Organic devices for photonics

Progress towards ITO-free devices

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Abstract— **In this contribution, the most relevant and recent progress on ITO-free organic devices will be reviewed. To illustrate some of the challenges present, we have focused on a specific device, namely the organic light-emitting diode (OLEDs). The possibility to use thin metal layer as a substitute to ITO will be investigated in detail.**

Keywords: Polymer, OLED, ITO, electrode, thin metal films

I. Introduction

Since the discovery of conductivity in polymers and certain organic molecules, remarkable progress has been made in synthesizing organic materials, in understanding their properties and in developing them for use in electronic and optical devices. Currently, organic light-emitting diodes (OLEDs), photovoltaic cells (OPV) and field effect transistors (OFT) are being pushed towards commercialization. But other interesting applications are emerging such as RFID tags (radio frequency identification), memory devices, sensors, single-use diagnostic devices and more, which represent a future multi billion market**.** A principle advantage of organic electronics is that large, flexible substrates can be used. Polymer films (like polyester) are most widely used today, but paper, cardboard, thin glass and stainless steel are also prominent candidates.

A successful entry of organic devices into the general market requires, apart from high performance levels, a significant cost reduction of the devices. One of the limiting factor for the industrial implementation of organic devices is the use of indium tin oxide (ITO) as bottom electrode, which apart from being an expensive and scarce material also requires high temperature process for obtaining thick layers ideal for device application (Fig. 1). Therefore various alternatives with high conductivity and transparency have been studied to function as the anode.

We will give here a brief report of the various approaches investigated recently. In addition, our recent proposal and demonstration of thin metal layers as substitute to ITO for OLEDs will be discussed.

II. Organic Light-Emitting Diode

In the last decades organic light-emitting diodes (OLEDs) have been extensively investigated as the potential next generation technology for flat-panel display and lighting. The interest in this technology has been triggered due to the reports of new breakthroughs in device efficiencies, lifetimes, and achievable colors, including white [1].

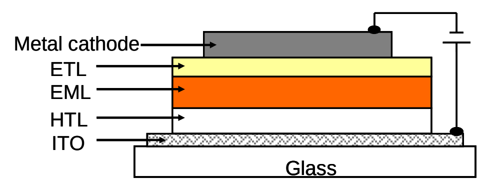

Figure 1: Schematic of the multilayer organic light-emitting device with the ITO as bottom electrode. EML is the emissive layer, ETL the electron transport layer and HTL the hole transport layer, all layers being organic.

An established method to obtain efficient OLEDs is use of multilayered device structures, consisting of many layers of organic semiconductor materials with different energy levels and functionalities, such as carrier transport, emission, and carrier blockage (Fig. 1). In such devices, indium-tin oxide (ITO), owing to its high optical transparency, good hole-injecting and commercial availability, has been used exclusively as a standard anode particularly for bottom emitting OLEDs. The surface of ITO glass is, however, chemically and physically ill-defined, which causes the detriment of its performance as the hole-injecting electrode in OLEDs. For example, its work function is known to dramatically depend on surface treatment methods and conditions. It has been reported that various species from the ITO will diffuse into the organic semiconductor layers leading to degradation in device performance.

A first approach to overcome several ITO limitations consisted in using thin metal layers (Ag, Cr) on top of ITO [2,3]. This double layer metal-ITO anode leads to an enhancement of the light output, even if its transmittance is lower than that of a single ITO layer. The metal-ITO anode is more favourable to device operation because of its optimized surface topography which leads to longer device lifetime. Adding a metal with a high work function to the ITO surface is then considered as a method with great potential for OLED applications. However for metal-ITO anode, improvement was observed only in hole injection efficiency, but not in power efficiency. This clearly implies reduced quantum efficiency, which is undesirable. Furthermore, such metals are only semitransparent, hence diminishing potential gains in efficiencies resulting from the metal buffer layer, while still using a thick ITO layer as part of the electrode. To be able to achieve ITO-free devices, extensive efforts have been made towards finding superior transparent conductive oxides (TCO) with no or little In. TCOs are usually n-type conductors either in a pure state or doped and in principle guarantee good charge injection, high transparency, good electrical conductivities, tunable morphology and the possibility of deposition on large areas with low cost techniques. Recently interesting results have been reported either using them like anode or cathode in the device [4]. A promising material is Al doped Zinc Oxide (ZnO) or AZO, which might replace ITO due to its high transmittance and low sheet resistance [5]. Still, a relatively thick layer of around 100nm is needed in order to obtain such a low sheet resistance and further work is needed to optimize its deposition. However, the most appealing examples of the use of this class of compounds are as air-stable electrodes in hybrid LEDs (HyLEDs) [6] where very efficient devices have been reported, but unfortunately, such approach still requires the use of ITO. The closest that has been achieved so far in using ITO free contact is the recent work by J. Meiss *et al* [7]. They have shown that multilayer metal contact made of ultra thin thermally evaporated Al and Ag films can be used for the top contact of an inverted organic bulk heterojunction solar cells obtaining up to 2.2 % in efficiency.

III. Thin Metal Films to replace ITO as Electrodes

In this work, we have investigated the possibility of using a thin nickel layer instead of ITO as anodes for bottom-emitting organic light-emitting diodes [8]. Identical single-layer devices based on a blue-emitting polymer were fabricated as bottom-emitting diodes, and equipped with either an ITO or nickel hole injecting electrode. The sputtering fabrication process gives very smooth, continuous and conductive nickel films, even for a film thickness as low as 4 nm. Metal films with a thickness between 50 and 100 Å are routinely used to prepare semitransparent contacts for a variety of optoelectronic devices [9]. Similar transmittance performance as for TCOs can actually be achieved if the metal film thickness is low enough (down to a few tens of angstroms) [10]. In addition, metals intrinsically show a significantly lower resistivity with respect to TCOs, even when they are very thin.

It was demonstrated that similar efficiencies were reached for devices with either ITO or nickel films less than 10 nm [8]. The thin nickel films show higher roughness, higher square resistance and a lower transmittance of about 2.5 times compared with ITO. These characteristics lead to a less efficient hole injection in the nickel-based device, which results in lower current densities at a given voltage and a slightly higher threshold voltage than the ITO-based device. Nevertheless, similar luminance levels were obtained for ITO-based and nickel-based devices. Most importantly, no optical modes could be observed within the nickel layer because the film is too thin for a light trapping mechanism. Lifetime measurements of the devices are underway

Another important aspect of the ITO-free electrode is the possibility to be deposited on flexible substrates. Preliminary work has been done in this direction, using flexible polyethylene terephtalate (PET) substrates. So far, the nickel films deposited on PET show good quality and good properties as on glass. Devices are now being implemented.

IV. Conclusion

In this paper, we have reported recent advances on ITO-free electrode for organic devices, focusing mainly on OLEDs. We have shown how thin nickel films could provide a route to ITO-free devices, as a semitransparent anode material for bottom-light-emitting diodes, with several advantages including simple deposition, no need for post-deposition treatment and lower cost.

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