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Silver grid transparent conducting electrodes for organic light emitting diodes

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ABSTRACT

Polymer organic light emitting diodes (OLEDs) were fabricated using thin silver hexagonal grids replacing indium tin oxide (ITO) as the transparent conducting electrodes (TCE). Previous literature has assumed that thick metal grids (several hundred nanometres thick) with a lower sheet resistance (<10 Ω/□) and a similar light transmission (>80%) compared to thinner grids would lead to OLEDs with better performance than when thinner metal grid lines are used. This assumption is critically examined using OLEDs on various metal grids with different thicknesses and studying their performances. The experimental results show that a 20 nm thick silver grid TCE resulted in more efficient OLEDs with higher luminance (10 cd/A and 1460 cd/m^2 at 6.5 V) than a 111 nm thick silver grid TCE (5 cd/A and 159 cd/m^2 at 6.5 V). Furthermore, the 20 nm thick silver grid OLED has a higher luminous efficiency than the ITO OLED (6 cd/A and 1540 cd/m^2 at 6.5 V) at low voltages. The data shows that thinner metal grid TCEs (about 20 nm) make the most efficient OLEDs, contrary to previous expectations.

1. Introduction

Transparent conducting electrodes (TCEs) are an important component in organic light emitting diodes (OLEDs). They allow the efficient extraction of light whilst conducting charge into the emission layer. Currently indium tin oxide (ITO) is the most commonly used TCE in OLEDs, as well as a host of applications such as organic photovoltaics (OPVs), displays and touch sensors. It has excellent sheet resistance (c. 15 Ω/□), high transmission in the visible wavelength range (typically 87% on average from 400 to 700 nm) and its fabrication process has been thoroughly optimised [1]. However, the cost of ITO is very high due to the scarcity of indium and the production process used to prepare the coatings. Indium migration has also been shown to limit the device lifetime [2,3]. Finally, ITO is also brittle, which is at odds with the mechanical flexibility of OLEDs [4] and other organic electronics.

Thus, there is a strong motivation to develop alternative TCEs to ITO [5–7]. TCEs in general must have a combination of high transmission at the emission wavelength and low sheet resistance. In addition, to lower the manufacturing cost and to allow new device architectures to be designed they should also be inexpensive and flexible. Conductive polymers such as poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) [8,9], silver nanowires (AgNWs) [10,11], nanometre thin metal films [12], metal grids [13–16], carbon nanotubes (CNTs) [17–20], graphene [17] and graphene oxides [21] have all been proposed as alternative TCEs. Whilst they are all potentially viable solutions for replacing ITO in specialist applications, this paper focuses on the use of nanometre thin metal grids in polymer OLEDs.

The transmission and sheet resistance of thin metal grids as TCEs have been previously investigated [12,13],

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and have been used to fabricate devices in proof of concept applications [14,22–25]. One of the advantages of metal grid TCEs is that their sheet resistance and transmission can be fine-tuned by adjusting the line width, spacing or thickness. For a given line width and line spacing, the transmission can be kept constant whilst the sheet resistance can be reduced by increasing the grid line thickness. It is suggested in the literature that thick metal lines (i.e. increasing perpendicular to the surface) will make the best metal grid-based devices as this minimises the sheet resistance, whilst the transmission is maintained at a high level. For example, Kuang et al. [16] reported a sheet resistance of 9.7 Ω/□ with a transmission of 80% using 1.2 μm thick parallel lines made of gold, and Galagan et al. [22] fabricated a 2 μm thick printed silver hexagonal grid which gave a sheet resistance of 1 Ω/□ with a metal coverage area of 8% (transmission was not specified, but it is presumed to be about 92%).

In this paper, we have investigated the performance of polymer OLEDs with respect to the line thickness of a silver grid TCE. Whilst many papers study the TCE in isolation and have made single devices (mostly OPVs) to demonstrate an application, there are no papers which study the variation in OLED performance with the metal grid thickness. Here we show that the perceived theory that thicker grids are optimal may actually be incorrect, with the better optimised device having a higher sheet resistance TCE than some of the other OLEDs.

2. Experimental methods

Silver hexagonal grids were fabricated by photolithography on a transparent 15 mm × 15 mm × 0.7 mm glass substrate. The photolithography process is described in the Supplementary Materials. Two masks with different hexagonal grid dimensions were used: one mask with 2 μm line width and 60 μm line spacing and the other with 3 μm line width and 10 μm line spacing. The silver grids produced from the two masks therefore had different sheet resistance and light transmission for a given grid line thickness. The grid line thickness was measured by AFM (Atomic Force Microscopy, Veeco Dimension 3100) after the lift-off process.

Silver grid TCEs of up to 40 nm line thickness can be used to make OLEDs as the surface was smooth enough and could be sufficiently planarised by a single layer of PEDOT:PSS. To make thicker grid lines, the grid fabrication method had to be adjusted. There have been reports in the literature of groups maintaining a smooth surface whilst using very thick grid lines [22], but they have not disclosed the method of planarisation. A simple approach would be to use a very thick layer of PEDOT:PSS, but that would be detrimental to the OLED performance. Therefore, we derived our own method of planarisation, with the aim of demonstrating the performance of OLEDs using a 100 nm thick silver grid TCE. There are a number of other routes that could be used to embed the grids in the substrate. The results surprisingly show that thick grid TCEs do not make the best OLEDs, so the concept of having to embed the grid lines may not be required.

The method used to make 100 nm thick grid lines for TCEs was the same as for making grid lines less than 40 nm thick, except that the lift-off resist PMGI SF6 (see Supplementary Materials) was not used and an extra step was inserted. After patterning the S1805 photoresist, it was hard baked for 2 h at 90 °C on a hotplate before etching the glass substrate for 1 min in buffered hydrofluoric acid (HF) diluted with deionised (DI) water in a 5:1 (DI water: HF) ratio. The result was troughs about 100 nm deep etched in the glass in which silver could be deposited in the required hexagonal grid pattern. Depositing 100 nm of silver through the openings in the photoresist therefore resulted in a flat TCE surface. Up to an extra 40 nm of silver protruding above the surface can be allowed before the device is short-circuited. The photoresist was then removed by leaving it in acetone overnight. Using this method, a 111 nm thick large spacing silver grid was produced for an OLED in this paper. The etched depth of the glass was 87 nm, and 24 nm of the silver lines were above the glass surface.

The TCE substrates were cleaned by sonicating for 10 min in acetone, isopropanol and methanol and were then blown dry with nitrogen. They were not plasma ashed as this damages the surface of the silver grid lines. Therefore, to maintain the same fabrication conditions for an accurate comparison, the ITO substrate was not plasma ashed either. This meant that the PEDOT:PSS does not wet as well to the TCE surface as it would if it was plasma ashed. However, after spin coating PEDOT:PSS outside the glovebox at a speed of 3000 rpm for 1 min with an acceleration of 330 rpm/s, it was observed that a uniform thin film is formed on the surface of both the silver grid and the ITO.

The remaining deposition steps were performed inside a nitrogen filled glove box. After depositing PEDOT:PSS (Clevios PVP AI 4083, Heraeus, Germany), the substrate was annealed on a hotplate at 150 °C for 10 min. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(N-(p-butylphenyl))diphenylamine)] (TFB) (ADS 259BE, American Dye Source) was then spin coated at 2000 rpm for 1 min at maximum acceleration (30,000 rpm/s). The substrate was baked again at 150 °C for 10 min. Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] F8BT (ADS 133YE, American Dye Source) was spin coated on the substrate at 1000 rpm for 1 min with an acceleration of 330 rpm/s, followed by a further anneal of 10 min at 150 °C. A mask was used to define the aluminium electrodes on the substrate. The mask (with the substrate) was placed inside an evaporator and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline BCP (5 nm) and aluminium (60 nm) were evaporated on to the substrate. The OLED was encapsulated using a UV-light cure adhesive (Loctite 3491) and a small piece of microscope glass slide to protect the organic layers from oxygen and water. The active area of the OLED was 8 mm^2.

3. Results

3.1. Silver grid TCE characterisation

The transmission of each grid TCE was measured prior to making OLEDs on them (Fig. 1(a) and (b)). The variation