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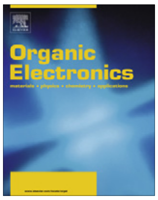

Ambient laser direct-write printing of a patterned organo-metallic electroluminescent device

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ABSTRACT

In this work we use laser direct-write (LDW) to fabricate patterned $[Ru(dtb\text{-}bpy)_3]^{2+}(PF_6^-)_2$ electroluminescent devices under ambient processing conditions. Device fabrication is accomplished via laser micromachining of a transparent conducting oxide top electrode, LDW printing the active organo-metallic material, and vapor depositing the bottom electrode. Nuclear magnetic resonance spectroscopy is used to ensure the transfer of damage-free luminophore material. Devices tested in air are shown to exhibit emission spectra, luminous efficiencies, and lifetimes similar to literature values for devices fabricated in nitrogen environments. The versatility of laser direct-write printing is then demonstrated by printing multi-color luminophore patterns with diameters down to 10 μm for future use in high-resolution device fabrication. This approach is compatible with large-area organic electronics that require the fabrication of high-resolution architectures.

1. Introduction

Advances in organic electronic materials have created an attractive alternative to traditional semiconductor devices. Organic materials have the advantage of being compatible with large area, lightweight and flexible plastic substrates and can be inexpensive to fabricate [1–4]. A particular subset of these materials, namely ionic transition metal complexes (iTMCs), has drawn much attention due to the high mobility of charge carrying ions in the organic layer. These materials enable single-layer device architectures that are more economical to manufacture and electronically more versatile than typical organic devices allowing the use of alternating currents [5]. Higher mobilities mitigate electrode work function limitations, permitting the use of oxygen-stable metal electrodes [6]. Lastly, the use of small molecule iTMCs alleviate problems with purification often encountered in polymer-based devices [7].

Device fabrication typically consists of spin coating solutions of iTMCs over transparent conducting electrodes. However, this approach is limited in its ability to produce high-resolution features without additional processing. Such features are important when fabricating multicolor displays and other more advanced light-emitting and electronic device architectures. Instead, direct-write printing techniques have the advantage of depositing organic material directly into high-resolution patterns without masks, molds, or the need for subsequent patterning steps [8,9].

Laser-induced forward transfer (LIFT) has emerged as a versatile technique for producing direct-write patterns of organic electronic materials [10–13] or direct printing of intact multilayer OLED structures [14–16]. In its conventional form [8], the bottom of a laser-transparent glass substrate (donor) is coated with an ink and placed 50–500 μm above a receiver substrate. Upon pulsed-laser irradiation, a confined region of ink near the glass interface is vaporized, and ink volumes as small as picoliters [17] are ejected onto the receiver substrate. User-programmable pattern generation is enabled through three-dimensional, sub-micron motion control of the donor/receiver assembly relative to the laser source. The direct-write nature of LIFT eliminates

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the need for masks used in vapor deposition and is often chosen over nozzle based methods when higher viscosity inks are required or the unreliable characteristic of nozzle clogging must be avoided. In addition, the entire LIFT process is conducted in ambient conditions making it a cost effective and convenient technique for the rapid prototyping of novel devices.

When dealing with organic molecules, LIFT presents a number of challenges. For instance, special care must be taken when the material of interest is particularly susceptible to thermal, optical, or mechanical damage [11]. Conversely, when the ink material does not strongly absorb incident laser energy, transmitted radiation inevitably interacts with the receiver substrate and can cause undesired vaporization of the transparent conducting oxide. The addition of foreign materials in the ink to absorb the laser can enable transfer in these cases but can also quench electroluminescence and hinder device operation.

To avoid these drawbacks we incorporate a polymer film absorbing layer (thickness = 2–8 μm) between the glass substrate and ink material on the donor [11,18,19]. Upon laser irradiation, a small volume of polymer nearest the polymer/glass interface absorbs the energy, forming an enclosed high pressure vapor that deforms the remaining polymer film into the adjacent ink and induces its transfer. This modified LIFT technique is termed blister-actuated laser-induced forward transfer (BA-LIFT) because the ink transfer is a consequence of laser-generated blister motion (Fig. 1a). BA-LIFT eliminates possible contamination issues associated with laser-absorbing additives or thinner laser absorbing layers by tuning the process for the absorption of laser energy solely in the polymer film and by selecting a thick enough polymer layer that will not fully decompose. In addition, BA-LIFT has been shown to successfully deposit weak laser-absorbing organic and biological materials, including systems that are optically and thermally sensitive [11,19].

In this work we use ambient laser direct-write techniques for fabricating patterned $[\mathrm{Ru(dtb\text{-}bpy)_3}]^{2+}(\mathrm{PF_6^-})_2$ (Complex **1**) electroluminescent devices. To confirm the viability of the BA-LIFT process for printing damage-free luminophore molecules, nuclear magnetic resonance (NMR) spectroscopy is employed. Our devices are characterized by acquiring emission spectra and measuring luminous efficiencies and lifetimes, which are similar to literature values of devices fabricated in nitrogen environments. Finally we demonstrate the versatility of BA-LIFT, by printing multi-color luminophore patterns for future use in high-resolution device fabrication.

2. Experimental

The two employed iTMC examples are tris(4,4′-di-tert-butyl-2,2′-bipyridyl)ruthenium, $[\mathrm{Ru(dtb\text{-}bpy)_3}](\mathrm{PF_6})$ [20] (Complex **1**), and bis(5-trifluoromethyl,2-(2′,4′-difluorophenyl)pyridyl), (4,4′-di-tert-butyl-2,2′-bipyridyl)iridium, $[\mathrm{Ir(F_5\text{-}mppy)_2(dtb\text{-}bpy)}](\mathrm{PF_6})$ [21] (Complex **2**), both of which are prepared as previously described [20,21]. In the absence of a blue-emitting iTMC, 9-anthracenemethanol (Aldrich, 97%, Complex **3**) is selected as a surrogate, and used without further purification.

Donor substrates are produced by soaking glass slides in a solution of NOCHROMIX and sulfuric acid to remove oils and loosen debris. Slides are subsequently washed in deionized water, rinsed with acetone and ethanol, and blow dried with nitrogen. Slides are then spin coated with commercially available polyimide (HD Microsystems PI2525) at different spin speeds (3000 and 6000 RPM), and cured as in previous work to produce final film thicknesses of approximately 7 μm and 4 μm, respectively [19]. Luminophore solution is subsequently spread onto donor substrates with a wirecoater, or an aliquot of solution is drop cast onto donor substrates and spun at 1000 rpm

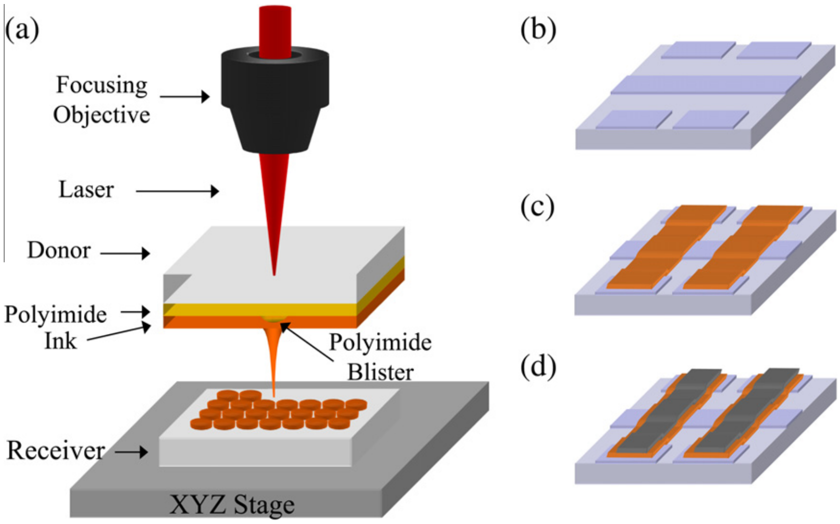

Fig. 1. (a) Illustration of the BA-LIFT process depicting ink transfer in the form of a coherent jet. Device fabrication begins with (b) laser micromachined indium tin oxide coated glass followed by (c) BA-LIFT printing of the organic ink in ambient conditions defining two 3.5 × 12.5 mm^2 pads. (d) Vapor deposition of the aluminum bottom electrode completes the fabrication process.