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Stability of the interface between indium-tin-oxide and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in polymer light-emitting diodes

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A cause for degradation of polymer light-emitting diodes is the oxidation of the polymer by oxygen diffusing out of the indium-tin-oxide (ITO) anode. This problem can be solved by the introduction of an organic hole-injecting film, poly-(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), between the ITO and the emissive polymer. Indeed, a dramatic improvement of the lifetime and also the luminous efficiency has been observed. However, our Rutherford backscattering (RBS) studies show that the ITO/PEDOT:PSS interface is not stable. In as prepared glass/ITO/PEDOT:PSS samples 0.02 at. % indium was found in the PEDOT:PSS film. Annealing in a nitrogen atmosphere at 100 °C during 2500 h increased the indium concentration to 0.2 at. %. Upon exposure to air much faster degradation of the ITO/PEDOT:PSS interface was observed; after several days in air the amount of indium reached a saturation concentration of 1.2 at. %. The degradation of the interface can be explained by etching of the ITO due to the strong acidic nature of PEDOT:PSS. © 2000 American Institute of Physics. [S0003-6951(00)05040-3]

The stability of interfaces in polymer light emitting diodes (*p*-LEDs) is considered crucial for the device performance. For devices in which the electroluminescent polymer is deposited on an indium-tin-oxide (ITO) anode, oxidation of the polymer by oxygen diffusing out of the ITO limits the device lifetime.¹ A possible way to get around this problem is the introduction of an organic hole-injecting film, poly-(3,4-ethylene-dioxythiophene) (PEDOT) doped with poly-(styrenesulfonate) (PSS), between the ITO and the emissive polymer. This has indeed led to a dramatic improvement of the lifetime and also the luminous efficiency.²⁻⁴ However, until now it has been unclear whether the interface between ITO and PEDOT:PSS is stable and which are the parameters that influence its stability. Moreover it has been demonstrated that the lifetime of *p*-LEDs depends on the exact nature of the ITO/PEDOT:PSS interface.⁵

It is well known that ITO is very sensitive to acid environments. In *p*-LEDs containing a sulfonium precursor route PPV deposited on an ITO substrate, the HCl released in the conversion of the precursor etches the ITO and products of this reaction are found in the PPV.⁶⁻¹⁰ Due to the strong acidic nature of PSS, the aqueous solution from which the PEDOT:PSS films are cast can also be expected to etch the ITO. We investigated the migration of etch products, i.e., indium containing species, into the PEDOT:PSS and PPV films of *p*-LEDs using Rutherford backscattering spectrometry (RBS).

PEDOT:PSS films were prepared by spin coating an aqueous solution of PEDOT:PSS¹¹ onto commercially available ITO-coated glass substrates (Merck Balzers). Directly afterwards, the samples were transferred to a glove box containing a nitrogen atmosphere in which the PEDOT:PSS

films were dried on a hot plate at 150 °C. In some cases, a solution of O-C₁-C₁₀-PPV in toluene was spin coated onto the PEDOT:PSS films. Samples were characterized both as-prepared and after various treatments: annealing in nitrogen, exposure to air, and annealing in air. The RBS experiments were performed using a 2 MeV He⁺ beam produced by the 2-30 MeV AVF cyclotron at Eindhoven University of Technology. The samples were transferred to the RBS setup in nitrogen using a load-lock system with a portable vacuum container.

A RBS spectrum of an as-prepared glass/(100 nm ITO)/(150 nm PEDOT:PSS)/(70 nm PPV) sample is shown in Fig. 1. The angle of incidence of the 2 MeV He⁺ beam was chosen perpendicular to the sample surface and the detector was placed at a backward angle of 110°. The energy axis was calibrated using the RBS spectrum of a glass/ITO reference sample. Simulations of the RBS measurements were performed with the RUMP code.¹² The atomic composition of O-C₁-C₁₀-PPV used in the simulations was 57% H, 39% C and 4% O, for PEDOT:PSS 43% C, 34% H, 17% O, and 6% S was taken. The composition of the ITO layer was assumed to be 60% O and 40% In, the Sn fraction was disregarded because In and Sn were indistinguishable in the RBS measurements. The composition of the glass substrate was 58% O, 24% Si, 12% Na, and 6% Ca.

The energy that corresponds to He⁺ ions scattered at indium atoms at the surface (1.82 MeV) is indicated with an arrow in the inset in Fig. 1. The large peak at about 1.6 MeV corresponds to indium in the ITO. At about 1.7 MeV a small step can be observed. Simulations of the spectrum showed that this step is due to 0.02 at. % indium in the PEDOT:PSS film. No detectable amount of indium is present in the overlying PPV layer. The measurement shows that in as-prepared samples products of the etch reaction between the PEDOT:PSS solution and the ITO substrate have been incorporated

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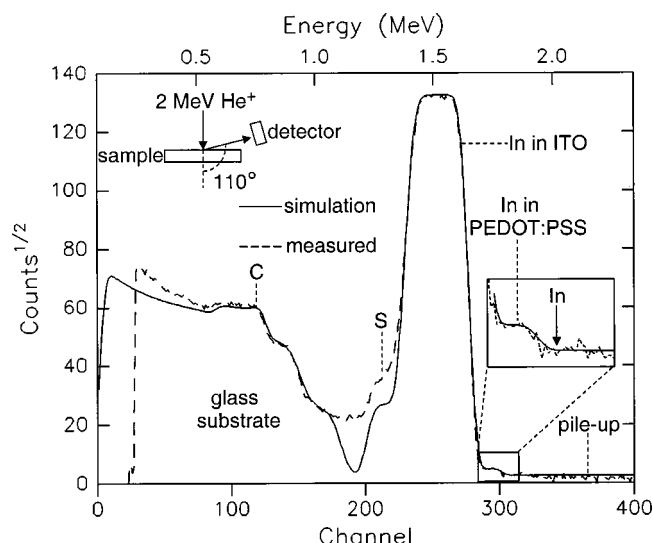


FIG. 1. RBS spectrum of an as-prepared glass/ITO/PEDOT:PSS/PPV sample. The features of C, S, In, and the glass substrate are indicated, as well as the surface energy of indium (the arrow in the inset). The signal that extends to energies above 2 MeV is due to pileup, which occurs when two particles are detected during a time interval that is smaller than the signal processing time. Note that the square root of the number of detected counts is plotted on the vertical axis.

in the PEDOT:PSS film. In samples that were stored in a nitrogen environment at room temperature for some time (days, months) no significant changes in the amount of indium in the PEDOT:PSS film have been observed. Etching of the ITO thus takes place during spin coating of the PEDOT:PSS solution. After removal of water from the film by heating the samples the etching stops or is at least slowed down considerably.

It is interesting to investigate whether the ITO/PEDOT:PSS system is stable upon prolonged heating and exposure to air, in order to study the long term interface stability. Figure 2 shows the RBS spectrum of a glass/(200 nm ITO)/(200 nm PEDOT:PSS)/(80 nm PPV) sample that was annealed in a nitrogen atmosphere for 2500 h at 100 °C.

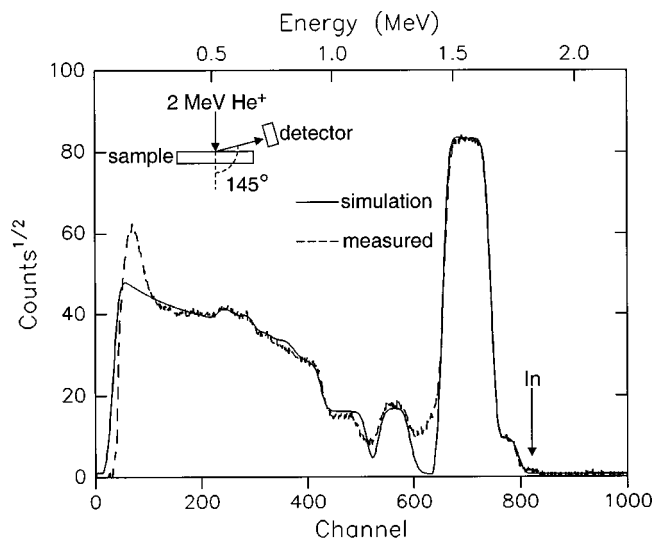


FIG. 2. RBS spectrum of a glass/ITO/PEDOT/PPV sample that was annealed in nitrogen at 100 °C during 2500 h. The In surface energy is indicated with an arrow. Note that the square root of the measured yield is plotted.

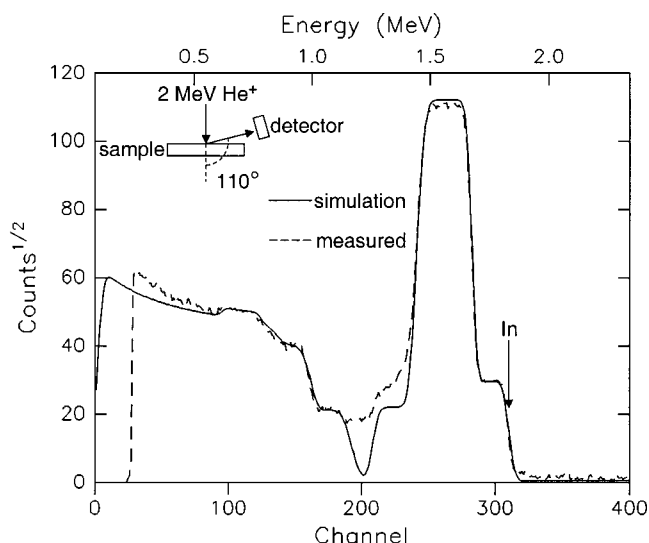


FIG. 3. RBS spectrum of a glass/ITO/PEDOT sample that was exposed to air during 10 days in a refrigerator at 8 °C. The In surface energy is indicated with an arrow. Note that the square root of the measured yield is plotted.

Comparison between Figs. 1 and 2 shows that there is a considerable increase in the amount of indium in the PEDOT:PSS film after annealing: 0.22 at. % indium in the annealed sample as opposed to 0.02 at. % in the as-prepared sample. Prolonged heating in nitrogen thus induces further intake of indium containing species in the PEDOT:PSS film, either due to a continued etching reaction or the diffusion of previously formed etch products from the ITO/PEDOT:PSS interface.

When samples are removed from the nitrogen atmosphere and exposed to air, much faster erosion of the ITO occurs. This can be seen from Fig. 3, which is a RBS spectrum of a glass/ITO/PEDOT:PSS sample that was exposed to air in a refrigerator at 8 °C during ten days. In this sample, 1.2 at. % (!) indium was found in the PEDOT:PSS film. This is also the maximum indium concentration that has been observed; prolonged exposure times had no further effect. Apparently the 1.2 at. % indium atoms in the PEDOT:PSS film correspond to the maximum amount of etch products that can be formed with the available acid groups in the PEDOT:PSS.

We also studied the migration of indium compounds into

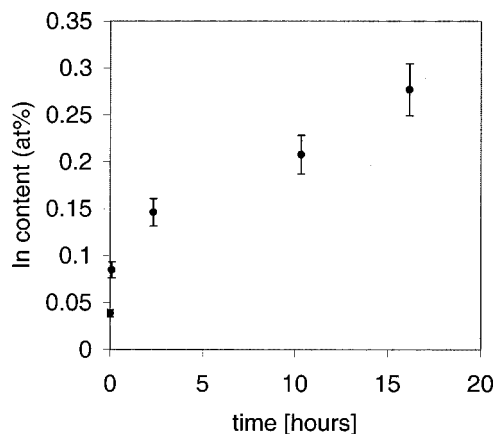


FIG. 4. In content in PEDOT:PSS films as a function of the time the films were exposed to air.

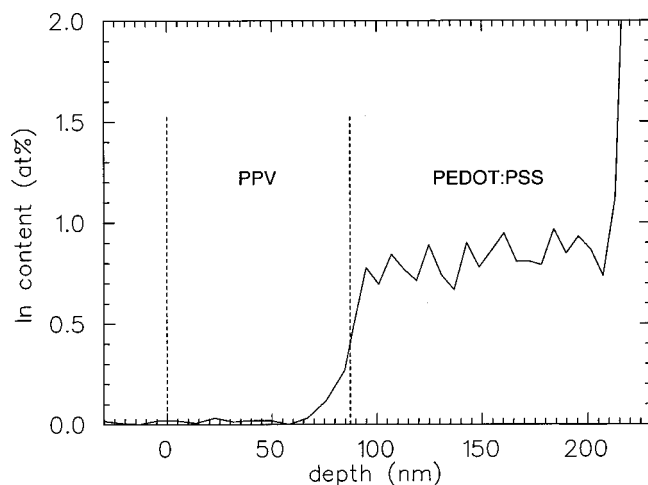


FIG. 5. Depth profile calculated with the RUMP code of indium in the PPV and PEDOT:PSS films of a sample that was exposed to air during two days. A sharp decrease in the indium concentration can be observed at a depth corresponding to the PPV/PEDOT:PSS interface.

PEDOT:PSS for exposure times in the range 0–20 h (see Fig. 4). After 10 h exposure to air 0.2 at. % indium was found in the PEDOT:PSS film, which is about the same concentration that was found in the sample that was annealed during 2500 h at 100 °C in nitrogen. It can thus be concluded that the ITO/PEDOT:PSS interface is very sensitive to air. The hygroscopic nature of PSS probably plays an important role. Upon exposure to air, water will be absorbed by the PEDOT:PSS film and an aqueous acid environment is formed due to the reaction $\text{H}_2\text{O} + \text{PSS}(\text{HSO}_3) \rightarrow \text{H}_3\text{O}^+ + \text{PSS}(\text{SO}_3)$. This will facilitate etching of the ITO and transport of the etch products throughout the PEDOT:PSS film. This hypothesis is confirmed by experiments performed on samples that were annealed in air at 170 °C, which showed a lower indium content in the PEDOT:PSS film than samples that were stored in air for the same time but were

not annealed. At 170 °C water is evaporated from the PEDOT:PSS film, resulting in less erosion of the ITO substrate in the heated samples.

In samples that contained a PPV film on top of the PEDOT:PSS film, a rather sharp decrease in the indium concentration was observed at a depth corresponding to the PEDOT:PSS/PPV interface (see Fig. 5). This implies that the indium containing etch products do not diffuse into the PPV film, but are trapped in the PEDOT:PSS layer.

In conclusion, we have shown that the interface between ITO and PEDOT:PSS is not stable. In as-prepared samples 0.02 at. % indium is present in the PEDOT:PSS film due to etching of the ITO during spin coating. Annealing in nitrogen at 100 °C leads to an increase in the indium concentration to 0.2 at. % after 2500 h. Exposure to air leads to a much more dramatic degradation of the interface; after several days in air the amount of indium reaches a saturation concentration of 1.2 at. %.

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