Organic light-emitting devices with laminated top contacts

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We demonstrate the fabrication of organic light-emitting devices based on a ruthenium complex with indium tin oxide anodes and laminated Au cathodes. Light emission was uniform over the whole device area, indicating a high-quality mechanical and electrical contact. The devices showed no rectification, indicating that the laminated contact was ohmic and caused no damage to the ruthenium complex. Comparison with devices using evaporated Au cathodes confirmed the quality of the lamination process. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1739270]

Organic light-emitting devices (OLEDs) are being developed for applications in flat panel displays and lighting.[1] In their usual configuration, one or more organic semiconductor layer(s) are sandwiched between two electrodes. Upon the application of a bias, electrons and holes are injected from the two electrodes into the organic layer(s) and recombine, giving rise to light emission. The fabrication of OLEDs requires the deposition of organic semiconductors on metal electrodes (bottom contacts), as well as the deposition of metals on organic semiconductors (top contacts).[1]

The formation of top contacts (metallization of the organic) is usually achieved by physical vapor deposition in vacuum, which is a time consuming process and can, in certain cases, lead to damage of the organic film by incident hot metal atoms.[2,3] This is true not only for OLEDs, but also for other organic semiconductor devices that use metal electrodes deposited on the organic, such as photovoltaics and transistors. Metallization becomes an extremely crucial process in molecular electronic devices, where a contact must be deposited on a layer of organic that is a single molecule thick.[4] Therefore, finding alternative techniques for depositing metal contacts on organic semiconductors using processes that are fast and noninvasive is desirable.

Recently, a noninvasive technique to deposit electrodes on organic semiconductors was developed by Loo *et al.*[5–7] The technique, termed soft-contact lamination, involves the deposition of a thin metal electrode on an elastomeric substrate. This substrate is then bought, metal side down, in contact with the organic layer, allowing van der Waals interactions to form the contact between the organic and the metal. The elastomer allows the metal electrode to follow the contour of the organic surface. This technique has been used for the fabrication of organic thin film transistors (OTFTs),[5–7] as well as the metallization of self-assembled monolayers.[8,9]

Applying this technique to the fabrication of contacts for OLEDs brings about several challenges: First, the contact area in an OLED is much larger, imposing strict demands from the metallization process. Charge injection in an OTFT takes place primarily from the edge of the contact, while, in an OLED, the entire area of a contact must inject charge uniformly. Second, typical OLEDs require a low work function metal for efficient electron injection, and this is usually the electrode that is deposited on the organic. Under typical lamination conditions, a low work function metal will form a thin oxide layer, which will lead to poor charge injection. Third, it is intrinsically more difficult to make an ohmic contact to an OLED than it is to an OTFT. This is because the injection efficiency of a nonohmic contact decreases as the distance between the two metal electrodes is reduced from a few tens of microns in a typical OTFT to about 100 nm in a typical OLED.[10] In addition, the presence of a high charge density induced in OTFTs by the field effect leads to band bending and helps make a contact more ohmic.[10] Based on these observations, it is not *a priori* clear that the lamination technique can be applied with success to the formation of contacts in OLEDs. The potential of using lamination in OLEDs based on conjugated polymers has been recently explored by Lee *et al.*[11]

In this letter, we demonstrate efficient laminated contacts in an OLED made from the transition metal complex $[\mathrm{Ru(dtb\text{-}bpy)_3}]^{2+}(\mathrm{PF_6^-})_2$, where dtb-bpy is 4,4′-di-*t*-butyl-2,2′-dipyridyl. OLEDs based on ruthenium complexes, pioneered by the MIT group in 1999,[12] are receiving a great deal of attention.[13–20] These devices work in a way similar to light-emitting electrochemical cells,[21,22] which allows the fabrication of efficient, single layer devices that use air stable metals for both anodes as well as cathodes.[15,19,23] This fact allowed us to fabricate OLEDs with laminated Au electrodes and show that they form ohmic contacts.

The synthesis and characterization of $[\mathrm{Ru(dtb\text{-}bpy)_3}]^{2+}(\mathrm{PF_6^-})_2$ has been reported elsewhere.[19] All films were deposited on glass with pre-patterned indium tin oxide (ITO) electrodes (Thin Film Devices, Anaheim, CA). ITO substrates were first cleaned in a de-ionized water bath followed by a

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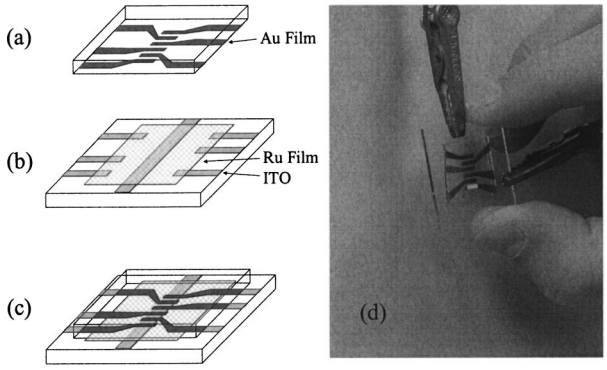

FIG. 1. Laminated device fabrication and operation. (a) Top component (patterned Au film on PDMS), (b) bottom component (ruthenium complex film on glass with pre-patterned ITO bottom contact and pads), (c) fully laminated device, and (d) laminated device operating in ambient conditions, as viewed through the glass substrate.

UV/ozone treatment. $[Ru(dtb\text{-}bpy)_3]^{2+}(PF_6^-)_2$ was then spin coated from acetonitrile solution onto the ITO substrates. Films were dried in a vacuum oven for 12 h at 60 °C, and the contacts were laminated as described below. Typical film thickness was 75–100 nm as measured by profilometry with a rms surface roughness of 4.4 Å, as measured by atomic force microscopy (AFM) over an area of 100 μm^2. Reference devices were fabricated with 200 Å Au electrodes that were directly deposited on the ruthenium complex film by thermal evaporation under high vacuum (10^{-6} mbar) at a rate of 1 Å/s. The Au deposition was done in an intermittent way to minimize damage to the ruthenium complex.[3] The current was measured with a Keithley 236 source-measure unit and the radiance with a calibrated UDT S370 optometer, attached to an integrating sphere.

The lamination technique is illustrated in Fig. 1. A ''bottom'' component [Fig. 1(b)] consists of a ruthenium complex film deposited onto glass with patterned ITO bottom contacts, as described above. A ''top'' component [Fig. 1(a)] utilizes a soft elastomeric material as a substrate onto which Au films are thermally evaporated. To fabricate the top component, Sylgard 184 polydimethylsiloxane (PDMS) was used as the elastomeric substrate. Sylgard 184 was mixed at a 10:1 base:curing agent ratio by weight. The mixture was cast on a silicon wafer and cured for 1 h at 60 °C. For all further processing, PDMS was cut to size and the previously exposed surface was mounted on a thin glass plate (not shown here), allowing the low roughness surface previously in contact with the Si wafer to be used for all further processing. Prior to thermal evaporation of Au contacts, PDMS was exposed to UV/ozone for 15 min. Longer exposure made the surface of the PDMS brittle, while shorter exposure led to poor adhesion to the bottom component. Ten angstroms of Cr (adhesion layer) and 200 Å of Au were then thermally evaporated under high vacuum onto the PDMS substrate at a rate of approximately 2 Å/s. A shadow mask was used to obtain the desired pattern, which resulted in devices with an active area of 3 mm^2. A rms surface roughness of 3.8 Å was measured for the Au films on PDMS by AFM, over an area of 100 μm^2. When placed in contact, the top component naturally wets the bottom component due to van der Waals bonding between the two elements [Fig. 1(c)].

A picture of a device with laminated contacts is shown in Fig. 1(d). The device is operated under a forward bias of 5 V, using the laminated Au contact as a cathode. Bright, uniform emission is observed throughout the whole device area. The temporal evolution of the current, radiance and external quantum efficiency of this device are shown in Fig. 2 (continuous line). The efficiency initially reaches a little over 1%, but decays gently over the course of 90 min. Efficient emission from an OLED that uses a high work function metal as a cathode might appear puzzling at first, but this behavior can be traced to the ionic nature of the $[Ru(dtb\text{-}bpy)_3]^{2+}(PF_6^-)_2$. Namely, the PF_6^- counter ions are mobile and can redistribute under the influence of the applied bias, leading to accumulation near the ITO electrode, and depletion near the Au electrode. This redistribution of ionic charge creates large electric fields at the contacts and enhances charge injection (by lowering the barrier for tunneling[22]).

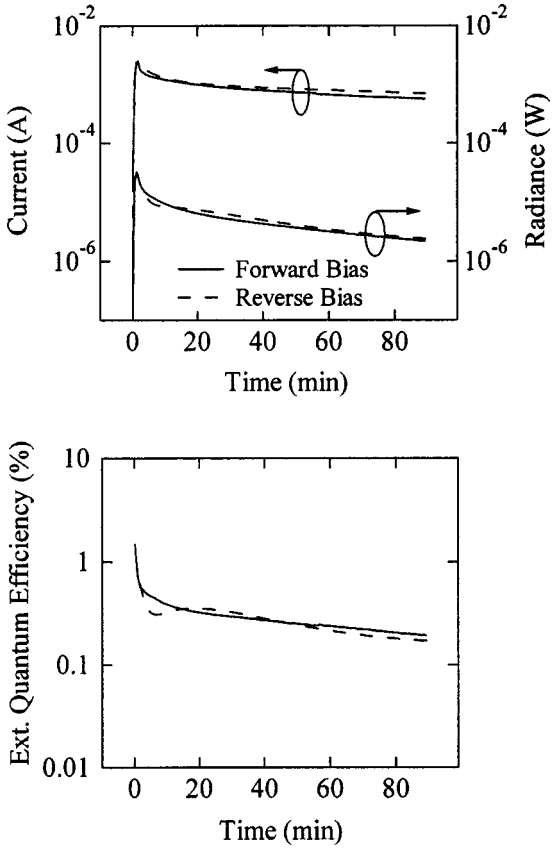

FIG. 2. Temporal evolution of current, radiance and external quantum efficiency of devices with laminated Au cathodes in forward and reverse bias (5 V, −5 V, respectively).

This fact is further validated by the absence of rectification, shown in Fig. 2. Namely, the current and radiance of a different device (on the same substrate), run at −5 V (dashed lines) are virtually identical to the ones from the first device (continuous lines). This is expected, since the redistribution of counter ions is reversed under −5 V, leading to enhanced electron injection from ITO and hole injection from the laminated Au contact. The absence of rectification indicates that under the influence of the ionic space charge, both the ITO as well as the laminated Au electrode become capable of injecting both electrons and holes with identical efficiency. Lack of rectification in a bipolar device with different electrodes is only possible when both contacts are ohmic, for both electron and hole injection.[24]

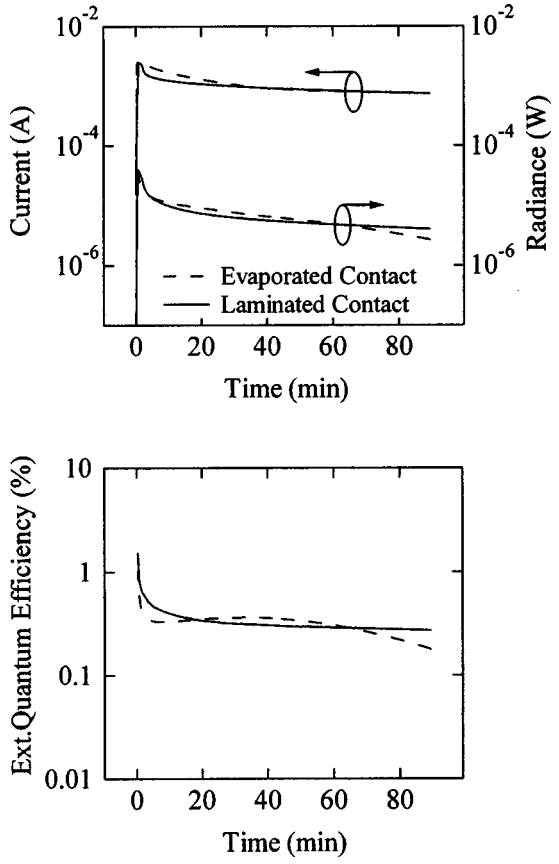

FIG. 3. Time evolution of current, radiance and external quantum efficiency of devices with evaporated and laminated Au cathodes in forward bias of 5 V.

Figure 3 compares the performance of OLEDs with laminated and with evaporated top Au electrodes. The two devices show similar performance, indicating that the lamination process works well. Small differences, namely the improved stability of the device with the laminated contacts, are mostly due to the differences in the quality of the ruthenium complex films, as these two devices were fabricated on different substrates. In order to gain some insight into the reproducibility of this technique, three separate laminations were performed on substrates that had six devices each. This produced 18 devices, which were run at forward bias for 10 min so their steady state efficiencies could be recorded. The resulting efficiencies make up a relatively tight distribution ranging between 0.4% and 0.9% (and one shorted device). The average external quantum efficiency (0.6%) was the same as that of devices with evaporated Au electrodes.

The lamination technique discussed here provides an easy way to make contacts to OLEDs from transition metal complexes, but its general applicability to OLEDs from traditional organic semiconductors remains to be proven. To a large extent, the success of the lamination described in this work is due to the ionic nature of the ruthenium complexes, which facilitates the formation of ohmic contacts. The uniformity in the emission of these devices, however, shows that it is possible to form a high-quality mechanical and electrical contact over areas of interest to OLEDs. In addition, the absence of rectification in these devises shows that no damage is induced by the lamination technique. This creates an opportunity to explore the regime of molecular electronics, where sensitivity to metallization induced damage is extreme.

In conclusion, we demonstrated the fabrication of OLEDs based on a ruthenium complex with ITO anodes and laminated Au cathodes. A good contact was obtained over an area of 3 mm^2, as seen by the uniformity of light emission. The devices showed no rectification, indicating that the laminated contact was ohmic and caused no damage to the ruthenium complex. Comparison with evaporated contacts confirmed the quality of the lamination process.

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