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Modification of PEDOT–PSS by low-energy electrons

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Abstract

The stability of conjugated organic materials under electron transport is of great importance for the lifetime of devices such as polymer light-emitting diodes (PLEDs). Here, the modification of thin films of poly(3,4-ethylenedioxythiophene) oxidized with poly(4-styrenesulfonate) (known as PEDOT–PSS, often used in the fabrication of PLEDs) by low-energy electrons has been studied using X-ray photo-electron spectroscopy. Thin films of PSSH and molecular solid films of EDOT molecules also have been studied. We find that electrons with kinetic energies as low as 3 eV result in significant modification of the chemical structure of the materials. For thin films of PSSH, the electron bombardment leads to a strong loss of oxygen and a smaller loss of sulfur. In addition, a large amount of the sulfur atoms that remain in the films exhibits a different binding energy because of scissions of the bonds to oxygen atoms. For condensed molecular solid films of EDOT molecules, we find that the carbon atoms bonded to oxygen react and form additional bonds, as evidenced by a new component in the C(1s) peak at a higher binding energy. In the PEDOT–PSS blend, we find both effects. The importance of these observations for light-emitting diodes incorporating PEDOT–PSS films is discussed. This work demonstrates that the combination of in situ low-energy electron bombardment in combination with photo-electron spectroscopy is a powerful method to simulate and study certain processes, associated with low-energy electrons, occurring in organic based devices, which cannot be studied directly otherwise.

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1. Introduction

Poly(3,4-ethylenedioxythiophene), or PEDOT [1,2] is an electro-chemically stable conjugated

polymer which can be oxidized (doped) to a high electrical conductivity [3] while maintaining moderate transparency [4–7]. Oxidized PEDOT, doped with poly(4-styrenesulfonate) or PSS, is used as a hole transport (buffer) layer in polymer based light-emitting diodes [7,8], so-called p-LED's. In such devices, PEDOT–PSS is used in between the indium–tin-oxide (ITO) substrate and the electroluminescent polymer, often poly(*p*-phenylenevinylene), or PPV. It has been shown that the presence of the PEDOT–PSS film leads to improved stability

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of LED's [9], and the device characteristics are less dependent upon the properties of the rough ITO substrate [10].

However, recent reports appearing in the literature indicate that degradation of p-LED's including a PEDOT–PSS film may be at least partially due to a degradation of the PEDOT–PSS film itself during operation of the devices. Rannou and Nechtschein [11] have reported on kinetic studies of the conductivity and conjugation of doped PEDOT thin films on polymer substrates. They have shown that the conductivity decay in air follows an Arrhenius law. This model provides an estimate for the half-life parameter of the conductivity in a device working in air at 100 °C to be about 150 h. In a recent study by de Jong et al., it was shown that migration of sulfur compounds occurs in devices containing PEDOT–PSS, leading to an accumulation of sulfur compounds at the PPV–cathode interface [12]. The migration occurred upon exposure to air, and under electrical stress in the absence of air. The latter results show that degradation of PEDOT–PSS is not only dependent upon air, but can also be induced by electrical transport. The causes of the degradation, however, are still unclear.

Recently, it was reported that PEDOT–PSS contains halogen impurities that can result in degradation of the material because of the high cross-section of dissociative electron-attachment reactions [13]. However, even low-energy electrons could, in principle, cause the degradation of materials. Here, we report on the effect of bombardment of low-energy (3 eV) electrons on the surfaces of PEDOT–PSS films. By studying the XPS core level spectra, C(1s), O(1s) and S(2p), of PEDOT–PSS films, PSSH films, and condensed EDOT films, it is shown that both bond breaking and composition changes are induced by low-energy electrons. Although the energy of the electrons in this study is high (3 eV) compared with energies of electrons injected into real devices, the dose used was three orders of magnitude lower than typical currents in p-LED's. The electron-impact-induced processes are expected to be similar to processes that occur during electron transport in devices containing PEDOT–PSS films, which is supported

by the similarity to observed effects in PEDOT–PSS containing devices under stress.

2. Experimental

PEDOT–PSS in aqueous solution was purchased from Bayer, while PSSH and EDOT were obtained from Aldrich Chemicals. Fig. 1 shows the chemical structures of the molecules. PEDOT–PSS films and PSSH films were prepared by first filtering the suspensions with a 1 µm filter in order to remove possible lumps, and subsequently spin-coating the suspensions on ITO substrates. The ITO substrates were prepared by ultrasonic rinsing, first in acetone and subsequently isopropyl alcohol, and finally normal rinsing in de-ionized water. The EDOT films were prepared in situ in the UHV system on ITO or Au substrates. The ITO substrates used for the condensed EDOT films were cleaned by ultrasonic rinsing in acetone and subsequently isopropyl alcohol, followed by UV–ozone treatment, immediately prior to insertion into the vacuum system. The Au substrates consisted of polycrystalline Au layers deposited on optically flat, naturally oxidized Si(110) wafers. Before inserting in the vacuum system, they were cleaned by ultrasonic rinsing in acetone and isopropanol. In the UHV system they were further cleaned by degassing at 150 °C, followed by a gentle etching using Ar⁺ ions. EDOT films were prepared by cooling the substrate to –150 °C and

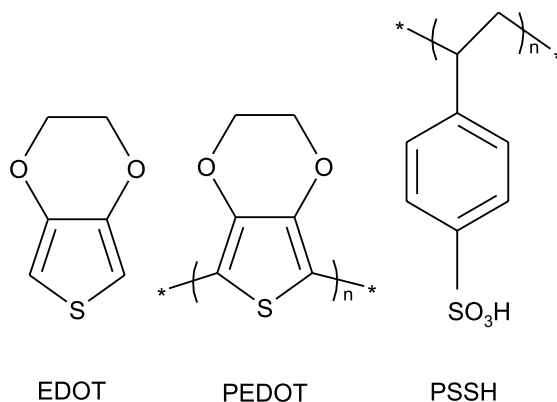


Fig. 1. Chemical structures of EDOT, PEDOT and PSSH.

subsequent adsorption of EDOT molecules which were let into the chamber to a pressure of 2×10^{-7} mbar for typically 10 min.

The XPS experiments were performed in a Scienta ESCA200 spectrometer with a base pressure in the low 10^{-10} mbar region of both the analysis and the preparation chamber (where the EDOT adsorption was carried out). Monochromatised Al(K α) X-rays were used for the analysis. All spectra shown here are “as recorded”, i.e., without smoothing, and with the binding energy referenced to the Fermi level of the substrate. The peak areas of the core level spectra were used to monitor changes in the elemental composition of the samples. It was checked that the pure EDOT and PSSH films gave consistent sensitivity factors for the relevant elements (C, O, S). Because the changes in the peak areas depend on the applied electron dose, and because after electron bombardment the samples are not homogeneous over the information depth of XPS, we do not give absolute values for the composition of the samples. Instead, we report the observed changes in relative signal ratios, which are sufficient to deduce which elements are involved in the species generated. In the standard geometry for the XPS experiments the photo-electrons leave the sample perpendicular to the sample surface. In some cases we show measurements for different exit angles, where the effects are more pronounced due to the enhanced surface sensitivity. It was verified on undamaged PEDOT–PSS films that the exit angle did not influence the peak position, shape and relative intensities significantly. In all the spectra shown here, the data points are represented by crosses, whereas the solid curves represent fits to the data used for the analysis.

Electron bombardment was done using a commercial “electron flood gun” mounted on the Scienta instrument. The energy of the electrons was determined by checking the voltages in the flood gun, and by measuring the sample current versus retardation potential applied to the sample. The values thus determined agreed with the settings of the flood gun controller. At 3 eV, a typical current density obtained at the sample was about $1 \mu\text{A}/\text{cm}^2$, which is more than three orders of magnitude lower than current densities common in

p-LED’s under operating conditions. We have also carried out experiments at higher electron energies (50 eV), the results of which are not shown here. These higher energy experiments yielded similar results as reported here for 3 eV. The fact that the changes presented here are solely due to the electron bombardment, and not induced by the X-rays employed for the analysis was carefully checked.

3. Results

3.1. PEDOT–PSS films

Figs. 2 and 3 show S(2p) and C(1s) XPS core level spectra obtained on a PEDOT–PSS/ITO

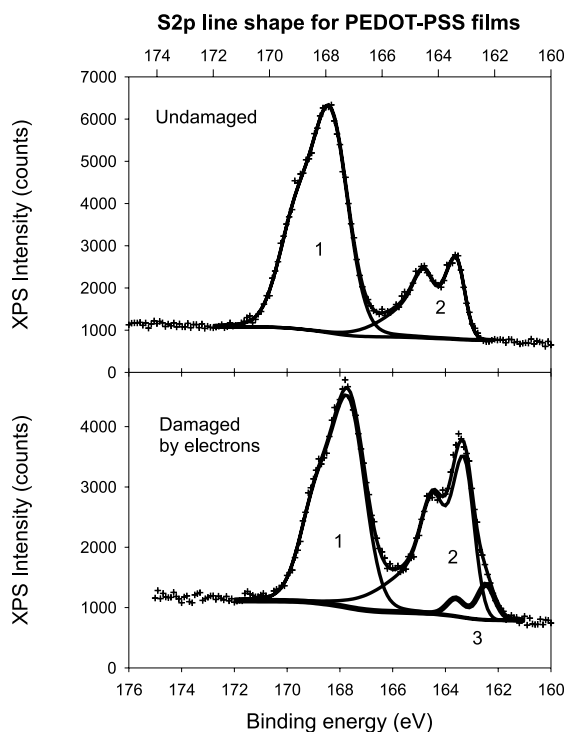


Fig. 2. Sulfur core level spectra of a PEDOT–PSS film before (top) and after (bottom) electron bombardment. In all spectra shown in this paper, experimental data are shown as crosses, and fits to the data are shown as solid curves. Peak 1 corresponds to S in the PSSH, peak 2 to S present in the PEDOT, and peak 3 is the new feature observed after electron bombardment.

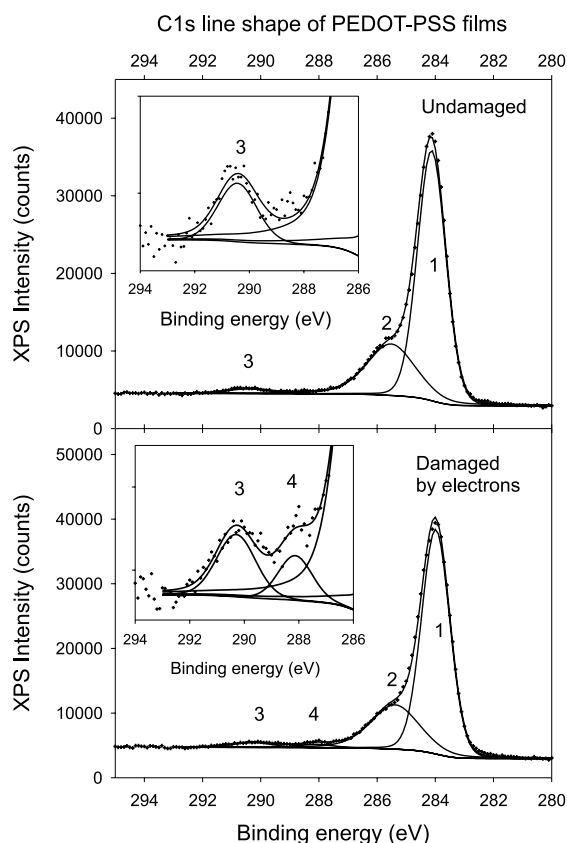


Fig. 3. Carbon core level spectra of a PEDOT-PSS film before (top) and after (bottom) electron bombardment. Peak 1 corresponds to C atoms in the PSS and the C atoms in the PEDOT which are not bonded to the oxygen atoms. Peak 2 corresponds to C atoms in PEDOT which are bonded to oxygen atoms, peak 3 is a shake-up peak. Peak 4 is a new feature observed after electron bombardment.

sample. The top panel shows scans obtained on the as-prepared films, whereas the scans in the bottom panels were obtained after bombardment by 3 eV electrons with a current density of about $1 \mu\text{A}/\text{cm}^2$ for 67 h at room temperature. These scans were obtained for an exit angle of the photo-electrons with respect to the sample normal of 45° . Integration of the peak area's for the C(1s), S(2p) and O(1s) peaks, before and after electron bombardment, show that the C/O signal increased by a factor of about 1.5, the C/S ratio by a factor of 1.2, and the O/S ratio by a factor 0.8. It thus appears that oxygen-containing species were detached, and

that these oxygen-containing species (or oxygen atoms) escaped from the sample surface. In addition, some sulfur-containing groups have been removed from the sample.

In analyzing the line shapes, the most obvious changes are visible in the S(2p) spectra of Fig. 2. The intensity in the S(2p) spectrum related to PSS (high binding energy) appears to decrease, compared to the portion of the S(2p) spectrum which is related to PEDOT. As shown below, for electron irradiated PSSH films, S-containing groups leave the surface. The scans in Fig. 2, however, over estimate the effect, because part of the sulfur signal from the PSSH shifts to lower binding energies by about 5 eV, and thus becomes almost indistinguishable from the PEDOT contribution. In the fits to the data points in Fig. 2(bottom), the S(2p) has been fitted with a third component at just 5 eV lower in binding energy, to take this into account. The C(1s) line shape in Fig. 3 also changes upon electron bombardment, although much less drastically. A small but significant and reproducible new feature develops on the high binding energy side of the main peak, near 288 eV, as is clearly seen in the insert in the figure (peak 4). In the O(1s) spectra (not shown here), the only change induced by electron bombardment is that the contribution from the oxygen in the PEDOT (higher binding energy) becomes somewhat stronger compared to the contribution from the oxygen-containing portions of PSSH (lower binding energy peak). This corresponds to a loss of oxygen, as discussed below, from the PSSH part of the films, which is enhanced by the segregation of PSSH towards the surface, making it more vulnerable to the electron bombardment. Angle dependent measurements showed qualitatively the same effects, but less pronounced for normal exit of the photo-electrons, and more pronounced for a glancing angle of 20° . This indicates that the changes to the PEDOT-PSS films are concentrated in the outermost region of the sample.

3.2. PSSH films

Fig. 4 shows the line shape of the S(2p) peak for a PSSH/ITO sample, both before and after exposure to the 3 eV electrons, about $1 \mu\text{A}/\text{cm}^2$ for 67 h.

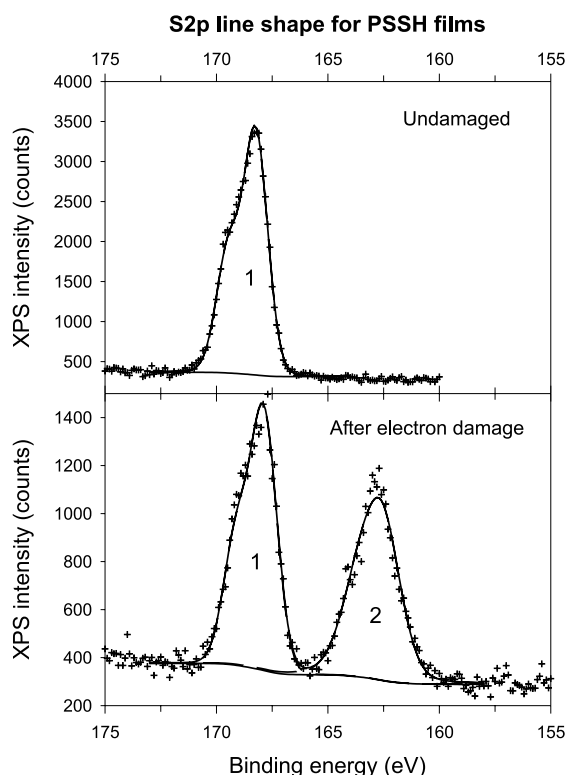


Fig. 4. Sulfur core level spectra of a PSSH film before (top) and after (bottom) electron bombardment. Peak 1 corresponds to the S atoms as present in undamaged PSSH, whereas peak 2 corresponds to S atoms for which the bond with the oxygen atoms has been broken.

The C/O signal ratio increases by a factor 3.9, the C/S ratio by a factor 1.7, and the O/S ratio by a factor 0.4. Clearly, electron bombardment leads to a very significant loss of oxygen-containing species (more than 30% over the information depth of XPS), and also a less but still significant loss of sulfur. The oxygen loss is underestimated, since about 15% of the oxygen signal in the as-prepared film originates from the substrate (as estimated from the O(1s) signal for a clean ITO substrate and the attenuation of the In(3d) peaks for the polymer film compared to that of a clean ITO substrate).

The S(2p) spectra in Fig. 4 show that 45% of the sulfur remaining in the sample after electron bombardment has moved to lower binding energy

by about 5.0 eV. This is consistent with detachment of the oxygen atoms from the sulfur atoms. The remaining portion of the S(2p) spectrum remains un-shifted, indicating that not all of the sulfur-containing species are affected by the electron bombardment. Angle dependent XPS measurements show that the fraction of sulfur observed at lower binding energies increases with decreasing exit angle (smaller information depth) of the photo-electrons, as expected, if the majority of the electron-induced damage is concentrated at the outermost surface of the sample. This is because the penetration depth of the 3 eV electrons is very small. The C(1s) and O(1s) peak shapes show very little change, and are therefore not shown here. It should be noted, however, that no new features appear in the C(1s) spectra around a binding energy of 288 eV, indicating that the new contribution observed in the C(1s) peak shape for PEDOT-PSS does not result from changes in the PSS part of the system. Only a small shift of the peak position is observed, which comes from a small change in the vacuum level upon electron bombardment. The only change in the O(1s) line shape is that the peak at 531.84 eV (associated with the oxygen in PSSH) becomes weaker compared to the contribution at 533.38 eV (from oxygen in the substrate). The difference between the two peak positions decreases slightly upon electron bombardment.

A simple model of the surface can provide a feeling for the magnitude of the electron-induced changes. In this model, the outermost 1.3λ thick surface layer is modified by the electron bombardment (here λ is the elastic mean-free-path of the photo-generated electrons in the XPS measurements). In this outermost 1.3λ (about 30 Å) thick layer, the oxygen has completely disappeared. In addition, in the outermost 0.5λ (about 12 Å) the sulfur has completely disappeared, and below this a layer of 0.8λ (about 12 Å) exists in which the S(2p) peak has shifted to a lower binding energy as a result of bond breaking with the release of oxygen atoms. Such a model is in agreement with the measurements for normal exit angle of the photo-electrons, although it should of course be kept in mind that the sharp transitions as modeled here are unlikely to occur in reality.

3.3. EDOT films

Because it is almost not possible to prepare pure PEDOT films, we have studied the effects of low-energy (3 eV) electron irradiation on ultra-thin films of EDOT molecules, condensed on a gold substrate (instead of ITO), in order to minimize the oxygen and carbon signals from the substrate itself. Because samples could be cooled only for a limited time, the electron beam bombardment was limited to only 22 h. The EDOT films needed to be thinner than the PEDOT-PSS films (above) in order to prevent sample-charging during XPS analysis, because of the lower conductivity compared to PEDOT-PSS or PSSH. In Figs. 5 and 6 are shown the C(1s) and O(1s) spectra of the ad-

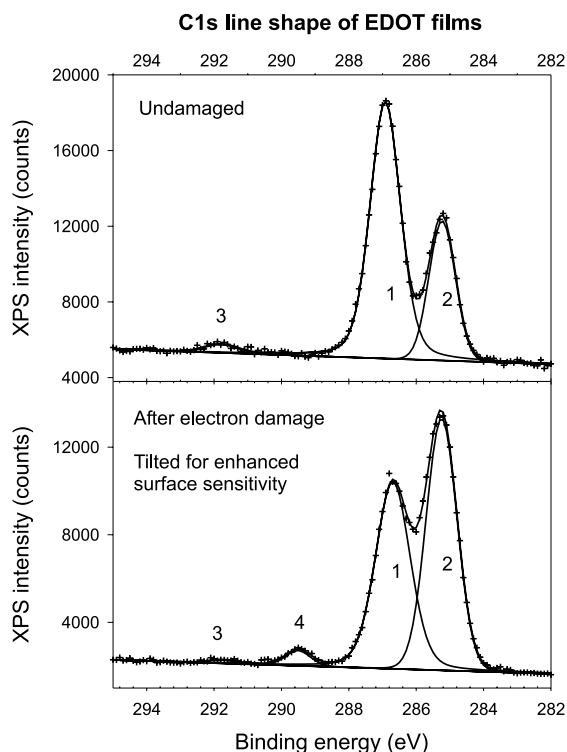


Fig. 5. Carbon core level spectra of an adsorbed EDOT film before (top) and after (bottom) electron bombardment (the latter spectrum was obtained for glancing exit angle in order to show the electron bombardment changes more clearly). Peak 1 corresponds to C atoms bonded to oxygen, peak 2 corresponds to C atoms bonded to sulfur. Peak 3 is a shake-up peak, and peak 4 corresponds to a new feature observed after electron bombardment.

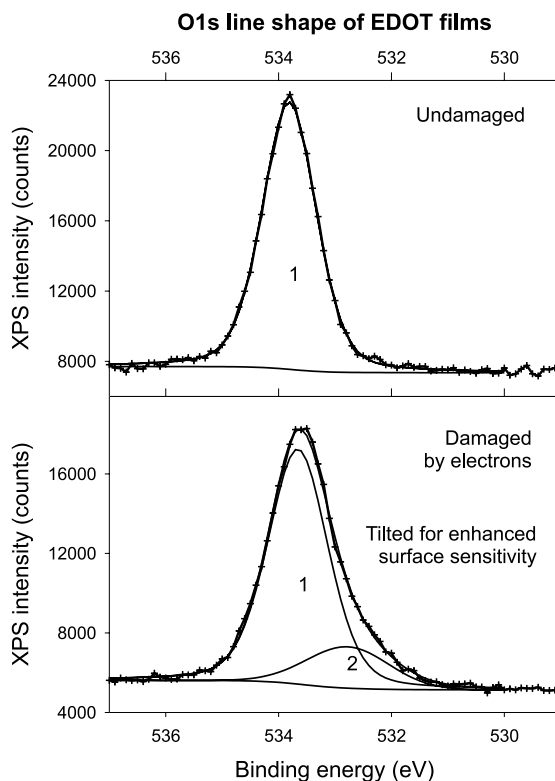


Fig. 6. Oxygen core level spectra of an adsorbed EDOT film before (top) and after (bottom) electron bombardment. The bottom spectrum was obtained for glancing exit angle in order to enhance the surface sensitivity to show the new feature (peak 2) after electron bombardment more clearly.

sorbed EDOT films, before and after 22 h of electron bombardment. The S(2p) line shape (not shown) did not change noticeably. The O(1s) line shape changes only slightly, and the changes are more easily visible by using a grazing exit angle (15°) of the collected photo-electrons as shown in Fig. 6; otherwise, the difference is hardly noticeable. In contrast, major changes occur in the C(1s) line shape. The C(1s) spectrum of the as-prepared EDOT film consists of two main peaks, the peak with the highest binding energy (labeled 1) corresponding to carbon atoms bound to oxygen atoms, and the peak at lower binding energy corresponding to the carbon atoms bound to the sulfur atoms (labeled 2). The intensity ratio of these two contributions is as expected based on the structure of the molecule (2:1). In addition, a small feature is seen at a higher binding energy (292 eV, labeled 3),

presumably due to shake-up processes. After electron bombardment, the ratio of these two peaks has changed completely. In addition, a small but significant additional peak arises at a binding energy of about 289 eV (labeled 4). To show the changes more clearly, the data shown in Fig. 5 for electron damaged material was obtained at a glancing angle of 15° with respect to the surface (the same features were also visible at normal exit angle, but less pronounced). Clearly, C atoms bonded to oxygen, react under influence of the electron beam. A small fraction of these C atoms form new bonds, leading to higher binding energies, but the main part is now observed at a binding energy close to the binding energy of the C atoms bound to S atoms, or in general C–C bonds. The C/O signal ratio for the standard XPS geometry was increased after electron bombardment by a factor 1.1, the C/S ratio by a factor 1.2, and the O/S ratio by a factor 1.04. For the grazing exit angle (15°) the effects are much more pronounced: C/O increases by 1.6, C/S by 1.8, and O/S by 1.14. This indicates that molecular fragments are generated by electron bombardment, and that smaller molecular mass fragments can escape from the surface. The angle dependence again confirms that the effects are stronger closer to the surface.

The modification of EDOT by electrons is also clear from measurements taken after the sample has warmed up to room temperature. For undamaged EDOT films prepared by adsorption on ITO substrates at -150°C and subsequently warming up to RT, no EDOT remains on the surface: the intensity of the S(2p) peak is below the noise limit, and from the signal to noise ratio in these experiments we estimate that if there is any EDOT remaining at the surface, it must be at least a factor 3 less than for the monolayer (ML) that chemisorbs on a Au substrate, as we have recently reported [14]. This indicates that in contrast to the chemisorption occurring on a gold substrate, there is no significant interaction between EDOT molecules and ITO. This in itself has consequences for the use of EDOT-based materials on ITO: even if an EDOT-based material would be developed which does not react with the ITO (like PEDOT–PSS does), then the lack of interaction will still result in weak adhesion at the interface. In con-

trast, if we warm up an EDOT film that has been exposed to 3 eV electrons, clear sulfur-derived peaks can still be observed at the surface at RT. This indicates that the electrons have modified some of the EDOT molecules, which subsequently remain on the surface. Since the films during bombardment are too thick to expect any of the electrons to reach the interface and induce a reaction there, we conclude that the electron damage leads to formation of molecules with a higher molecular weight than EDOT, which do not desorb in UHV at room temperature. UPS spectra (not shown) of the remaining higher mass components, do not resemble EDOT oligomers. This indicates that it is unlikely that e-beam polymerization of EDOT could be used to prepare PEDOT films directly on the surface of a substrate by electron beam irradiation.

4. Discussion and conclusions

The changes in the XPS spectral line shapes and peak intensities of PEDOT–PSS, upon irradiation by 3 eV electrons, can be interpreted by comparison with corresponding spectra of PSSH and EDOT films. The decrease in intensity of the oxygen signal, and, to a lesser extent, sulfur signal, in the PEDOT–PSS films bombarded by electrons indicates degradation of the PSSH. In addition, the shape of the S(2p) spectral peak for the PEDOT–PSS shows the presence of S-containing species at lower binding energies, although this is seriously camouflaged by the presence of the contribution to the S(2p) peak from the PEDOT itself. For condensed molecular solid films of EDOT molecules, the composition changes less drastically, but the additional feature observed in the EDOT C(1s) peak is also present for the PEDOT–PSS sample. Thus, this additional feature is caused by modification of the PEDOT part of the PEDOT–PSS blend.

The electron-induced degradation of PEDOT–PSS has important consequences for use of this material as an electrical transport (buffer) layer in devices such as p-LED's. The degradation of the PEDOT likely leads to a decrease of the conjugation of the conducting polymer, and an expected

deterioration of the charge transport properties. In addition, certain bond-breaking effects lead to the release of O- and S-containing moieties that are free to move within the device structure. Free O atoms would be extremely reactive, and may attack the light-emitting polymer or the cathode in the p-LED's. In addition, S-containing species may become mobile, and the distribution of such species throughout the device may influence charge transport.

Note that the present experiments were carried out with 3 eV electrons, an energy which is rather higher than the average electron energies expected in p-LED's. However, the current densities employed in this study are more than three orders of magnitude lower than those in operating devices, and the exposure times are orders of magnitude below the life time requirements for devices. Thus even if only a very small fraction of the electrons in a real device would obtain such an energy, the present results show that this would lead to rapid deterioration of the conducting polymer. Studies at lower electron energies could not be carried out, because the electron emission component (the "flood gun") did not function well below 3 eV. At realistic current densities and operating times as encountered in devices, however, the process still occurs. This is supported by the observation of the accumulation of S-containing species at the PPV-cathode interface of a device under stress by high-energy ion scattering techniques [12], and the density of S atoms accumulated was found to be about 1 ML (6×10^{14} atoms/cm²). However, ion scattering analysis does not allow to determine which chemical groups of the start material is sensitive to the degradation, and only the photo-electron spectroscopy experiments discussed in this paper show this unambiguously. In addition, we find that oxygen is released, which could not be observed in the ion scattering experiments on buried interfaces.

Finally, we would like to point out that the combination of high-resolution XPS with in situ electron bombardment is a promising way to study the sensitivity of materials to electron transport, and to obtain a basic understanding of effects occurring in real devices under stress. However, in order to more closely approach energies and current densities in real device conditions, specialized

electron sources must be used that can deliver electron densities above 10 mA/cm² at well defined energies between 0.1 and 5 eV.

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