Top Electrode Engineering in Organic Light-Emitting Devices Formed by Soft Contact Lamination (*Invited*)

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Abstract

We describe a new approach for building organic light-emitting diodes (OLEDs), which is based on physical lamination (i.e. soft contact lamination (ScL)) of thin metal electrodes supported by an elastomeric layer (polydimethylsiloxane) against an electroluminescent organic. We find that the devices fabricated have much better performance than those constructed with conventional vacuum deposition process. In addition, the ScL is intrinsically compatible with the technique of soft lithograph so that it is easy to build patterned OLEDs with feature sizes into the nanometer regime.

1. Introduction

Organic optoelectronic materials enable new classes of devices that could be important for consumer electronics. Organic light emitting diodes (OLEDs)[1,2] for example, form the basis of ultrathin and power efficient mechanically flexible display systems. In addition, miniaturized devices that have features in the micro and nanometer regime also have the potential to be important for applications in photonics, chem/biosensing and other areas. There are significant technical and scientific challenges associated with building high performance devices of this type and with understanding the details of their behavior. In particular, the nature of the interface between an organic semiconductor and a metal electrode is critical to the performance of these as well as other organic electronic and optoelectronic devices such as photovoltaic cells,[3] and transistors[4]. It is known that evaporation of metals onto organics, which represents the most common way to establish electrical contacts, leads to in-diffusion of the metal, changes in the morphology of the organic and, in some cases, disruption of chemical bonds.[5,6] These effects are important because they can lead to the generation of luminescence quenching centers in OLEDs[5-7] and large interfacial resistances in transistors.[8] The interfaces are difficult to control, however, since they depend sensitively on complex chemical and physical interactions between the metal and the organic, and also on the detailed processing conditions. A new technique, soft contact lamination (ScL)[3,8,9,10], provides a means for establishing electrical contacts at room temperature in ambient conditions without the externally applied pressures and heating that are associated with other lamination techniques[3,11] or the disruption of the organic that can be associated with evaporation. It thereby minimizes chemical, physical and morphological changes to the organic. This paper shows that the OLEDs built with this ScL method significantly outperform identical devices produced by direct evaporation. The paper concludes by demonstrating that these good characteristics persist in micron and nanometer-scale OLEDs fabricated by the combined use of ScL and soft lithographic techniques, including a form of near field optical lithography to define electrodes with dimensions of ~150 nm.

2. Experimental

Figure 1 schematically illustrates an OLED fabricated by ScL. The ScL device consists of two parts: a transparent elastomeric element coated with a thin metal film and a transparent substrate that supports an electrode and a film of an electroluminescent organic. When these two components are brought together, van der Waals interactions pull them into intimate contact to complete the device. This soft, laminated contact is robust (i.e. the device can be turned upside down without the pieces coming apart), it is reversible (i.e. the components can be peeled apart with no visual damage to either) and it can be established at room temperature without any applied pressure. The elastomer that we use for the experiments is PDMS (Sylgard 184, Dow Corning Inc.) cast and cured (60 °C for 3 hours) against the flat surface of a silicon wafer. Exposing the PDMS (typical thickness between 1 and 5 mm) to an oxygen plasma (~2 s, 30 sccm, 30 mT, 100 V; Plasma-Therm reactive ion etcher) followed by electron beam evaporation at ~5×10^{-7} torr of ~1 nm Ti (adhesion promoter; 0.3 nm/s) and 20-60 nm Au (1 nm/s) generates thin electrically continuous metal films that are strongly bonded to the PDMS. Evaporating through a shadow mask placed near the PDMS enables coarsely patterned OLEDs. Micron and nanoscale devices can be achieved by using various soft lithographic methods. Spin casting forms a

uniform film of the electroluminescent material on a thin (~100 nm) layer of indium tin oxide (ITO; ~15 Ω/□) on a glass slide (0.4 mm thick). When the bottom and top pieces are brought together, van der Waals forces pull the electrodes into intimate contact with the EL layer at room temperature, without application of external pressure. Typically this contact initiates on one side of the structure; a wetting front then progresses naturally across the sample until the entire surface is in contact.

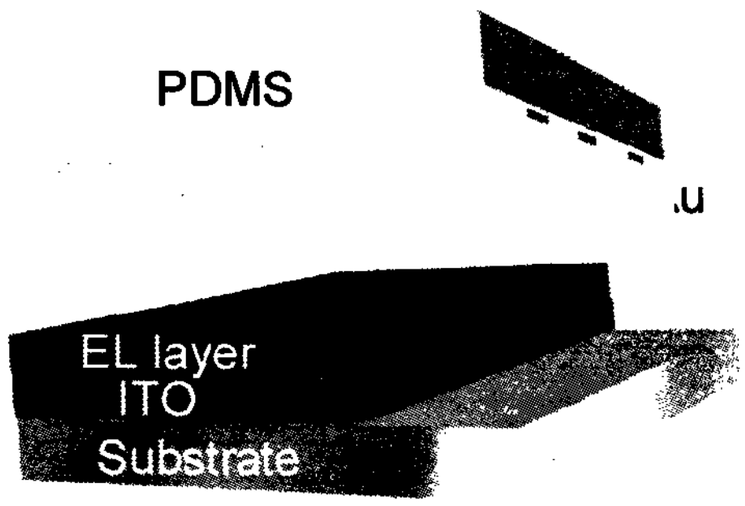

Figure 1. Schematic illustration of organic light emitting devices formed by soft contact lamination.

3. Results and discussion

We first compare the performance of OLEDs built by ScL and by direct evaporation of Au electrodes (conventional devices) onto thin (~65 nm) films of poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) spin cast onto ITO/glass. The Au was evaporated on MEH-PPV at a relatively high rate of 10 Å/s with a long distance (~ 40 cm) between the metal source and the sample, and with a rotating sample mount, in order to reduce in-diffusion.[5] The current and light output of these devices were measured while biasing the voltage positively to either the ITO or the Au. Qualitatively, the emission from both types of devices is spatially uniform as viewed by eye or through a microscope. Figure 2a shows typical current-voltage behavior. The similar current-voltage characteristics, together with the uniform emission, suggest that the two types of devices have similar electrical properties. Figure 2b displays typical external EL quantum efficiencies[12] as a function of current density. Since the work function of ITO (~4.7 eV) is smaller than that of Au (~5.1 eV), the efficiencies are higher when Au is biased positively than when ITO is biased positively because of enhanced electron injection. In contrast to the similar electrical properties, the ScL devices have efficiencies that are more than a factor of ten larger (maximum quantum efficiency: 0.015 % photons/electron (hereafter, ph/el) for ITO+ direction and 0.056 % ph/el for Au+ direction) than the conventional ones (maximum quantum efficiency: 0.0015 % ph/el for ITO+ direction and 0.003 % ph/el for Au+ direction). The quantum efficiencies of ScL devices with Au electrodes in both bias directions are also comparable to or a little higher than conventional ITO/MEH-PPV/Al devices with a lower work function metal (Al) we fabricated (maximum quantum efficiency: 0.01 % ph/el for ITO+ direction and 0.04 % ph/el for Au+ direction) and the previous reported values in the literature.[13,14] Because the MEH-PPV is primarily a hole transporting material, most of the excitons form near the Au in both types of devices when the ITO is biased positively. Nonradiative energy transfer from these excitons to metal (i.e. luminescence quenching by metal) represents one mechanism that reduces the efficiency.[15] This effect occurs in both conventional and ScL devices. The one order of magnitude lower efficiency in the conventional devices suggests the presence of additional quenching mechanisms. These could arise from various pathways associated with metal in-diffusion, changes in morphology, bond disruption and other effects caused by deposition of the Au. The large difference in efficiency is also present when the Au is positively biased. While most excitons in this case are

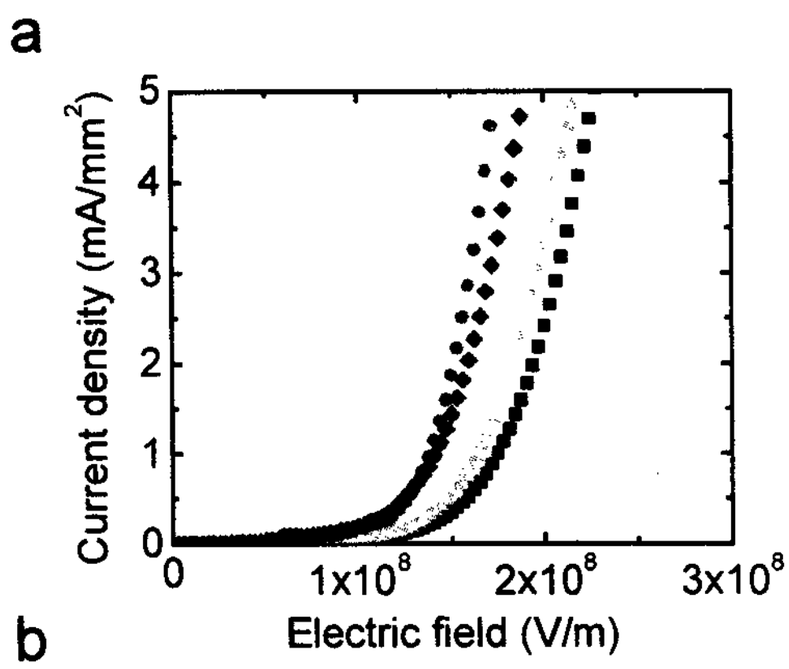

Figure 2. Characteristics of OLEDs formed from a stack of ITO (100 nm) / MEH-PPV (65 nm) / Au (20 nm), fabricated by soft contact lamination (ScL) and by evaporation (conventional) of the Au layer.

generated near the ITO, they can readily diffuse towards the Au side of the device during operation because their characteristic diffusion length is ~20 nm,[16] which represents a substantial fraction of the thickness of the MEH-PPV. In addition, the peak recombination zone moves towards the Au electrode due to the enhancement of charge-carrier mobility in increasing electric fields.[17] As a result, the excitons can be quenched through the same pathways, independent of the direction of the bias.

Although the absolute efficiencies of even the ScL devices are relatively low when Au is used, the performance can be improved through various strategies. For example, blending organic salts (tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$)) into the emitting polymer (MEH-PPV: $TBABF_4$=0.865: 0.135 by wt.), produces field-induced dipoles that enhance hole and electron injections from both electrodes.[17] For a ScL device made of 190 nm film of the MEH-PPV and $TBABF_4$ blend with 60 nm Au/PDMS, a maximum external efficiency of 2.5 % ph/el was measured at 3.4 V. Pure MEH-PPV ScL devices can also be improved by depositing a thin (~10 nm) electron injecting layer (the blend of polyethylene oxide and $TBABF_4$)[18] onto MEH-PPV. With this strategy, we obtained maximum external quantum efficiency of 0.53 % ph/el at 6.8 V for ScL devices.

In addition to high efficiencies and non- invasive, reversible electrical contacts, ScL provides unique opportunities for using soft lithography to make patterned OELDs with high resolution. Here we demonstrate three different approaches, using a polyfluorene derivative[19] as the electroluminescent layer because of its better stability than MEH-PPV: (i) the PDMS element itself can provide surface relief to pattern the contacts (Fig. 3a),[8,9,20] (ii) the Au on the PDMS can be chemically modified by microcontact printing patterns of insulating thiols as barriers to charge injection (Fig. 3b) and (iii) photolithography with conformable phase masks[21] and etching can be used to pattern directly the Au on the PDMS with nanometer resolution (Fig. 3c). Each of these approaches achieves high contrast patterned emission by modifying the top electrode prior to lamination. The spatial homogeneity of the emission in the patterned areas is, in all cases, comparable to that of unpatterned devices formed by evaporation. The nanoscale OLEDs (Fig. 3c) have ~150 nm wide Au line electrodes, but show emission profiles of ~600 nm linewidth, which is comparable to the resolution of the optical imaging system. The efficiency of these nanodevices is nearly as good (0.23 % ph/el with 15 nm Au) as unpatterned ones. Ultrasmall, flexible OLEDs such as these could potentially be useful, for example, as conformable light sources for subwavelength storage or lithography systems, or nanoscale optoelectronics. These and other more conventional applications, as well as fundamental investigations of electrode/organic semiconductor interfaces represent some of the many

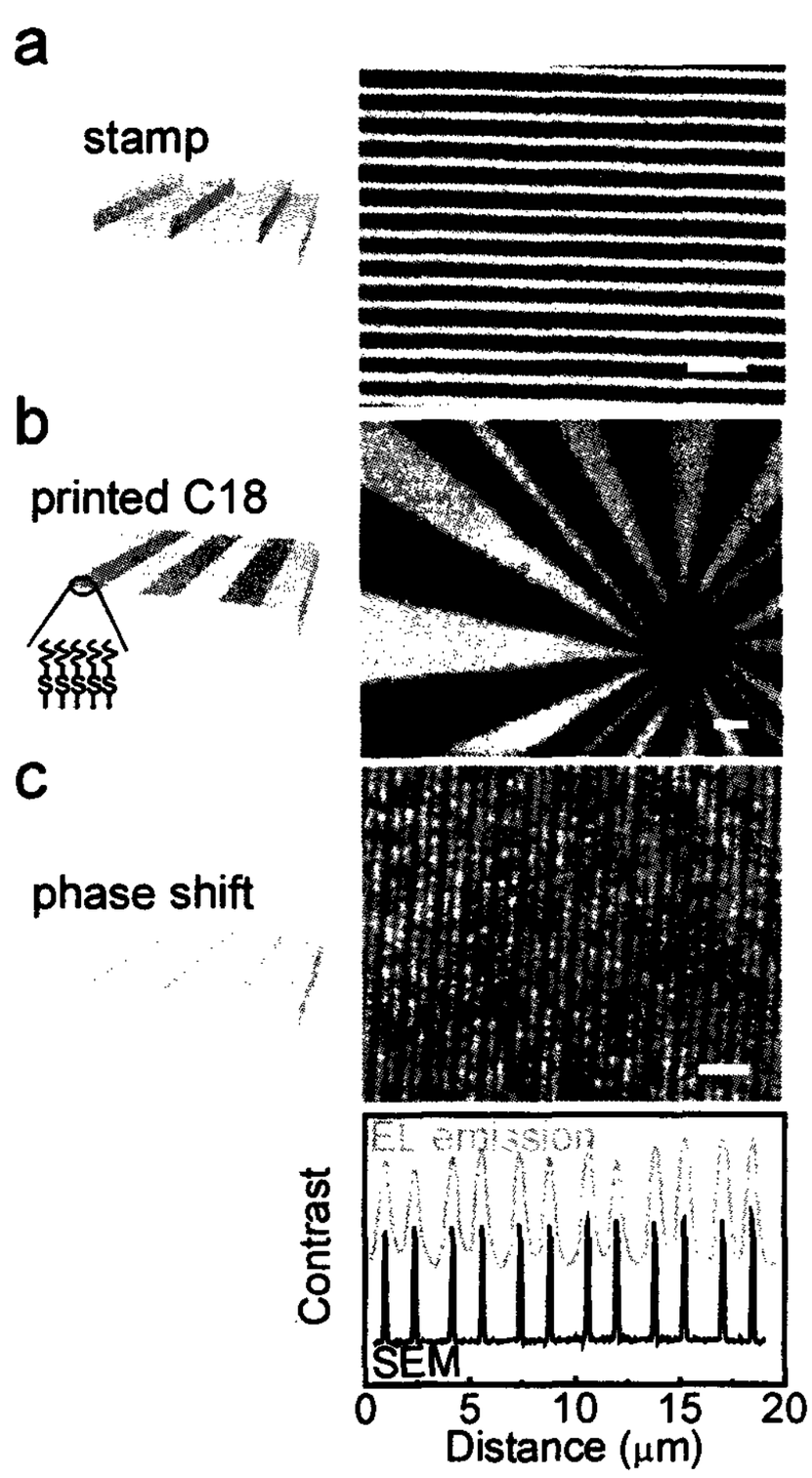

Figure 3 Patterned OLEDs formed by the combined use of soft contact lamination and soft lithography (a) Molding features of relief into the PDMS followed by blanket deposition of the electrode generates emission in the pattern of the raised features. The scale bar is 100 μm. (b) Microcontact printing an insulating self-assembled monolayer (octadecanethiol; C18) prior to lamination yields emission only in the bare Au regions. The scale bar is 100 μm (c) Photolithography with a conformable phase mask followed by etching directly patterns lines (150 nm wide) of Au on the PDMS. The averaged linewidth (~600 nm) of the pattern of emission (bottom graph) in this case is comparable to the resolution of the optical imaging system. The scale bar is 5 μm. The Rayleigh diffraction limit for the 0.55 NA microscope objectives is 590 nm at wavelength of 540 nm. The EL image was taken through the ITO (100nm)/glass (0.4 mm), which reduces the effective numerical aperture.

promising areas of use for soft contact lamination.

4. Conclusion

Organic/polymer EL devices formed by ScL exhibit homogeneous physical contacts and greatly improved quantum efficiency compared to conventional devices. This latter feature results because ScL avoids the detrimental effects caused by metal evaporation that give rise to non-radiative decay channels for excitons. In addition to excellent performance, micro and nanoscale devices based on chemically or physically modification of the top electrodes prior to lamination demonstrates the power of ScL for fabricating high-resolution organic optoelectronic devices.

5. References

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