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P-48: Patterning of OLED Cathodes by Metal Dry Etching

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Abstract

A method to pattern the metal cathode of OLEDs by conventional photolithography and dry etching in a chlorine plasma is introduced. Sharp lines are obtained with feature sizes down to 20 μm. The performance of polymer LED fabricated this way is discussed. In addition, the growth of the non-emissive region at the edge of the cathodes is analyzed in the context of this patterning technology.

1. Introduction

Displays based on organic light-emitting diodes (OLED) show a remarkable potential to compete with conventional display technologies in the near future because of their emissive nature and low fabrication costs [1, 7, 13, 14, 18].

However, the sensitivity of the organic thin film (polymer as well small molecules) to oxygen, water and solvent vapor poses a serious design problem because it severely limits available patterning techniques [2, 3, 5, 17]. Once the organic film is deposited, it is not possible to process the device by conventional photolithography without damaging the organic film. The use of photoresist on top of the polymer film has been demonstrated [11]. But in this case, the materials were carefully chosen to be compatible with photoresist chemicals. This clearly restricts the choice of material. To pattern the cathode layer, a shadow mask is commonly employed which patterns the cathode metal film during the evaporation process. But it is problematic to obtain very small feature sizes over a large area with this technique. In addition, alignment is difficult due to the vacuum environment. Another method employed is the use of “cathode separators”, which are photoresist pillars deposited by conventional photolithography before the deposition of the organic film and the cathode. The pillars then separate the devices [15, 19]. This technique is difficult to apply to OLEDs based on polymers, because polymeric materials cannot be thermally evaporated, but are usually formed by spin-casting from solution. In this paper we demonstrate that dry processing can be used to pattern a blanket cathode metal film on an OLED. Small features are achieved despite the incompatibility of the photoresist materials with organic LED materials.

2. Device Fabrication

The OLED polymer film was deposited on a glass substrate coated with indium-tin-oxide (ITO) (30 Ω/□). The polymer used was poly(9-vinylcarbazole) (PVK, MW~ 1 100 000 g/mole, 71.5% by weight in the final solution) as the hole transport material and 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD, 28.5% by weight in the final solution) as the electron transport material [20]. Both, the PVK and the PBD, were obtained from Aldrich and used as received. The polymer blend also contained the coumarine 6 (C6, obtained from Lambda Physik, emission peak at 505 nm).

Cathode materials are often chosen to be metals with a low work function to facilitate electron injection into the organic film. In previous work, the alloy magnesium silver was used and yielded reasonable external quantum efficiencies. However, these metals are difficult to etch by plasma processing. Aluminum, on the other hand, has a relatively high work function. But we chose aluminum in this work because of its high etch rate in chlorine plasma and its stability in air. Some very efficient devices have been reported using aluminum cathodes [6, 9] or aluminum-lithium cathodes[8, 10]. A 100 nm thick blanket aluminum layer was deposited by thermal evaporation on the ITO substrate previously coated with the polymer.

The etching process of the aluminum cathode was performed using conventional photoresist as masking material in a chlorine/borontrichloride plasma. The photoresist AZ 4210 was deposited at 4000 rpm, and subsequently pre-baked. The sample was then exposed to UV light and developed. Due to pinholes in the aluminum film and the exposure of the organic film at the edge of the substrate, water and developer came into contact with the polymer film. The metal film blistered off within seconds. To circumvent this problem, we deposited two layers of aluminum: The first layer covered only the central area of the device where future devices were to be formed. After the first Al deposition (800 nm), the organic layer was removed outside this area using a solvent drenched swab. The second Al deposition (1500 nm) covered the whole device, as shown in Fig. 1. This processing step served two purposes: First, the number of pinholes in the Al film is drastically reduced due to the second metal layer. Second, the organic film is not exposed to water and developer on the edge of the device.

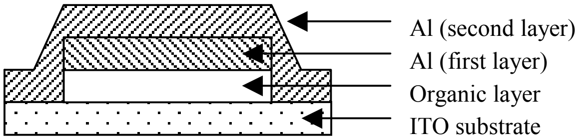

Figure 1: Device structure to avoid blistering of the aluminum film due to contact with water and developer during the lithography process, and to reduce aluminum pinholes.

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The substrate processed in this fashion did withstand the photolithography step without any blistering and was subsequently transferred into a parallel plate plasma etching chamber for further processing. Chlorine plasma etches aluminum very rapidly. However, re-deposition of non-volatile etching products (namely $AlCl_3$) is often observed [4, 16]. In addition, chlorine does etch aluminum oxide only very slowly. To alleviate these problems, a mixture of chlorine and borontrichloride (Cl_2 and BCl_3) in a carrier gas is conventionally used. However, BCl_3 also reduces the etch rate of pure aluminum. In our work, a mixture of 1:2 (Cl_2:BCl_3) did not produce any re-deposition, and the etch rate was sufficiently high (7.5 nm/min). At a plasma power density of 0.27 W/cm^2 and a pressure of 200 mtorr, etched features down to 20 μm were obtained. In this process, argon was used as the carrier gas (200 sccm) and Cl_2 and BCl_3 (10 sccm, 20 sccm, respectively) as the etchants. Fig. 2 shows etched Al lines with a width of 20 μm aluminum stripes on a patterned ITO sample (ITO lines run perpendicular to the Al lines).

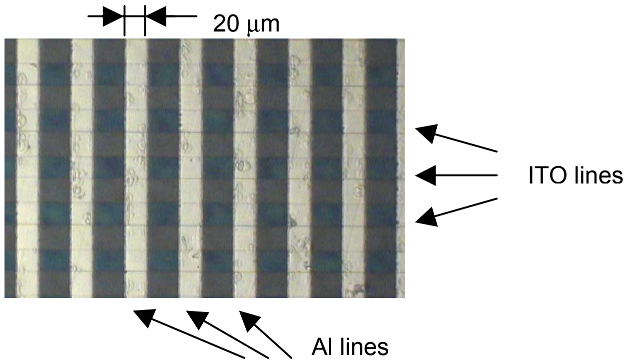

Figure 2: Micrograph of a sample with Al cathode lines fabricated with plasma etching. The width of the ITO lines and the Al lines is 20 μm.

3. Device Characterization

Measuring the individual OLEDs formed at the intersection of ITO lines and cathode lines (Fig.2), we noted that none of these devices emitted light. However, samples fabricated the same way but with larger area (1 mm^2, 0.25 mm^2 and 0.04 mm^2) were working as shown in Fig. 3. From these micrographs it can be seen that the emissive region of the OLED is smaller than the area covered by the aluminum cathode. Along the edge of the cathode, a non-emissive zone formed with a width independent of the feature size of the device. In all devices, the non-emissive zone was about 65 μm (± 5 μm) wide. All devices were tested in air four hours after the cathode was deposited. From this observation, it can be understood why the 20 μm wide devices did not emit any light due to the fact that the non-emissive region consumed the whole device.

The current-voltage characteristics along with the light output for these devices are very similar as shown in Fig. 4. The external quantum efficiency is about the same for all devices (0.14% for the 1 mm^2 device, 0.12% for the 0.25 mm^2 device, and 0.11 % for 0.04 mm^2 device). That means that the detector-current scales with the emissive area of the device rather than the area of the device. Thus the non-emissive zone does not contribute much to the diode current.

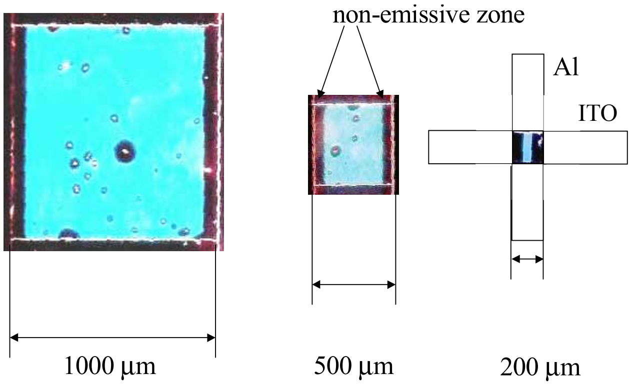

Figure 3: Electroluminescent micrograph of devices of different sizes fabricated with plasma etching of the cathodes. The ITO lines run horizontally, the aluminum lines vertically. Note the non-emissive zone in all samples along the edge of the aluminum line. The devices were exposed to air for approx. 4 hours.

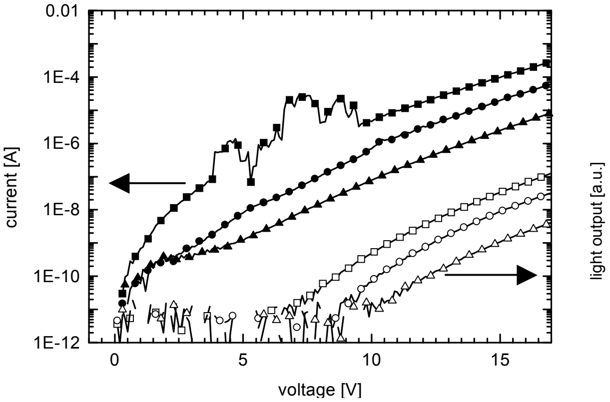

Figure 4: Current-voltage characteristics and emitted light of OLEDs with plasma etched cathode: The cathode area was 1mm x 1mm (squares), 0.5mm x 0.5mm (circles), and 0.2mm x 0.2mm (triangles). The devices were exposed to air for approx. 4 hours.

It could be argued that the plasma etching process caused the non-emissive zones, especially after the aluminum film was etched away and the organic layer was completely exposed to the plasma. Chlorination of the oxadiazole groups of the PVK as well as other reaction with chlorine radicals could cause the breakdown of π-bonds and thereby reduce the electrical conductivity of the organic layer. On the other hand, the non-emissive zones can also be explained by the growth of dark spots, i.e. degradation of the device by exposure to air/water vapor through a pinhole in the cathode [12]. In our case, the non-emissive zones could be formed this way because the entire edge along the aluminum cathode was exposed to air.

It is important to distinguish between these two mechanisms to evaluate the usability of the etching technology. To this end, we compared the growth of the non-emissive zone (Δ*L* in Fig. 5) with time in a dry-etched device and in a device fabricated by evaporation of aluminum through a shadow mask. In both cases, the cathode was 300 nm thick. The growth was observed in air. No significant difference in growth rate can be inferred. Therefore, we conclude, that the damage to the organic film caused by the plasma treatment is negligible compared to the damage due to exposure to air.

The growth rate of the non-emissive zone in devices with aluminum cathodes can be dramatically reduced when the samples are kept in a nitrogen atmosphere (dew point -50 °C), stressing the need for device encapsulation.

For all devices, the width of the non-emissive zone shows an approximate square root dependence on time suggesting that the reaction of the organic material is limited by the diffusion of a reactant from the device edge.

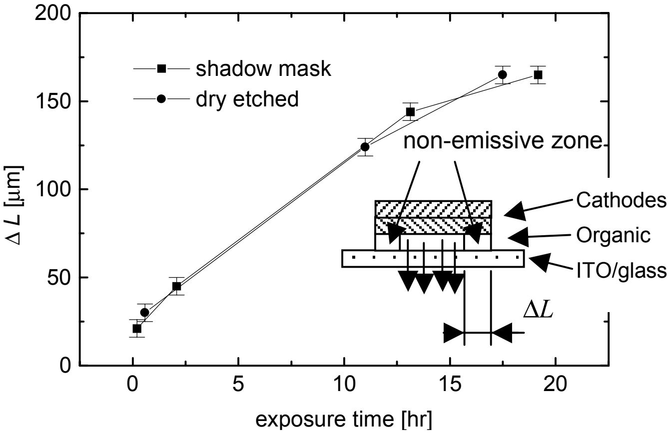

Figure 5: Growth of the non-emissive zone with time in air after (a) aluminum cathode (300 nm) patterning with plasma etching (circles), and (b) patterned cathode formation by aluminum evaporation through a shadow mask (squares). Δ*L* is the width of the non-emissive zone (inset).

4. Conclusion

Conventional photolithography and dry etching with a resolution of 20 µm can be applied to pattern aluminum cathodes of polymer OLEDs. It is critical that the cathodes have no pinholes, and the edges of the device are sealed to prevent the photoresist developer from damaging the aluminum layer.

Devices showed a non-emissive zone along the edges where the metal was exposed to air. However, comparing these devices with devices fabricated using a shadow mask, we conclude that the damage is not due to the etching process but rather a consequence of exposure to air and subsequent dark spot formation.

5. Acknowledgements

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