3HT interface to 300 K, which makes our approach very interesting for practical applications. In combination with other parameters that influence the interface morphology, such as deposition rate, an optimization of the deposition temperature for individual metal/polymer combinations provides a strong tool for the precise control of chemistry and morphology of metal–polymer interfaces.

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Supporting Information Available: Experimental details, low-energy ion scattering (LEIS) spectra (Figure S1), Ca 2p photoelectron spectra (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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