Fabrication of organic light-emitting diode pixels by laser-assisted forward transfer

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Fabrication of a polymer light-emitting device was achieved by a laser forward transfer technique using the decomposition of a thin triazene polymer film by a XeCl excimer laser. The dry deposition process allows transfer of a bilayer consisting of the electroluminescent polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] covered with an aluminum electrode onto a receiver substrate. The soft transfer results in laterally well resolved pixels ($\approx 500~\mu$m), whose fluorescence as well as electroluminescence spectra remain unaltered. The rectifying and smooth current-voltage characteristics add to the merits of this laser-based transfer method that opens up the possibility of direct-writing heat- and UV-sensitive materials. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2759475]

Laser-induced forward transfer (LIFT) has been developed as a direct-write method for the defined microdeposition of metals, ceramic powders, or organic materials.[1–4] In conventional LIFT procedures, a layer of the transfer material is coated on a transparent donor substrate (e.g., fused silica). Irradiation by a laser pulse coming in through the substrate leads to an evaporative forward ablation of the transfer material. A receiver substrate that is placed in close vicinity of the donor substrate receives the material to be transfered. Mainly robust and heat-resisting materials can be transferred by this method because of the high thermal load induced by direct light absorption. Sensitive materials, such as organic dyes or semiconductive polymers, are damaged by laser irradiation. To avoid direct laser damaging, an additional dynamic release layer (DRL) was introduced for light-to-heat conversion needed to transfer sensitive materials.[2,5–8] The common issue of these intermediate layers, predominantly used with infrared lasers, is the intrinsically high thermal load on the sensitive materials to be transferred.[9]

To prevent heat- and light-induced damages, we developed an advanced LIFT process using an intermediate sacrificial layer of a UV-absorbing dialkyltriazene polymer. Thin films of this photopolymer are excellent DRLs because they decompose integrally into volatile fragments at very low ablation thresholds [$\approx 25~\text{mJ/cm}^2$ (Ref. 10)]. Recently, living mammalian cells were deposited onto a bioreceiver substrate with a pulsed ArF excimer laser using such a triazene polymer DRL.[11] In a similar manner, pixel arrays of sensitive multispectral nanocrystal quantum dots were smoothly transferred with good resolution.[12] Therefore, this LIFT method should be ideally suited to transfer sensitive optoelectronic polymers for the fabrication of organic light-emitting diodes (OLEDs) as well. Unlike solution-based screen printing,[13] ink-jet methods,[14] and photolithographic techniques,[15] the laser deposition process is a dry transfer method that bears two

principal advantages. Firstly, it is able to produce high-resolution patterning required for pixelated displays. Secondly, it bears the potential to fabricate well-defined multilayer structures. This is difficult if not impossible to achieve using solution based methods if more than two layers are to be deposited. In contrast with a resonant infrared pulsed laser ablation method, recently applied to fabricate polymer light-emitting diodes (PLEDs),[16] the advanced LIFT process does not rely on vacuum deposition and shadowing mask techniques.

In this letter, we report the LIFT method for the fabrication of polymer light-emitting devices using the archetype poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV).[17] We demonstrate microdeposition of a polymer/metal cathode bilayer from a fused silica donor to a transparent conducting oxide receiver using the high-quality triazene photopolymer as sacrificial DRL (Fig. 1). Photoluminescence, electroluminescence, current-voltage characteristics, as well as structural properties of the transferred pixel devices are discussed.

With the goal to produce OLEDs according to the simple device architecture tin-doped indium oxide (ITO)/MEH-PPV/Al, the multilayer donor films were prepared by depositing successively triazene polymer (100 nm), aluminum (70 nm), and MEH-PPV (90 nm) on fused silica substrates (see Fig. 1). The triazene polymer (poly[oxy-1,4-phenylene(3-methyl-1-triazene-1,3-diyl)-1,6-hexanediyl(1-
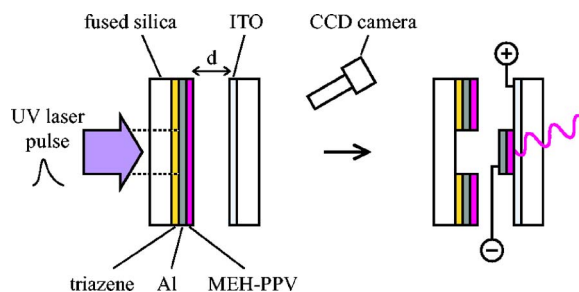

FIG. 1. Scheme of the transfer principle.

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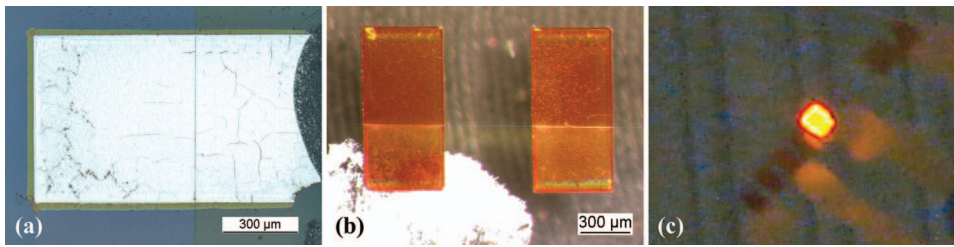c)Electronic mail: thomas.lippert@psi.ch

FIG. 2. (Color) Digital photographs of transferred pixels. (a) Detail of the back side of a pixel (Al layer on top). (b) View of two pixels through the ITO substrate, the one on the left is contacted with Ag paste. (c) Pixel in operation.

methyl-2-triazene-1,3-diyl)-1,4-phenylene]) was synthesized, as described in Ref. 18, and spin coated from solutions in chlorobenzene and cyclohexanone (1:1 w/w). Aluminum was deposited by thermal evaporation in high vacuum. MEH-PPV (Aldrich, $M_n = 40\,000 – 70\,000$ g/mol) was purified by flash chromatography (THF, silica gel) before use and spin coated from a 1 wt % solution in chlorobenzene. The entire film fabrication was carried out in inert atmosphere. Patterned ITO (140 nm, 20 $\Omega/\square$) glass substrates were used as receivers after cleaning. The transfer was achieved using a single pulse from a XeCl excimer laser ($\lambda = 308$ nm, $\tau = 30$ ns). The donor and receiver substrates were placed in close contact ($d < 1$ μm) on a translation stage. The laser fluence was controlled by an attenuator and a homogeneous part of the beam was imaged by a lens onto the backside of the DRL. A camera with a microscopic objective was used to follow the deposition. Samples were exposed to air only for the time needed to achieve transfer and put back into the protective atmosphere immediately after, where they were kept for the characterization. The Al cathodes of the pixels were contacted individually with silver paste. Current-voltage curves were measured with a Keithley 2400 source-measure unit. The photoluminescence was measured in air with a Jobin Yvon Horiba FL311 Fluorolog using front face detection. Electroluminescence spectra and luminance were recorded with a Minolta CS1000 spectroradiometer.

State-of-the-art PLEDs utilize layers smaller than 100 nm. Therefore, the challenge here is to transfer very thin layers of functional materials. Obviously, such thin films are very sensitive to mechanical and thermal solicitations, requiring a careful tuning of the laser fluence and DRL thickness. Optimal transfer conditions in air were obtained with a triazene thickness of 100 nm and a laser fluence of 250 mJ/cm^2. At significantly lower fluences, laser ablation was not sufficient to propel the Al/MEH-PPV bilayer to the receiver substrate. At higher fluences, the Al layer was disintegrated, demonstrating the limited cohesion of the metal film. Figure 2(a) shows a microscopy picture of a transferred pixel viewed from the aluminum side. The Al layer is visible on top, below is MEH-PPV, and the round dark shape on the right is silver paste. The pixel is homogeneous and exhibits extraordinarily sharp edges which have never been reported for a LIFT technique up to now. However, some cracks are present on the Al layer which are more pronounced at higher fluence.

No redeposited debris of triazene or transfer material are visible on the pixel and on the side, pointing out the benefits of using the former as sacrificial release layer. Interestingly, there is a thin MEH-PPV border surrounding the aluminum pixel [see Fig. 2(a)]. The ablation crater on the donor substrate confirms that the MEH-PPV pixel is slightly larger than the Al pixel. We attribute this feature to the different mechanical behaviors of the polymeric layer compared to the

aluminum film. This effect is particularly helpful in the construction of light-emitting diodes, since it avoids short circuits between the transferred aluminum electrode and the ITO. A bottom view from the ITO side of two pixels is shown in Fig. 2(b). The top rectangle of the pixels in contact with the ITO anode is the active area. The bottom part is on glass, where the contact to Al was applied using silver paste. Here again, it appears that the pixels have a regular and clean shape, corresponding to the spot of the laser beam. A diode pixel in operation is shown in Fig. 2(c). Other noncontacted pixels can be recognized as well on the picture. The pixel emits light, demonstrating that the device is functional after the transfer.

Operating devices were then characterized by current-voltage (I-V) and electroluminescence (EL) measurements. Figure 3(a) presents a typical current-voltage curve. The I-V curve exhibits a smooth, rectifying shape up to 16 V, which is free from short-circuit spikes, indicating that transferred diodes are of good quality and no layer mixing occurs upon transfer. Simultaneous I-V and EL measurements were carried out. The luminance-current characteristics are linear, which is a typical diode behavior [see inset to Fig. 3(a)]. A luminance of 6 cd/m^2 was measured at 14 V. This value is not very high and reflects the yet unoptimized device architecture. In particular, the high current and light onset voltage are due to the poor electron injection at the aluminum cathode as well as the rather thick MEH-PPV layer which limits charge transport. The luminous efficiency at 14 V of 2 $\times 10^{-2}$ cd/A is typical of simple MEH-PPV light-emitting diodes using a bare Al cathode.[19] However, the choice of this device architecture offers the advantage of being well characterized in the literature. Most importantly, the MEH-PPV emission spectrum depends strongly on thermal annealing,[20] which permits the assessment of possible heating effects oc-
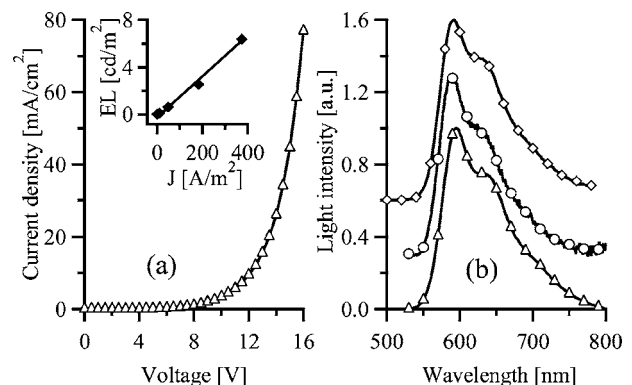

FIG. 3. (a) Current-voltage curves of a typical pixel device. Inset: EL intensity vs current density (other sample). (b) Normalized photoluminescence spectra of a donor film ($\triangle$) and a transferred pixel ($\bigcirc$), and electroluminescence spectrum of the same pixel ($\diamond$). For clarity, the spectra were vertically offset.

curring during laser transfer. Photoluminescence (PL) and electroluminescence spectra are presented in Fig. 3(b). The PL spectra were taken from both a donor film and a transferred pixel, which was also used for measuring EL. The vibronic structure of the spectrum is the characteristic of the interchain packing of the polymer and origins from the aggregation state of the polymer in the spin coating solution.[20] If annealed, the emission spectrum of the film exhibits a very broad redshifted peak at 650 nm with poor emission efficiency. No such peak is observed neither in the EL nor in the PL spectrum of the transferred pixel. Due to poor electron injection in the single layer devices, the recombination and EL emission zone is very close to the aluminum cathode. The EL spectrum is therefore particularly sensitive to structural changes occurring in the vicinity of the aluminum electrode. The fact that both PL and EL spectra of the pixel are similar points out that thermal load effects are very limited. Future work will focus on the detailed influence of the various parameters such as layer thicknesses and laser fluence on the pixel transfer. Different device architectures and lifetimes of the diodes will also be investigated.

This work shows that functional OLED pixels can be fabricated by a modified LIFT process. The visual aspect of the transferred pixels is very good, especially the sharpness of the edges. Therefore no limitation is expected with regards to miniaturization, which is a necessary requirement for producing flat panel displays. Our laser transfer method combines two further unique features. It can be applied to sensitive materials without altering their properties but it also allows to direct-write multilayer systems in a solvent-free single step, without requiring any shadowing mask or vacuum installation. This opens the way to alternative manufacturing processes for the OLED technology.

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