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

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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. A possible way to get around this problem is 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.
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.

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 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
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 H₂O + PSS(HSO₃⁻) → H₃O⁺ + PSS(SO₃²⁻). 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. %.