Macromol. Symp. **2004**, *212*, 225-230

Degradation Effects in Polymer Light Emitting Devices Due to Heat Treatment

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Summary: The characteristics of polymer light emitting diodes (PLEDs) (ITO/PPV/Ca) depend strongly on the conditions during preparation and operation. We studied the effects of heat treatment (during and after preparation) of PLEDs with OC_1C_{10}-PPV as active layer. PLEDs showed a reduction of both the current and the light output to 40 % after annealing for only 30 min at 65 °C. Effects on *I-V* characteristics were studied by measuring single carrier devices (hole- and electron-dominated devices). The current reduction after heat treatment can be ascribed to degradation of the ITO/PPV and the Ca/PPV interfaces.

Keywords: annealing; conjugated polymer; degradation; interfaces; light emitting diodes (LED)

Introduction

Polymer light emitting diodes (PLEDs) are considered promising candidates for full-colour, cheap, flexible displays, which are easy to process [1]. Polymer LEDs consist of an emitting polymer layer (in our case dialkoxy-*p*-phenylenevinylene (OC_1C_{10}-PPV)), which is spin-coated on anode (indium-tin-oxide (ITO) covered glass) and covered with calcium cathode prepared by evaporation.

The temperature history during preparation is considered to be important for the PLED performance. The glass/ITO/PPV layer is usually heated before application of the cathode in order to remove impurities from the PPV. The device will also be heated when a protective Al layer is applied onto Ca, because of the radiation of the evaporator. Furthermore, in commercial applications, some temperature resistance is necessary.

We studied the effects of heat treatment on PLEDs with calcium cathodes by electrical characterisation of PLEDs, hole-only (ITO/PPV/Au and Au/PPV/Au) and electron-only (TiN/PPV/Ca) single-carrier devices.

DOI: 10.1002/masy.200450822

Preparation of PLEDs

Substrates of glass covered with ITO (100 nm ITO, 30 Ω/□, Merck) were cleaned in an ultrasonic bath successively with acetone (Uvasol, Merck) and propan-2-ol (Uvasol, Merck). Next, a UV ozone treatment was conducted for 20 min. Subsequently, the samples were transferred without air access to a glove box (O_2 and $H_2O < 1$ ppm), where an OC_1C_{10}-PPV layer was spin-coated onto the ITO. Then, the samples were transferred to the evaporation chamber which is connected to the glove box. Here a 80-nm thick calcium cathode was evaporated from an effusion cell, at a deposition rate of 0.3 nm/s. The pressure during the evaporation process was $\sim 1*10^{-5}$ Pa.

Electrical and optical characteristics were measured in the evaporation chamber. Heat treatment was performed in the evaporation chamber with an infrared lamp, temperature was measured with NTC thermistors, which were in contact with the glass of the PLEDs. After the heat treatment, the samples were left to cool down before electrical and optical characteristics were measured.

Hole-dominated single-carrier devices were prepared consisting of glass/ITO/PPV/Au and glass/Au/PPV/Au structures. Electron single-carrier devices were made according to Bozano et al. [2] consisting of glass/TiN/Ca/PPV. For both glass/Au and glass/TiN, the same cleaning procedure as for glass/ITO was performed apart from the UV ozone treatment, which was omitted.

Characteristics of PLEDs

Figure 1 shows the light output against current at 6 V bias for untreated and annealed PLEDs (glass/ITO/PPV/Ca). It is clear from Figure 1 that thermal treatment leads to reduction in current and light output. The power efficiency at 6 V is not influenced much by the heat treatment. It can be seen that the current and light output reduction depends strongly on the treatment temperature.

The reduction of current and light output after evaporation of 50 nm of aluminium onto the top of the calcium is also shown in Figure 1. The temperature of the PLEDs increased during evaporation, because of the radiation of the aluminium evaporator. Temperature measurements on the rear side of the PLED indicated temperatures of 48 °C immediately after evaporation of aluminium.

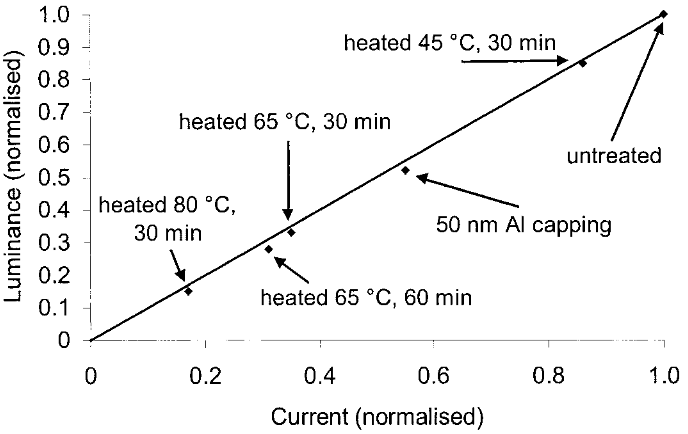

Figure 1. Relative current and brightness at 6 V bias for thermal treatments at different temperatures and time scales. The current and brightness are normalised to the current and brightness measured on the same devices before heat treatment. Experiments were performed with PLEDs with 130 nm OC_1C_{10}-PPV and a calcium cathode. Heat treatment was performed at pressure ~10^{-7} Pa. The line indicates points were the relative losses in current and brightness are equal (constant power efficiency). All devices were measured at equal temperatures.

It was verified that the electrical characterisation itself does not cause the degraded PLED performance by comparing *I-V* and *E-V* characteristics of annealed PLEDs, which were and were not characterised before the annealing step.

Subsequently, annealing at 65 °C for 30 min was carried out at different stages of the production process to find causes of the current and light output reduction. The results of these experiments are shown in Figure 2. Heat treatment before application of the calcium cathode also led to a reduced current and light output, but the reduction was smaller than for samples treated after application of the cathode. Heat treatment both before and after application of the cathode resulted in almost the same current and light-output reduction as heat treatment after application of the cathode.

Apparently, calcium causes a part of the current reduction and another part is caused by ITO and/or the PPV. In order to study the influence of the calcium and ITO more thoroughly, single-carrier devices were prepared.

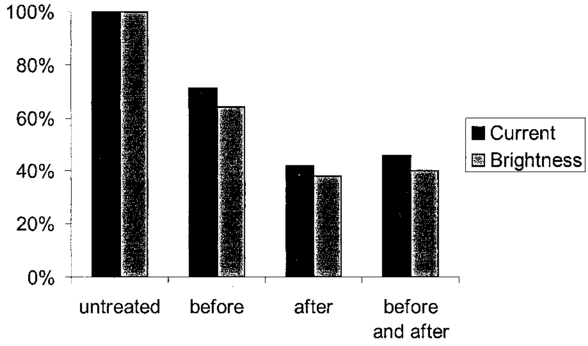

Figure 2. Current and light output at 6 V of ITO/PPV (130 nm)/Ca PLEDs, normalised to the current and light output of untreated devices. Devices were heat-treated for 30 min at 65 °C *before, after* and both *before and after* application of the calcium cathode. If the devices were treated before application of the cathode, they were left to cool down before the calcium was applied.

Hole-only single-carrier devices

In order to find the mechanism that caused the current reduction, hole-only single-carrier devices consisting of ITO/PPV/Au structures were prepared. The high work function of gold blocked the injection of electrons and, therefore, these devices were considered as hole-only single-carrier devices. Heat treatment (30 min at 65 °C) before, after or both before and after application of the Au cathode, all resulted in a reduction of the current to 80 % (at 6 V) compared with untreated devices. In order to separate the effects of the degradation of the ITO/PPV interface and the PPV itself, hole-only devices with a gold anode and a gold cathode were prepared (Au/PPV/Au). These devices did not show any reduction of the currents after annealing at 65 °C for 30 min. It can be concluded that the ITO caused the current reduction in ITO/PPV/Au devices and that the heat treatment of PPV itself did not cause the decreased PLED performance.

Electron-only single-carrier devices

Next, measurements were performed on electron-only single-carrier devices. In these devices the ITO anode was replaced with TiN in order to block the holes [2]. The TiN/PPV/Ca did not show light output in the used voltage range (0-6 V) and impedance spectroscopy confirmed that these samples can be described as single-carrier electron-only devices.

Heat treatment before application of the calcium cathode did not result in reduction of the current; moreover, the current-voltage characteristics of treated and untreated devices were equal. If the devices were heated after (or before and after) application of the calcium cathode, the current at 6 V decreased to 40 % and the shape of the current-voltage characteristics changed. We concluded that heat treatment influences the electron currents; this occurred only when the calcium was present. The PPV did not cause the decreased electron current, because heat treatment before application of the cathode did not have any effect on the performance.

Modification of the Ca/PPV interface

In the previous paragraph, we concluded that calcium caused the decreased electron current. In order to get a better understanding of the effects of electron current reduction on PLED performance, we tried to modify the Ca/PPV cathode without performing heat treatment.

It can be expected that, by heating the device, calcium atoms diffuse into the PPV and modify the Ca/PPV interface. An alternative approach, to modify the Ca/PPV interface, changes the evaporation rate of the calcium. If the evaporation rate is very low, the probability of clustering of calcium particles on the PPV surface is very small, as shown in ref. [3] for other metals on polymers. Free calcium atoms are therefore considered to diffuse easier into the PPV.

Devices with calcium cathodes deposited at two different evaporation rates (0.3 and 0.003 nm/s) were prepared by evaporating calcium at two different temperatures (510 °C to 380 °C) and characterized (Figure 3). It can be seen that devices with cathodes deposited at 0.003 nm/s have a worse characteristics; the current was reduced by 45 % and the brightness by 50 % at 6 V.

The time needed to evaporate the cathode is obviously different for the two evaporation rates, which could lead to different temperatures during evaporation of the devices due to the radiation of the evaporator. However, the temperatures measured on the glass of the PLED immediately after evaporation are equal (38 °C) for both deposition rates.

In the case of slow evaporation, the calcium at the PPV interface is exposed longer to impurities, (e.g. oxygen), which might be present in vacuum. Oxidation of the cathode leads to decreased performance [4]. Our mass spectrometer did not detect impurities in vacuum, which means that the partial pressures of oxygen and water vapor were below 10^{-7} Pa. Furthermore, in ref. [4], it is shown that oxidation of calcium during evaporation leads to a decreased power efficiency. The power efficiency, however, was (nearly) unchanged in our experiments, so it can be concluded that impurities did not influence our experiments.

Therefore, following [3], we expect that a low evaporation rate induces calcium diffusion into the PPV, which apparently reduces electron injection as indicated by a lower current and light output.

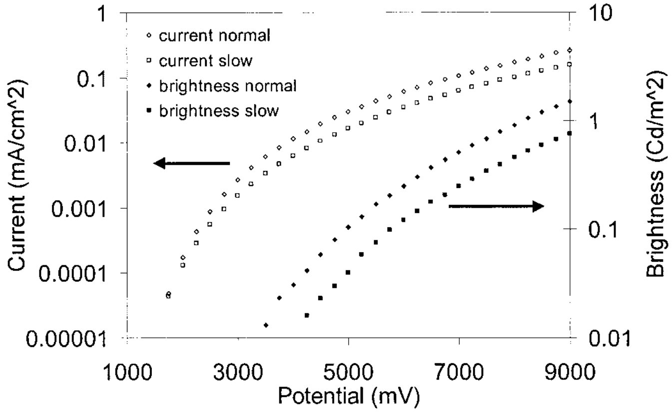

Figure 3. Current and brightness characteristics of ITO/PPV (250 nm)/Ca PLEDS. The first 20 nm of calcium is deposited onto the PPV at different rates. For the 'normal' devices, the evaporation rates were 0.3 nm/s and for the 'slow' devices it was 0.003 nm/s

Conclusions

Annealing of PLEDs (ITO/PPV/Ca) at various stages of preparation leads to reduction of current and the light output. This reduction is caused by the ITO/PPV and the Ca/PPV interfaces. Changes in the PPV itself (if present) do not influence the performance. It was shown that modification of the Ca/PPV interface by lowering the evaporation rate of the calcium resulted in worse device characteristics. Probably more calcium diffuses into the PLED, which apparently leads to worse PLED performances due to, example, the formation of (electron) traps. Heating PLEDs after application of the calcium cathode can also be assumed to induce calcium to diffuse into the PPV and cause a part of the observed current reduction.

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