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Highly efficient fully flexible indium tin oxide free organic light emitting diodes fabricated directly on barrier-foil

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ABSTRACT

We present a simple method for the fabrication of highly conductive and fully flexible metal/polymer hybrid anodes for efficient organic light emitting diodes (OLEDs). By incorporating ultra-thin metal grids into a conductive polymer, we fabricated anodes with very low sheet resistances and high transparency. After optimizing the metallic grid, OLEDs with these hybrid anodes are superior to OLEDs with standard indium tin oxide (ITO) anodes in luminous efficacy by a factor of ~2. Furthermore, the sheet resistance can be reduced by up to an order of magnitude compared to ITO on polyethylene terephthalate (PET). The devices show a very low turn-on voltage and the hybrid anodes do not change the emissive spectra of the OLEDs. In addition, we fabricated the anodes directly on a barrier foil, making the double sided encapsulation of a typically used PET-substrate unnecessary.

1. Introduction

Organic light emitting diodes (OLEDs) can be processed on almost every substrate. Flexible substrates such as polyethylene terephthalate (PET) foils [1–3] are especially interesting, as OLEDs can be built as freely shapeable light sources. This enables special applications in display technology and general lighting which cannot be realized with traditional light sources. To reach commercial competitiveness, flexible devices still have to overcome some obstacles, such as device efficiencies and a bendable device encapsulation [4,5].

Typically, OLEDs use indium tin oxide (ITO) as a transparent anode. ITO has some disadvantages that are especially critical for flexible devices. Since ITO is brittle, its use in flexible devices is limited [6]. Furthermore, ITO is difficult to process, especially on PET-foil, since high temperatures are required to achieve good conductivity and transparency [7]. Therefore, alternatives to ITO have been discussed. Polymeric anodes are a promising candidate [8,9], but the conductivity is still too low for large area applications. Silver nanowires are promising [10] but they can easily create shorts, due to the thin layers used in OLEDs. Different vacuum deposited as well as solution processed transparent conductive oxides were proposed [11–13], but on flexible substrates they have similar drawbacks as ITO (brittle, high temperatures required, complex doping necessary, etc.). Metallic grids have been used to enhance the conductivity of ITO [14], which did not resolve the problems with ITO in flexible devices. Rather thick (d > 0.4 μm) and wide (w > 300 μm) grids were also used in ITO-free devices, but are very complex in fabrication since the used thicknesses and geometries made a complicated passivation necessary to prevent shorts [15]. Furthermore, most approaches towards flexible OLEDs have been demonstrated on PET-foil. Since PET is permeable for moisture and oxygen [16], it is pivotal to remove moisture within the PET and to encapsulate the devices to operate them under ambient atmosphere. Therefore, OLEDs fabricated on (typically ITO covered) PET-foil have to be encapsulated with barrier foil from both sides, making the device less flexible and more susceptible for degradation.

Here we demonstrate a method to fabricate ITO-free organic light emitting diodes directly on a barrier foil. As an anode we demonstrate a hybrid of a highly conductive polymer and an ultrathin metallic grid. The sheet resistance can be reduced up to one order of magnitude compared to commercially available ITO covered PET-foil. As we demonstrate here, this simple fabrication method for a completely flexible anode is based on the direct use of an encapsulation foil. This makes it unnecessary to encapsulate a PET-substrate from both sides. This method has the further advantage, that all OLED-layers have no contact to PET, so that the here presented devices are less vulnerable towards oxygen and moisture emitted from the highly hygroscopic PET [16].

2. Experimental details

2.1. Anode fabrication

As a substrate for our devices we used a transparent barrier film on a PET cover (3M, FTB3-125) with a combined thickness of 125 μm, see

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Fig. 1(a). The substrates were cleaned in isopropyl alcohol in an ultrasonic bath for 1 min. After 1 min of oxygen plasma treatment, a layer of ma-p 1215 photoresist (purchased from microresist technology GmbH) was spincast at 2000 rpm for 30 s resulting in a ~1.1 μm thick layer on the barrier side of the substrate. After a prebake at 80 °C for 60 s the grid structure in the respective sizes was illuminated into the resist via standard photo lithography. After development (developer: ma-D 331 from microresist technology GmbH) the respective metal was evaporated under vacuum at a pressure of $\sim 5 \cdot 10^{-4}$ Pa. To improve the adhesion of the gold on the barrier layer, we evaporated ~5 nm chromium below the gold layer. Thus, the gold grids in this report comprise the combination of chromium and gold. Aluminum and silver were directly processed on the barrier layer. After a lift-off with acetone and isopropyl alcohol, the metal grid remained on the barrier side of the substrate (see Fig. 1(b)). The substrates with the metal grids were then treated in oxygen plasma for 1 min. A layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, "PH 1000", purchased from Heraeus Clevios GmbH, diluted with 5 vol.% dimethyl sulfoxide and 5 vol.% isopropyl alcohol) was spincast at 2000 rpm for 120 s resulting in an ~80 nm thick layer (see Fig. 1(c)). The hybrid consisting of the ultrathin metal grid and the highly conductive polymer PEDOT:PSS was used as the anode in our devices.

2.2. Device fabrication

The following steps were performed in a glovebox under nitrogen atmosphere to avoid any degradation due to oxygen and moisture. The later referred ITO-anode device was fabricated on commercially available ITO-covered PET foil (purchased from VisionTek Systems, PET50). These reference devices were fabricated the same way as the devices with the hybrid anode, but without the metallic grid. The substrates with the metal grid or ITO and PEDOT:PSS layer were heated at 80 °C in a vacuum oven for 12 h to get rid of any H_2O residues. As an emitting layer the phenylene substituted poly(para-phenylenevinylene) (Ph-PPV; "Super Yellow" purchased from Merck OLED Materials GmbH) was used. The solution at a weight/volume ratio of 3 mg/ml in toluene was spincoated at 1000 rpm for 55 s resulting in a ~60 nm thick layer. As a cathode 0.7 nm thick lithium fluoride (LiF) and a 200 nm thick aluminum layer were evaporated under high vacuum ($\sim 10^{-5}$ Pa), see Fig. 1(d). Four luminous areas were defined on the substrate, each with a size of 5 mm × 5 mm. For the encapsulation a transparent barrier film with a PET cover and a pressure sensitive adhesive (PSA) on the barrier side (3M, FTB3-125a) was laminated on the OLED (Fig. 1(e)). After encapsulation the devices were measured under ambient conditions. Fig. 1(f) shows a photograph of a finished (bended) device.

2.3. Measurement setups

The transmission measurement presented in this report was performed with a UV/VIS/NIR spectrometer (Perkin Elmer 1050) with a 150 mm integrating sphere and an InGaAs detector to measure all potential scattered light of the grid samples.

The device efficiencies were measured in an integrating sphere (Gigahertz-Optik, UMBB-210) coupled via a multimode fiber to a spectrometer (Acton Research Corporation SpectraPro-300i) with an attached ICCD-camera (Princeton Instruments PiMax: 512). To record the I–V characteristics simultaneously with the efficiency measurements a source-measure unit (Keithley SMU 236) operated the devices.

To measure the sheet resistances the anodes were structured in a rectangle. An electrically conductive silver adhesive was processed at two ends of the rectangle in a manner that the shape of the anode was

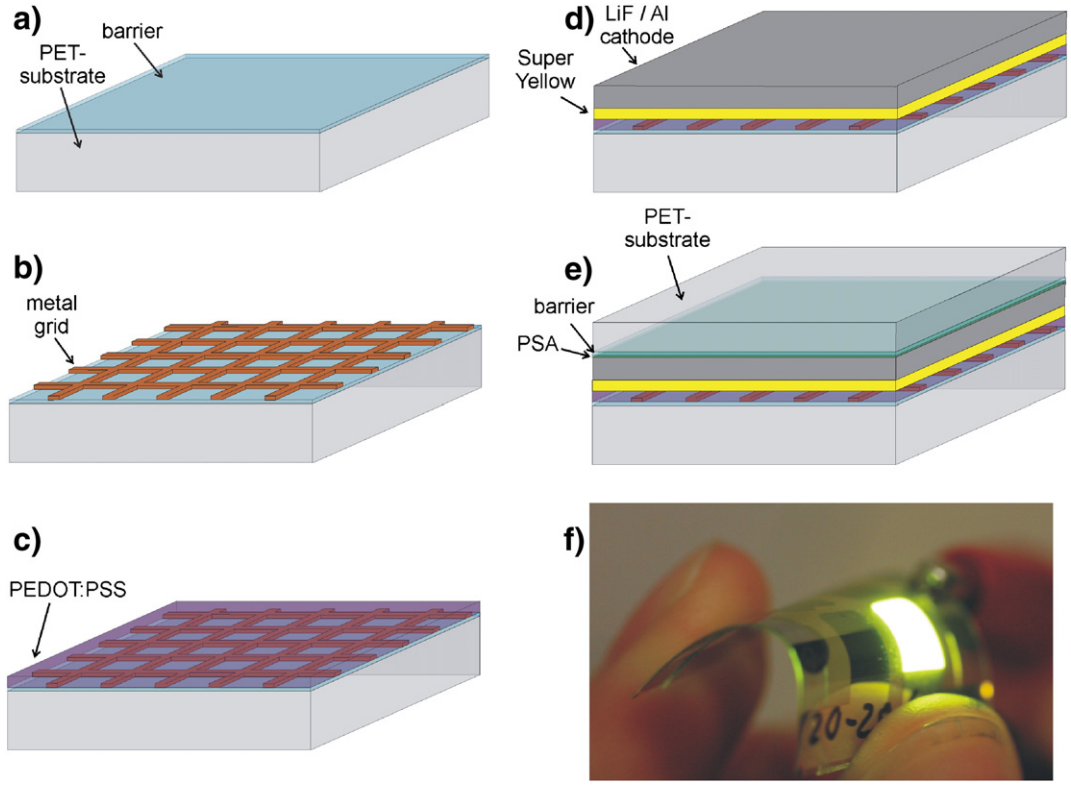

Fig. 1. Fabrication scheme. (a) A transparent barrier with a PET cover film was used as a substrate. (b) The metal grid was fabricated via standard photolithography and evaporation of the metal with a subsequent lift off process on the barrier side of the substrate. (c) A layer of PEDOT:PSS (PH 1000) with 5 vol.% DMSO and 5 vol.% IPA was spincoated on the metal grid. (d) As the emissive layer the Ph-PPV derivative "SuperYellow" was used and a LiF/Al layer served as the cathode. (e) For the encapsulation a barrier film with a PET cover and a pressure sensitive adhesive on the barrier side was used. (f) Photography of a finished device.