Investigation of the Effects of Doping and Post-Deposition Treatments on the Conductivity, Morphology, and Work Function of Poly(3,4-ethylenedioxythiophene)/Poly(styrene sulfonate) Films**

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We investigate the influence of annealing conditions on the physical properties of thin films of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS). In particular, we describe how annealing temperature, the ambient gas, and choice of dopant affect the conductivity, morphology, and work function of the films. Two specific dopants are considered, sorbitol and glycerol, and broad guidelines are developed for using PEDOT/PSS as a hole-injection electrode in polymeric light-emitting devices, solar cells, and photodetectors.

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the best-known π-conjugated polymers, and has attracted considerable commercial and scientific interest during the last decade owing to its excellent conducting and electro-optical properties. PEDOT is an insoluble polymer that exhibits several desirable properties in its oxidized state: high conductivity (ca. 550 S cm^{-1}); good thin-film transparency; and high stability.[1–4] The low solubility of pure PEDOT may be circumvented by using a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS) as a charge-balancing dopant during polymerization in water to yield a PEDOT/PSS aqueous composite.[5] The composite is believed to be a colloidal suspension in which PEDOT chains decorate segments of higher-molecular-weight PSS chains, and in which there is a modifiable excess of PSS. This combination has been developed extensively by researchers at the Bayer AG research laboratories in Germany, resulting in a water-soluble polyelectrolyte system with good film-forming properties, moderately high conductivity (ca. 10 S cm^{-1}), high visible-light transmission, and relatively good stability.[4–6]

The aqueous dispersion of PEDOT/PSS can form a thin and uniform intermediate layer between films of organic materials and indium tin oxide (ITO, a hole-injecting contact) that helps to limit the influence of asperities and to enhance adhesion. In addition, PEDOT/PSS has a higher work function than ITO, even after O$_2$-plasma treatment[7,8] and chemical modification[9,10] of the ITO. This combination of properties has lead to widespread use as an electrode/hole-transport layer in organic devices, such as light-emitting diodes and photodetectors.[11–14] Whilst the conductivity of the best (soluble) PEDOT/PSS films is reasonably high, there remain some applications for which higher electrical conductivities (> 10 S cm^{-1}) are required (such as stand-alone transparent anodes in flexible electronic devices). There have been several reported attempts to increase the conductivity of PEDOT/PSS films and improve their hole-injection properties, as described below:

- *Chemical modification of PEDOT during synthesis*. Kiebooms et al., for instance, prepared PEDOT$^{(+)}$(PF$_6^-$) by anodic oxidation of EDOT;[15] Groenendaal et al. prepared alkylated PEDOT derivatives;[16] and Randriamahazaka et al. used semi-interpenetrating polymer networks based on modified cellulose and PEDOT.[17]
- *Mixing the PEDOT/PSS dispersion with an organic solvent*, e.g., dimethyl sulfoxide, *N,N*-dimethylformamide, or tetrahydrofuran. It is believed that the screening effect due to the polar solvent between the PSS dopant and the PEDOT polymer main chain plays an important role in charge-transport properties.[18]
- *Addition of a small amount of a surfactant* to improve the wetting of the ITO surface by aqueous PEDOT/PSS, e.g., poly[oxyethylene(12)tridecyl ether].[19]
- *Addition of a dopant to modify the morphology*, e.g., glycerol, sorbitol, or a mixture of sorbitol, *N*-methylpyrrolidone, and isopropanol. It is considered that morphological changes induced by the presence of the dopants are important factors in the increased conductivity for doped films of this type.[14,20–22]

Taking into account the greater level of activity focused on the latter approach, in this paper we have chosen to focus our attention on studies of the effects that this doping approach has on other important parameters. In particular, we study the influence of post-deposition treatment atmosphere and treat-

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ment temperature on the conductivity, the work function, and the morphology for both doped and undoped PEDOT/PSS films, and we compare and contrast their differences.

## 2. Results and Discussion

2.1. Conductivity

Electrical properties of conducting polymers are strongly dependent on film morphology and chemical and physical structure, which are in turn affected by the annealing temperature and atmosphere. Winter et al.[3] found that sustained heating at 150 °C under atmospheric conditions causes irreversible structural changes in the PEDOT main chain. Aasmundtveit et al.[23] reported that heating PEDOT to 200 °C increases the crystalline order. PEDOT/PSS systems are hygroscopic and after treatment in air any observed thermal changes are generally unstable against the rapid uptake of atmospheric moisture.[24] In order to further investigate the different effects of moisture and oxygen on the electrical properties of PEDOT/PSS films, we investigated the effects of thermal treatment in air, O_2, and N_2 atmospheres,.

Figure 1 shows data after thermal treatment in air, O_2, and N_2 together with data for untreated films in these same atmospheres. The conductivities of the untreated films are different
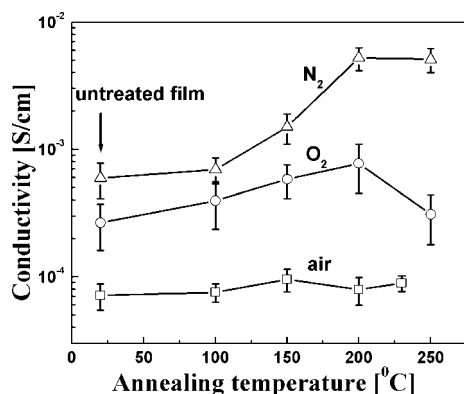
Figure 1. Conductivity of thin (~ 50 nm) PEDOT/PSS films measured in a coplanar electrode geometry before and after treatment at elevated temperature. The samples were stored, thermally treated, and then allowed to cool in air (squares), in N_2 (triangles), or in oxygen (circles). The conductivity was measured only following equilibration at room temperature.

due to varying levels of residual water in the different atmospheres as we discuss later. The conductivity for the treated films was measured only after the films had completely cooled to room temperature (after several hours) and had reached a stable value. We observed in all cases that the conductivity of the films decreases monotonically after the heating has ceased (Fig. 2a). The conductivities of the films treated and measured in O_2 and N_2 reached a stable saturation value at room temperature. The conductivities of those treated and measured in air decreased continuously over about ten hours until the conduc-
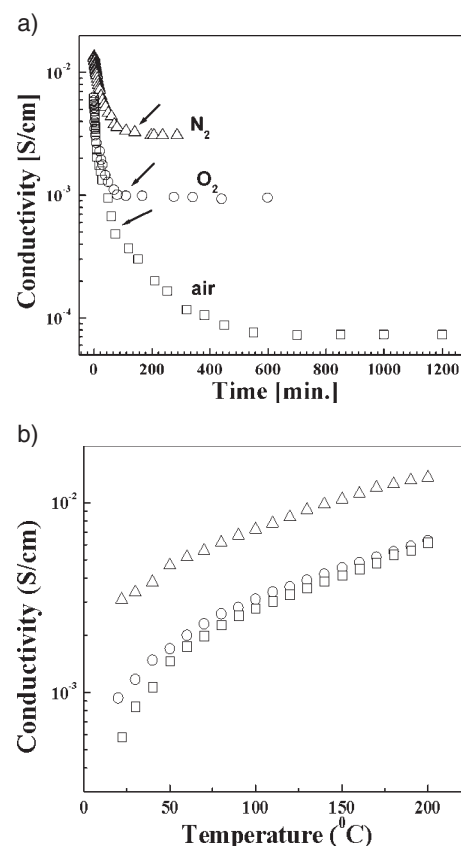
Figure 2. a) Conductivity of PEDOT/PSS films treated at 200 °C as a function of the time after the heating had ceased. b) Dependence of the conductivity on temperature in all cases measured during cooling from the annealing temperature. For both parts of the figure, triangles are for measurements in N_2, squares for measurements in air, and circles for measurements in O_2. The three arrows mark the times at which the temperature just reaches room temperature. Under N_2 and O_2 atmospheres there is then very little further change. In contrast, the conductivity continues to decrease for the samples in air.

tivity reached a saturation value (Fig. 2a) equal to the conductivity before treatment irrespective of the treatment temperature. From Figure 2a it is apparent that the conductivities measured in air, O_2, and N_2 have almost parallel dynamics during the initial cooling (temperature above 50 °C), but the conductivity measured in air subsequently decreases more rapidly.

The PEDOT/PSS films are hygroscopic and the degree of water uptake is expected to scale with the amount of PSS. The ratio of PEDOT to PSS used here was 1:6. Air-annealed films start absorbing water from the air when they cool below a certain critical temperature of 50 °C (Fig. 2b). The increasing discrepancy, as the temperature falls further, between the conductivity of air- and O_2-annealed films implies a steadily rising influence of moisture on the conductivity. It is worth noting that on first cooling to room temperature, the difference in conductivity between the air- and O_2-annealed films is only about a factor of two. However, this difference continues to rise with time yielding a final conductivity for the air-annealed films that is about thirteen-times lower than that of O_2-annealed films. The immediate implication for device fabrication

is that annealing should be undertaken in a moisture-free atmosphere.

It is common knowledge that PEDOT/PSS films are very stable; they can be treated for up to 1000 h at 100 °C with no change in conductivity.[5] This implies that the O_2 molecules in the air do not have an adverse effect on the conductivity of PEDOT/PSS films, at least below 100 °C. It might therefore be expected that there should be no difference between the conductivities of O_2- and N_2-annealed films below 100 °C but this is not the case and N_2-annealed films were found to have markedly higher conductivities (Fig. 1). The discrepancy is attributed to higher levels of "residual" water in the O_2 atmosphere rather than any specific influence of the O_2 itself; it should be remembered that O_2 annealing was performed in a continuous-flow experimental arrangement, whereas N_2 annealing was performed in a glovebox with active H_2O removal. The importance of residual water was confirmed when a second batch of N_2-annealed films were prepared with the same continuous-flow arrangement used for O_2 annealing; in these circumstances, N_2- and O_2-annealed films yielded broadly comparable results, confirming the highly detrimental influence of water vapor on PEDOT/PSS film conductivity, even at relatively low atmospheric levels. The variations in residual water levels for the films tested in the different atmospheres account for the different conductivity values of the untreated films reported in Figure 1. As the annealing temperature is raised from 100 to 200 °C, the conductivities of the O_2- and N_2-annealed films increase, those annealed in N_2 always being more conductive than those annealed in O_2 (in Fig. 1). Apart from the influence of residual water, it suggests that oxygen itself may play a role in the acceleration of film degradation at high temperature.

The changes in the conductivity of N_2-annealed films should relate to thermally induced changes in the nature of the PEDOT/PSS films. Since the conductivities of the films annealed at 100 °C are almost identical before and after treatment, it appears that this temperature is too low to substantially alter the polymer films. The conductivities of the films then increase with annealing temperature, reaching a peak value at 200 °C, for which annealing temperature the final room-temperature conductivity is about ten-times higher than that of unannealed films. The conductivity of films treated at 250 °C is slightly lower than those at 200 °C but not substantially so, suggesting that thermal degradation of PEDOT/PSS is relatively mild compared with the case for O_2-annealed films.

The chain alignment in thin polymer films often changes with temperature, leading to modified morphologies. Heating may also affect the colloidal particle interactions in the PEDOT/PSS composite. PEDOT/PSS is an aqueous gel dispersion in which the hydrated or swollen gel particles consist of PSS interlinked by PEDOT chains. The conductivity of dried PEDOT/PSS films depends critically on the gel particle size distribution as is the case for many granular conductors where grain size and connectivity control conductivity. The increase in conductivity with increasing grain size follows directly from the reduction in the number (and/or height) of inter-grain hopping barriers. The number of such barriers may be reduced at elevated annealing temperatures by coalescence of PEDOT/PSS parti-

cles, e.g., by softening/melting of PSS and PEDOT. This can lead to the polymer chains adopting a more crystalline structure as reported by Aasmundtveit et al.[23]

An undesirable side effect of heating is thermal degradation; in a previous report we investigated how the treatment time at 200 °C affects the conductivity of N_2-annealed PEDOT/PSS films.[24] We found a 27 % decrease in conductivity when the treatment time is increased from 10 to 50 min. Kiebooms et al.[15] and Winter et al.[3] separately reported thermal ageing studies showing that PEDOT films undergo continuous degradation above a treatment temperature of 150 °C. In light of the findings of Aasmundtveit et al.,[23] the variations in conductivity with treatment time that we report here may be the result of a competition between enhanced crystallization and the onset of material degradation. If the temperature is too high (above 250 °C, from our data) degradation of the materials becomes a severe problem and the conductivity falls.

We turn our attention now to doped PEDOT/PSS films. Figure 3 shows the conductivities of sorbitol- and glycerol-doped PEDOT/PSS films (referred to here as S-PEDOT/PSS and G-PEDOT/PSS, respectively) for various doping ratios; data
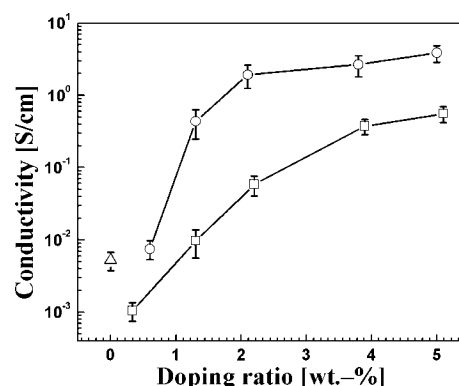
Figure 3. Comparison of the conductivities of the S-PEDOT/PSS (circles) and G-PEDOT/PSS (squares) films as a function of doping ratio. The pristine PEDOT/PSS film conductivity is also shown (triangle). The annealing temperatures for S-PEDOT/PSS, G-PEDOT/PSS, and pristine PEDOT/PSS films are 180 °C, 160 °C, and 200 °C in N_2, respectively. As before, the conductivity was measured only following equilibration at room temperature.

for an undoped PEDOT/PSS film prepared under the optimum annealing conditions is also shown for comparison. The optimal annealing temperatures for sorbitol- and glycerol-doped PEDOT/PSS films were empirically found to be 180 °C for 8 min and 160 °C for 40 min, respectively. In both cases, the conductivities increase with the doping ratio and tend to a saturation value. Of the two dopants, sorbitol is the more effective as a means of increasing film conductivity; significant improvements in conductivity are observed even for low doping ratios of 0.6 wt.-%; at 2 wt.-% the conductivity is about 500 times higher than that of the best undoped films. In contrast, at the lowest measured doping ratio (0.33 wt.-%), the conductivities of the 160 °C annealed G-PEDOT/PSS films were found to be lower than those for the best undoped PEDOT/PSS films (an-

nealed at 200 °C). They are, however, comparable with those for undoped PEDOT/PSS films annealed at a similar temperature (compare 150 °C data shown in Fig. 1 with conductivity for G-PEDOT/PSS annealed at 160 °C, shown in Fig. 3). This suggests that glycerol has an essentially negligible effect on the film morphology (and hence conductivity) when present at low concentration (0.33 wt.-%).

The increased conductivities of the films in the presence of (sufficient levels of) the two dopants are believed to arise from the rearrangement of the PEDOT/PSS morphology at high temperatures leading to better connections between the conducting PEDOT chains. Greczynski et al.[25] reported X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements showing that heating of undoped PEDOT/PSS films causes phase segregation. This results in a surface entirely covered by an excess of PSS that behaves as an insulator. It is likely that a composition gradient exists from the surface to the bulk of the film. PEDOT molecules, which are responsible for conduction in the blend, are not uniformly distributed. As a result, the conductivity is not uniform through the entire film but varies in the direction perpendicular to the plane of the film. Jönsson et al.[22] reported that sorbitol-doped PEDOT/PSS films lose significant quantities of dopant material during heating, suggesting that the dopant molecules themselves are not the key mechanism for the improved conductivity. The same situation would be expected to occur for glycerol molecules since they should be even more easily evaporated during heating than sorbitol. The morphological and physical changes during PEDOT/PSS film formation are considered more likely to account for the improved conductivity. Compared with undoped films, doped films show a two- to three-fold increase in the PEDOT/PSS ratio within the surface layer.[22] This results in a more uniform distribution of PEDOT molecules throughout the PEDOT/PSS film, which in turn improves overall connectivity between PEDOT grains. This should in turn create better pathways for charge transport perpendicular to the film.

2.2. Morphology

Atomic force microscopy (AFM) topography images of undoped and doped PEDOT/PSS films were recorded to study possible changes in morphology. Figure 4 shows the surface roughness of undoped PEDOT/PSS, S-PEDOT/PSS, and G-PEDOT/PSS films as a function of treatment temperature. For comparison, the roughness of bare ITO and ITO coated with films of unannealed PEDOT/PSS, S-PEDOT/PSS, and G-PEDOT/PSS were also measured (see Fig. 4). Upon increasing the doping ratio for both sorbitol and glycerol systems, the conductivities of the films increase but the film quality decreases (surface roughness increases shown in Fig. 5). Considering both the conductivity and film uniformity, doping ratios for S-PEDOT/PSS and G-PEDOT/PSS of about 2.2 and 1.2 wt.-%, respectively, are considered optimum.

It is very clear that deposition of doped and undoped unannealed PEDOT/PSS films on top of ITO reduces the surface
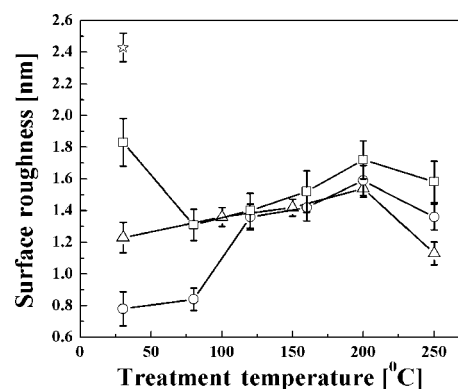
Figure 4. Dependence of the surface roughness of pristine PEDOT/PSS films (triangles), S-PEDOT/PSS films (circles), and G-PEDOT/PSS films (squares) on treatment temperature in N_2. The doping ratios for S-PEDOT/PSS and G-PEDOT/PSS are about 2.2 and 1.2 wt.-%, respectively. The measurements were taken after equilibration at room temperature. Also shown for comparison is the surface roughness of the underlying ITO (star).
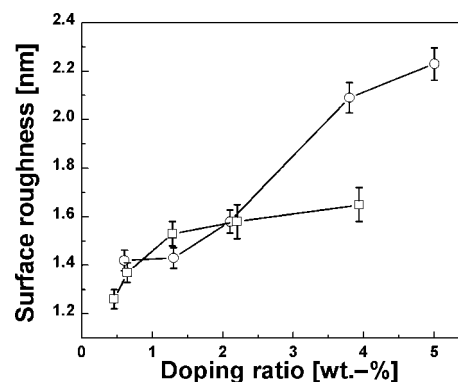
Figure 5. Comparison of the surface roughness of the S-PEDOT/PSS films (circles) and G-PEDOT/PSS films (squares) with different doping ratios. The annealing temperatures in N_2 for S-PEDOT/PSS and G-PEDOT/PSS are 180 °C for 8 min and 160 °C for 40 min, respectively. The surface roughness was measured after equilibration at room temperature.

roughness. A roughness of 2.43 nm was found for our untreated ITO and this reduced to 1.23 nm after coating with an undoped PEDOT/PSS layer. The surface roughness of the undoped films increases, however, when the PEDOT/PSS is heat-treated and reaches its maximum value at a treatment temperature of 200 °C. The roughness then drops as the treatment temperature is further increased. One possible reason is that thermal degradation is minimal at low temperatures and the primary effect of increasing temperature is to increase the effective colloidal particle size, leading to greater surface roughness. The reduction in roughness above 250 °C is consistent with the onset of film degradation. This is in agreement with previous AFM studies[25] that suggested a grain-like structure of PEDOT/PSS films with an inhomogenous distribution of the PEDOT and the PSS species within a single grain.

Prior to annealing, the G-PEDOT/PSS films are somewhat rougher than unannealed PEDOT/PSS films (with the surface

roughness increasing sharply at higher glycerol concentrations): Unannealed S-PEDOT/PSS films by contrast are considerably smoother than G-PEDOT/PSS and undoped PEDOT/PSS films. This may be due in part to different degrees of adhesion to the substrate. The surface roughness of G-PEDOT/PSS films decreases substantially after an initial thermal treatment, even for relatively low annealing temperatures of 80 °C. S-PEDOT/PSS films are, however, little affected by annealing at 80 °C due to the high melting point of sorbitol (98–100 °C) relative to glycerol (20 °C). Both types of doped film show similar behavior to that for undoped PEDOT/PSS for annealing temperatures above 80 °C for G-PEDOT/PSS and 120 °C for S-PEDOT/PSS. This indicates that the surface roughness of the doped films is controlled by thermally induced changes in film morphology. These are in turn expected to be influenced by the rate of evaporation of the dopant molecules at any given annealing temperature.

2.3. Work Function

PEDOT/PSS films have been widely used in organic and polymeric devices as hole-injection layers. The contact between ITO and PEDOT/PSS is effectively Ohmic and the pertinent barrier to hole injection is actually determined by the work function of PEDOT/PSS. Therefore, the work function of PEDOT/PSS films plays a central role in determining the efficiency and performance of light-emitting diodes (LEDs). The measured work function is an extremely sensitive indicator of surface quality since gases or other adsorbed species may induce substantial variations of the energy required to remove an electron from the Fermi level. As described above, the conductivity and morphology of PEDOT/PSS film vary according to the specific conditions of thermal annealing and, as such, we expect to observe associated changes in the work function according to treatment conditions.

The work-function measurements reported here were carried out by means of the Kelvin probe method.[26] This technique measures the contact potential of a sample relative to a reference electrode and is therefore a relative measure of the work function. The values obtained from the Kelvin probe measurements may differ from those obtained using UPS because the former yields a value averaged over the area of the electrode whereas the latter is a localized measurement. The Kelvin probe technique yields values that tend to be slightly higher than those from UPS but has the important advantage that it may be used under ambient conditions. It therefore provides a convenient and inexpensive tool for fast screening of contact potential differences. All measurements reported here were undertaken inside a N_2-filled glovebox in a shielded metal box to eliminate stray electric fields. In the course of the measurements, the reference electrode was inevitably exposed to the ambient gas (N_2) introducing the possibility of progressive changes in its work function. To minimize this effect, freshly prepared metal samples were periodically measured for calibration purposes.

Figure 6 depicts the dependence of the work function of PEDOT/PSS films on thermal treatment in air, O_2, and N_2. The subsequent changes in work function on prolonged exposure to humid air (a sealed box with saturation vapor at room temper-
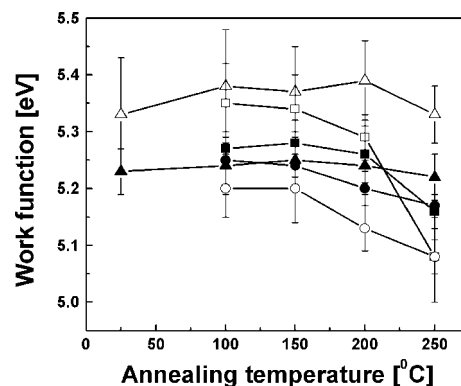

Figure 6. Dependence of the work function for the pristine PEDOT/PSS films on thermal treatment in air (open squares), under O_2 (open circles), or under N_2 (open triangles). The work function was measured only following equilibration at room temperature. The work function values after subsequent overnight exposure at room temperature to moist air are also shown (corresponding filled symbols).

ature) are also shown in Figure 6. The work functions for the treated films were measured only after they had completely cooled to room temperature. The work functions of N_2-annealed films were found to be higher than those treated in air or O_2. The work functions of air- and O_2-annealed films decrease monotonically with increasing annealing temperature. The reasons for the difference between the work functions of the air- and O_2-annealed films are not yet clear but we suggest a few possibilities. The morphology of the hygroscopic films treated in (hydrated) air may be different from those treated in a dry gas; in addition, the measured work function is sensitive to the surface properties. Any change in the electrical character of the specimen surface — for example, due to adsorption of atoms, molecules or ions — will change the work function. The films treated in air are likely to have been exposed to other impurity particles in addition to gas molecules, and the dipole moment of any absorbed species can directly induce contact potential-difference shifts.[27]

Interestingly, after prolonged exposure to high-humidity air (allowing water uptake to reach its saturation value), the work functions of the annealed films are quite similar (~ 5.25 eV), except for those treated in air and in O_2 at 250 °C. The latter have slightly lower values (see Fig. 6). The hygroscopic PEDOT/PSS gel particles swell after water uptake. The films after thermal treatment have a PSS-rich component on the surface, which is especially hygroscopic and may cause H_2O molecules to form a thin layer above the PSS chains. The surface layer of H_2O molecules may suppress the influence of thermal and ambient gas on the morphology of the films. The films treated in air and O_2 at 250 °C show substantial thermal degradation.

Figure 7 shows work functions for doped PEDOT/PSS films with different glycerol and sorbitol doping ratios. All of these samples were prepared in air and then annealed in dry N_2. The
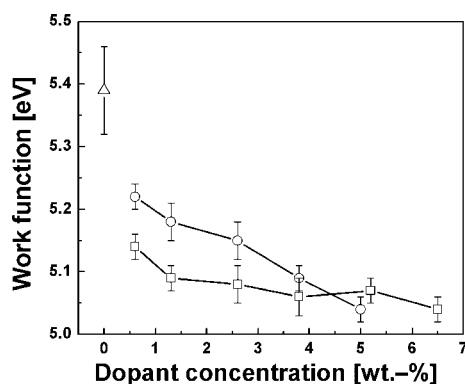
Figure 7. Comparison of the work-function values for S-PEDOT/PSS (circles) and G-PEDOT/PSS (squares) films with different doping ratios, and for a pristine PEDOT/PSS film (triangle). All of these samples were spincoated in air and then annealed in a glovebox filled with N_2. The pristine PEDOT/PSS, S-PEDOT/PSS, and G-PEDOT/PSS films were treated at 200 °C for 10 min, 180 °C for 8 min, and 160 °C for 40 min, respectively.

undoped PEDOT/PSS, S-PEDOT/PSS, and G-PEDOT/PSS were treated at 200 °C for 10 min, 180 °C for 8 min, and 160 °C for 40 min, respectively. The work functions show a steady decrease with increasing dopant concentration. The results for G-PEDOT/PSS films lie in the range 5.1 ± 0.05 eV for different doping ratios, which are in agreement with previously reported values of 4.9–5.0 eV.[14] The morphological changes in the PEDOT/PSS films and variations in the ratio of PEDOT to PSS at the surface of the films after doping may be responsible for the changes in work function.

Finally, we fabricated polymer LEDs with doped and undoped PEDOT/PSS films as the hole-transport layer. Poly(9,9-dioctylfluorene) (95 wt.-%) blended with poly[(9,9-dioctylfluorene)-*co*-benzothiadiazole] (5 wt.-%) was used as the emitter and Ba/Al as the cathode. All devices were fabricated under the same conditions except for the use of a pristine or a doped PEDOT/PSS layer. We note that although the work functions of doped PEDOT/PSS films are deduced to be some 0.2–0.3 eV lower than those of undoped films, we did not find the turn-on voltage of such devices to be correspondingly higher than those for devices using pristine PEDOT/PSS. They all had a turn-on voltage around 2.3 V. The reason for this apparent "pinning" effect is not yet clear, but may be related to field-enhanced injection due to trap sites at the PEDOT/PSS–polyfluorene interface, as previously described by Brewer et al.[28] A further study of the injection mechanism for these devices is underway.

3. Conclusion

We have investigated the influence of annealing conditions on the physical properties of thin films of poly(3,4-ethylenedi-

oxythiophene) oxidized with poly(styrene sulfonic acid) (PEDOT/PSS). In particular, we have investigated how annealing temperature, the ambient gas, and the choice of dopant affect the conductivity, morphology, and work function of the films. The presence of water and O_2 in the ambient gas reduces the conductivity and work function of the undoped PEDOT/PSS films. Inert gases such as N_2 are therefore recommended for the treatment of PEDOT/PSS films. The improvements in conductivity after annealing are attributed to morphology changes that lead to larger grain sizes and lower inter-grain hopping barriers. The introduction of dopants leads to substantial increases in conductivity, by up to a factor of about 500, depending on the exact doping ratio. The surface roughness is also found to increase, with the degree of roughness at a given annealing temperature, apparently dependent on the rate of evaporation of the dopant molecules. The work functions for sorbitol- and glycerol-doped PEDOT/PSS films are lower than those for undoped films and they decrease with increasing dopant concentration. Further studies of the influence of these treatments on device performance are underway for polymer LEDs, solar cells, and photodetectors.

4. Experimental

An aqueous dispersion of PEDOT/PSS, known commercially as Baytron P VP AI 4083, was obtained from HC Starck. To prepare doped films, various concentrations of sorbitol or glycerol (Sigma–Aldrich, used as received) were added to the PEDOT/PSS dispersion as appropriate. All dispersions were filtered with a 0.45 μm syringe filter. Thin films of approximately 50 nm were spin-coated in air at ~2000 rpm onto patterned ITO substrates. The films were subsequently heated on a hot plate at temperatures between 100 and 250 °C in air, O_2, or N_2. O_2 annealing was carried out by continuously flowing O_2 over a heating stage (Linkam HFS91). Annealing under N_2 was carried out in a glovebox with H_2O and O_2 levels of less than 1 ppm and 0.1 ppm, respectively. The resistance of the films was determined using coplanar ITO contacts separated by 1 mm; the surface roughness of the films was measured in air with an atomic force microscope (Burleigh SPM); and work functions were measured using the Kelvin probe technique (Kelvin Control 07 from Besocke Delta Phi GmbH).

Note added in proof: Timpanaro et al. (*Chem. Phys. Lett.* **2004**, *394*, 339) recently reported a scanning probe microscopy study of PEDOT/PSS and the influence of sorbitol doping on conductivity. Their conclusions on morphological factors are in general agreement with those reported here for S-PEDOT/PSS.

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