

Influence of water on the work function of conducting poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)

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The influence of water exposure on the work function (ϕ) and surface composition of conducting poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDT:PSS) was investigated with ultraviolet and x-ray photoelectron spectroscopies. It was found that annealing PEDT:PSS in vacuum to 220 °C yields a high ϕ of 5.65 eV. Subsequent exposure to water vapor or air reduces ϕ to \sim 5.15 eV, and the film surface becomes enriched with PEDT. These observations were fully reversible for repeated annealing–water exposure cycles. The reduction in ϕ is attributed to (i) the inclusion of water leading to a larger dielectric constant and (ii) polymer swelling-induced rearrangements of surface dipoles. © 2007 American Institute of Physics.
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The use of intrinsic conducting polymers (ICPs) as electrodes and hole injection layers in optoelectronic devices based on conjugated organic materials is a key for the successful implementation of organic electronics. Most widely used ICPs today are based on aqueous dispersions of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) [PEDT:PSS, chemical structure shown in Fig. 1(a)].¹ For instance, PEDT:PSS has been used for the fabrication of highly efficient organic light emitting diodes^{2,3} and field-effect transistors.^{4,5} One of the reasons for this success is the relatively high work function of PEDT:PSS, which results in low hole injection barriers at interfaces between the ICP and the active layers made of both small molecules^{6,7} or polymers.^{8–10} However, reported values for the work function (ϕ) of PEDT:PSS exhibit a significant spread from \sim 4.8 to 5.2 eV,^{6,11–13} mainly due to different formulations and processing conditions. This inconsistency makes it difficult to predict hole injection barriers in actual devices, in particular, when they are fabricated under varying conditions. For instance, Huang *et al.*¹² have recently shown that ϕ of a commercial PEDT:PSS formulation varies by about 0.2 eV, depending on the atmosphere employed during the annealing of the ICP. However, very little influence of the device efficiency on annealing temperature was found. In addition, it has been shown that also the surface composition of PEDT:PSS is an important factor governing device function and efficiency.^{14–17}

In the present ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) study we have investigated the commercial PEDT:PSS formulation Baytron® P CH8000, which is presently being used as standard ICP as buffer layer in organic light emitting devices. Controlled processing and treatment schemes (including ultrahigh vacuum conditions) allowed us to show that the intrinsic work function of

PEDT:PSS can be as high as 5.65 eV and that it is strongly reduced by residual water (down to \sim 5.05 eV). In addition, water uptake of the ICP is accompanied by pronounced surface composition changes, which contribute to changes in ϕ .

A commercially available aqueous dispersion with a PEDT:PSS weight ratio of 1:20 (Baytron® P CH8000, H.C. Starck GmbH & Co. KG) was used to spin cast thin films onto freshly cleaned and UV/O₃-treated (30 min) indium tin oxide (on glass) substrates under ambient conditions. Such samples were directly transferred into the ultrahigh vacuum (UHV) system for further *in vacuo* treatment and photoemission experiments. Some samples were heated at 200 °C for 5 min in air prior to loading into the UHV system. Photoemission experiments were performed at the endstation SurfCat at synchrotron light source BESSY GmbH (Berlin). This system comprises the interconnected preparation and analysis chambers. The base pressure in the chamber used for sample annealing (via a resistively heated wire integrated in the sample holder) and the analysis chamber was 1×10^{-10} mbar, and 2×10^{-8} mbar in the chamber used for H₂O dosing. The pressure during sample annealing always remained below 8×10^{-9} mbar. Water (de-ionized) dosing was achieved through a leak valve. The excitation energies for UPS and XPS were 35 and 630 eV, respectively. Photoemission spectra were collected with a hemispherical electron energy analyzer set to an energy resolution of 100 meV. In order to determine the sample work function the secondary electron cutoff (SECO) was recorded with a -10 V sample bias.

The dependence of the work function of PEDT:PSS (spin cast in air and loaded into the UHV system without *ex situ* annealing) on the annealing temperature *in vacuo* is shown in Fig. 1(b). ϕ increased from its initial value of 5.05 eV to slightly above 5.65 eV for an annealing temperature of 220 °C. Higher temperatures led to lower ϕ values and probably degradation of the polymers. The dependence shown in Fig. 1(b) was the same for individual samples an-

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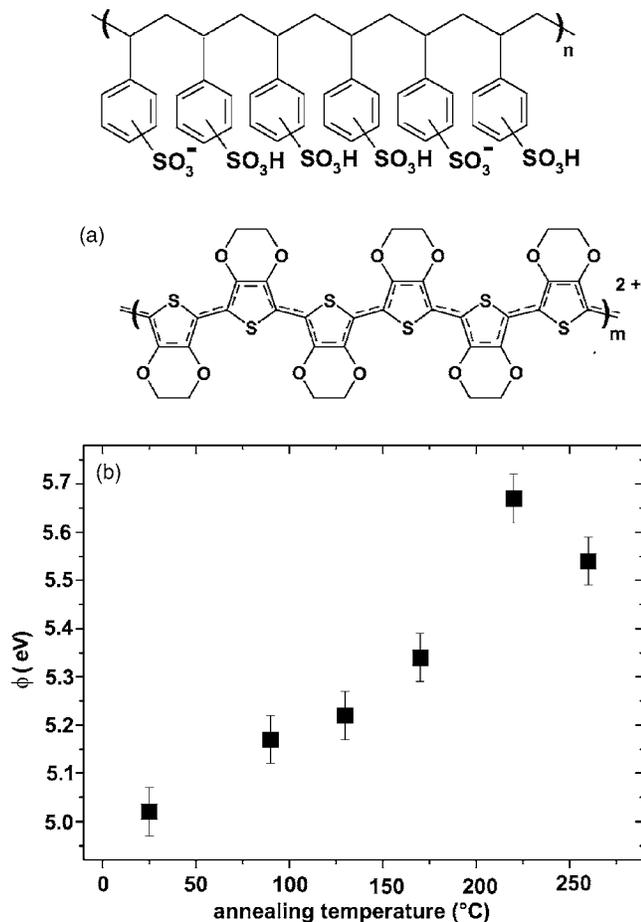


FIG. 1. (a) Schematic chemical structure of PEDT:PSS, and (b) relationship between PEDT:PSS (Baytron® P CH8000) work function ϕ and annealing temperature in ultrahigh vacuum.

nealed at just one specific temperature and also for samples where all annealing steps were performed sequentially with increasing temperature. Saturation of ϕ was achieved for annealing times of ~ 15 min. For comparison, PEDT:PSS samples annealed *ex situ* at 200 °C for 5 min (as recommended by the supplier) exhibited typical ϕ values of 5.20 eV. Longer annealing times in air did not result in changes of ϕ . Interestingly, such samples could also be brought to $\phi=5.65$ eV by subsequent annealing to 220 °C *in vacuo*. These initial results let us propose the hypothesis that

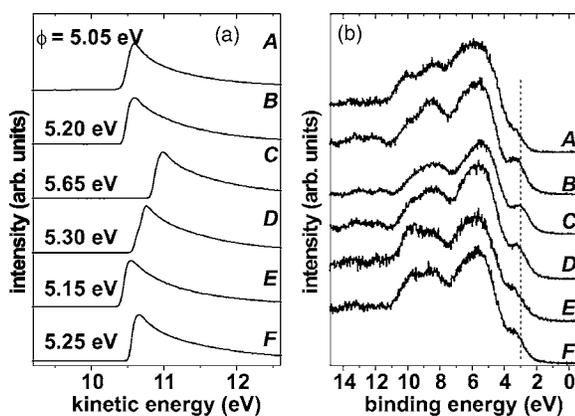


FIG. 2. (a) Secondary electron cutoff and (b) valence region photoelectron spectra of PEDT:PSS samples after different treatments A–F (as explained in the text).

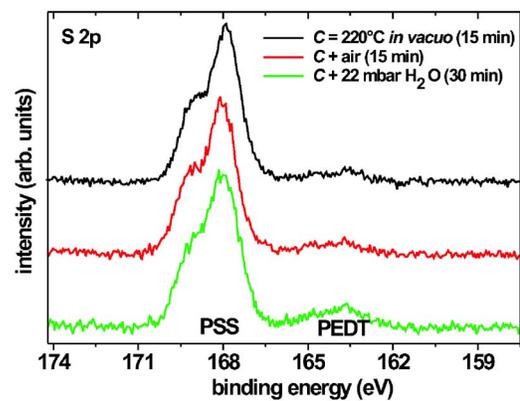


FIG. 3. (Color online) $S\ 2p$ core levels of PEDT:PSS samples after treatments C, F, and E (from top).

residual water within the ICP film causes the changes in ϕ . In order to explore this further, we exposed high- ϕ samples (prepared by *in vacuo* annealing at 220 °C; in the following referred to as treatment C) to pure water at a pressure of 1×10^{-3} mbar for 30 min (treatment D). This corresponds to the partial pressure of water in a typical inert gas box with 1 ppm H_2O content, simulating the conditions often prevailing during device fabrication. Another type of exposure consisted of pure water at ~ 22 mbar pressure for 30 min (E) and to ambient air for 15 min (F). The resulting SECO and valence region spectra are shown in Figs. 2(a) and 2(b), together with those obtained for PEDT:PSS not annealed (A) and *ex situ* annealed (B). While changes in the valence region were rather moderate, significant reductions in ϕ were observed, which can now clearly be related to the exposure of PEDT:PSS to water.

As ϕ decreased for increasing water exposure, also the surface composition (and thus morphology) of the PEDT:PSS films was changed. This is evidenced by the XPS spectra from the $S\ 2p$ core level in Fig. 3 (approximate information depth of 2–3 nm). While the surfaces for samples after treatments B, C, and D were enriched with PSS (expected bulk stoichiometry of 1:15.4 for Baytron® P CH8000), a significant increase in the signal from PEDT was observed after extended water (E) and air exposures (F), i.e., the surfaces became richer in PEDT. All corresponding values are summarized in Table I. Note that all effects of exposure to water and ambient air (containing ubiquitous water) on PEDT:PSS, i.e., change in ϕ and surface PEDT:PSS ratio, were *fully reversible* upon subsequent annealing to 220 °C *in vacuo*.

We suggest two simultaneously operative mechanisms that can lead to the observed lowering of the PEDT:PSS

TABLE I. Work function ϕ of PEDT:PSS (Baytron® P CH8000) films, and surface PEDT:PSS ratio measured in UHV as function of various treatments in air and vacuum.

| PEDT:PSS treatment | ϕ (eV) (in UHV) | PEDT:PSS ratio |
|---------------------------------------|----------------------|-----------------|
| A: vacuum dried | 5.05 | ... |
| B: 200 °C in air (5 min) | 5.20 | 1:22(± 5) |
| C: 220 °C <i>in vacuo</i> (15 min) | 5.65 | 1:20(± 5) |
| D: C + 10^{-3} mbar H_2O (30 min) | 5.30 | 1:24(± 5) |
| E: C + 22 mbar H_2O (30 min) | 5.15 | 1: 8(± 2) |
| F: C + air (15 min) | 5.25 | 1:12(± 3) |

work function upon exposure to water. First, the surface morphological changes induced by swelling of the polymer cause a higher surface concentration of PEDT. It has been suggested that the charges of PEDT⁺ and PSS⁻ cause local dipoles.⁷ A preferential orientation of these dipoles with their negative end towards vacuum (i.e., for a PSS-rich surface) on the surface leads to an increase in ϕ . Accordingly, we observed lower ϕ values for samples with lower surface PSS concentration (for treatments E and F). Second, the incorporation of water increases the dielectric constant ϵ of the sample [dielectric constant of water: 78 (Ref. 18)]. This in turn reduces the dipole-induced changes of ϕ ($\Delta\phi$) according to the Helmholtz equation,¹⁹ where $\Delta\phi \sim 1/\epsilon$.

Besides reducing the high work function of PEDT:PSS, the presence of residual water in conducting polymers (except when annealed *in vacuo*) may lead to earlier device degradation due to chemical reactions of water with conjugated organic materials and/or the cathode. Furthermore, a change in the ICP surface composition can have a significant influence on the function and efficiency of organic light emitting devices. It has been shown that PSS-rich surfaces lead to efficient electron blocking at the interface towards luminescent polymers, which increased exciton generation and thus device efficiency.¹⁴⁻¹⁷ This electron blocking effect of PEDT:PSS is reduced by the surface compositional changes induced by significant water exposure, i.e., the surface became PEDT rich in the present study. In addition, the surface composition might also determine the dipole formation and the hole-injection properties at the interface.⁷⁻¹⁰ Controlling the residual water content in conducting polymers involving PSS seems therefore of fundamental importance for device performance and possibly longevity. It will, however, remain an experimental challenge to confirm this hypothesis. All device processing steps following the deposition and postbaking of PEDT/PSS films have to be conducted at a partial water pressure in the ppb range, which is not readily accessible with standard equipment.

In conclusion, we have shown that residual water in *ex situ* annealed thin films of the conducting polymer PEDT:PSS is the cause for the large variation of ϕ observed for different preparation conditions. The work function of water-free PEDT:PSS samples was as high as 5.65 eV, while it was only 5.05 eV for high water content, i.e., without an-

nealing. Water exposure of *in vacuo* annealed samples caused swelling-induced increased PEDT concentration on the polymer surface, which explains ϕ lowering. Additional lowering of ϕ may be related to an increase of the sample dielectric constant by incorporation of water. Efficient removal of residual water in ICPs could be beneficial for device performance.

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