

Super-high-resolution transfer printing for full-color OLED display patterning

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Abstract — A transfer-printing method for the patterning of thin polymer layers is described. A hard stamp with a raised feature is brought into contact with a spin-coated organic film under elevated pressure and temperature to break the films. The patterned film is then transfer printed onto the devices. This method is used to print red/green/blue subpixel arrays with a pattern size as small as $12\ \mu\text{m}$ at a resolution of 530 ppi to demonstrate its ability for full-color organic light-emitting-display fabrication. Devices with printed organic layers have similar performance to spin-coated controls under optimized printing temperature and pressure settings. The critical physical parameters include a soft intermediate plate for the sharp breaking of edge patterns, control of surface energies, and printing at moderate temperature and pressure to achieve intimate contact between the printed layer and the underlying substrate.

Keywords — OLED, patterning, printing.

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1 Introduction

An important challenge for OLED-display manufacturing is to find a simple and low-cost method for patterning the organic materials used for different colors. Conventional photolithography is usually not capable of patterning organic materials because the solvent used in the process may degrade the materials to be patterned. Ink-jet printing^{1–4} has been widely used, but it suffers from potential drawbacks such as poor resolution, low throughput, and non-uniform thickness. Other alternative patterning methods demonstrated includes laser-induced thermal imaging^{5,6} and laser-induced sublimation transfer.^{7,8} With laser-induced thermal imaging, sharp-edge patterns are difficult to achieve for polymer layers, and laser-induced sublimation can only be used to pattern small molecules. In this paper, we demonstrated a transfer-printing technique over a large area to pattern active polymer layers. OLEDs with the transferred layers were fabricated and tested.

2 Transfer printing

Figure 1 illustrates the procedures of our transfer-printing method. The process begins with the fabrication of a hard stamp [Fig. 1(a)], where the raised features correspond to the final regions without the polymer on the final device plate. A silicon wafer is used for the hard stamp and conventional lithography and etching is used. In this work, rectangularly shaped patterns of two dimensions ($12 \times 40\ \mu\text{m}$, $24 \times 80\ \mu\text{m}$) are etched into the stamp to a depth of $\sim 700\ \text{nm}$. A second flat plate, also silicon for convenience, is coated with a poly(dimethylsiloxane) (PDMS) layer and used as a backing layer for the active polymer layer to be patterned.

The PDMS is spin-coated from a PDMS prepolymer which is a mixture of Sylgard 184 and its hardener (Dow Corning) dissolved into cyclohexane solvent. The PDMS prepolymer solution is syringe-filtered by using a $0.1\text{-}\mu\text{m}$ filter before use. The PDMS film after spin-coating is baked at 150°C for 2 hours on a hotplate for cross-linking. The final PDMS film is about $1.2\ \mu\text{m}$ in thickness after baking.

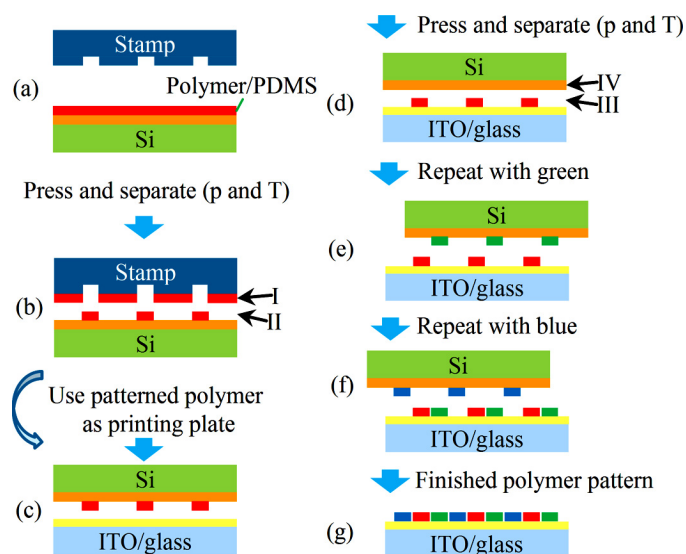


FIGURE 1 — Schematic illustration of the transfer-printing method for full-color display patterning. (a) A hard stamp with raised features and a polymer-coated (e.g., red-light-emitting) PDMS/Si substrate. (b) The stamp is pressed onto the polymer layer at elevated temperature (p and T). Upon separation, two patterned polymer layers are formed on each side. (c) The patterned polymer on the PDMS side is used as the printing plate and (d) is pressed onto a device plate (p and T) to transfer the polymer layer. Steps (a–d) are repeated for (e) green- and (f) blue-light-emitting polymer to finish the pattern (g) required for a full-color display.

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The control of surface energies for transfer printing is critical. The PDMS film is treated with oxygen plasma treated for 5–10 sec in order to make the surface hydrophilic so that spin-coating is possible.⁹ Longer plasma treatment, however, will make the PDMS surface too sticky and the polymer layer would not detach easily from the PDMS layer during the printing steps.

For the active light-emitting organic layer, a mixture of polymer and small molecules is used.¹⁰ Poly(9-vinylcarbazole) (PVK) ($M_w = 1.1$ M, $T_g = 200^\circ\text{C}$) is used as the host polymer. It is doped with 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) for electron transport and the dyes nile red, coumarin 6 (C6), or coumarin 47 (C47) for red, green, and blue color tuning, respectively.¹⁰ The entire blend is spin-coated onto the PDMS-coated silicon substrate, using chlorobenzene as the solvent to yield a thickness of 70–90 nm.

The stamp is then pressed against the polymer film under elevated temperature in order to break the polymer film [Fig. 1(b)]. A broad range of temperatures (50–150°C) and pressure (50–400 psi) settings have been used in our experiments. The pressure and temperature is maintained for 2–6 minutes before the system is cooled down for separation. For this step, we use a commercial nano-imprinter (Nanonex NX-2000) because it can control both the pressure and temperature. Under pressure, the PDMS layer deforms and a large stress field is concentrated at the stamp edge (discussed later).⁹ As a result, the polymer film breaks at the stamp edges. After the system cools down to 50°C, the pressure is released and the stamp is separated from the substrate. Upon separation, polymer film in contact with the raised regions of the silicon stamp is transferred onto the stamp and a complementary pattern is left on the PDMS side.

It is possible to use either of the patterned layers (on the stamp or on the PDMS/Si substrate) for further transfer printing. In this work, the pattern left on the PDMS is used because the soft PDMS allows a conformal contact to be more easily realized between the patterned polymer layer and the device substrate [Fig. 1(c)], if any non-idealities (non-planar substrate, particles, *etc.*) are present.

Next, by a similar press and separate step, the patterned polymer film is transferred from the PDMS onto a device plate [Figs. 1(c) and 1(d)]. For simplicity, silicon or glass is used as the device plate for printing demonstration, while ITO-coated glass is used for electrical property testing. In all three cases, the surface is oxygen plasma treated to achieve a higher surface energy, and thus a more successful transfer of the polymer layers. The oxygen plasma treatment of the ITO surface also lowers the barrier for hole injection and improves OLED efficiency.¹¹ In our work, the same temperature and pressure conditions are used for the two transfer-printing steps for simplicity [Figs. 1(b) and 1(d)]. Finally, for full-color OLED-display patterning, we only need to repeat the previous steps twice so that three

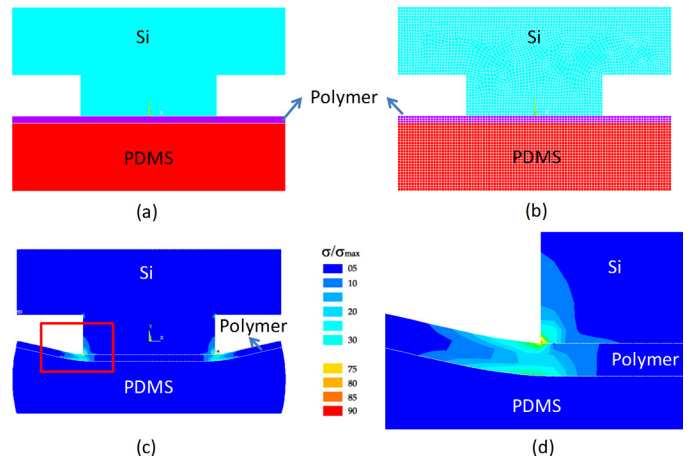


FIGURE 2 — Finite-element analysis. (a) Model geometry, (b) finite-element mesh plot, (c) von Mises stress distribution, (d) a magnification of (c) showing the region marked with the square, where large stresses are localized.

(red-, green-, and blue-emitting) polymer blends are created [Figs. 1(e)–1(g)].

Finite-element analysis of a silicon stamp pressing onto a polymer-coated PDMS layer is performed by ANSYS. All layers are modeled as linear, isotropic, and elastic materials. The Young’s modulus and Poisson’s ratio used for our simulation are silicon (181 GPa, 0.3), polymer (PMMA as an example, 900 MPa, 0.499), and PDMS (3 MPa, 0.48).^{9,12} The simulation results are shown in Fig. 2. The sample geometry used is shown in Fig. 2(a), where the polymer layer is 100 nm thick, and the PDMS is 500 nm thick, the silicon protrusion is 300 nm in depth and 1 μm in width. The bottom edge of the PDMS is fixed to have no displacement. A normal pressure of 0.15 MPa is applied to the top edge of the silicon stamp. The mesh plot used for the simulation is shown in Fig. 2(b). The calculated deformed shape with the von Mises stress distribution is shown in Fig. 2(c). Clearly, the distribution of stresses is not uniform within the polymer layer, with large stresses localized along the edges of the silicon-stamp protrusions. Figure 2(d) shows a magnification of the region with localized stresses.

A similar two-step method has been demonstrated to pattern passive polymer, such as polymethyl methacrylate (PMMA) and polyvinyl acetate (PVAc).⁹ However, in their work, the electrical properties of the transferred layers were not measured and no sequential printing of different layers onto a single substrate was demonstrated.

3 Printing results

The transfer-printing technique is first demonstrated to print a single-color array, as shown in Fig. 3. The polymer layer to be patterned is the green-light-emitting blend PVK + PBD + C6 of about 75 nm in thickness, which is put down on the PDMS surface by spin-coating. Micrographs shown in Figs. 3(a) and Fig. 3(b) were taken after the first transfer-printing step, with Fig. 3(a) taken on the stamp side (corresponding to label I in Fig. 1) and Fig. 3(b) on the PDMS side

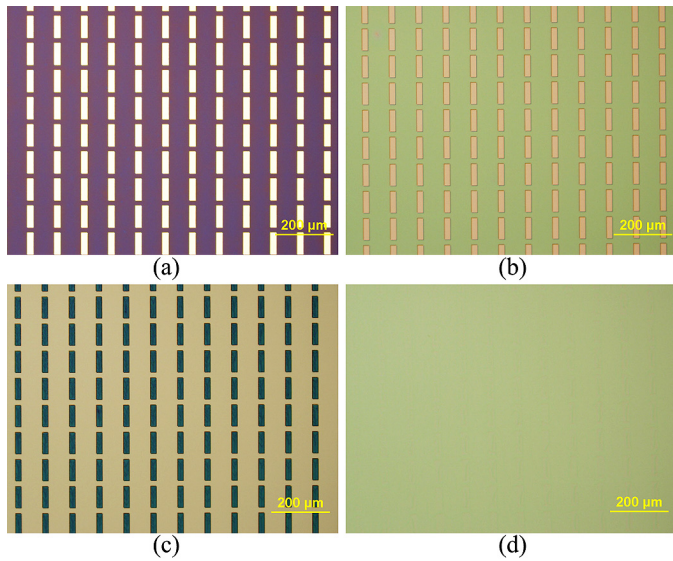


FIGURE 3 — Optical micrographs of polymer patterns at different steps. (a) Polymer pattern on stamp side (labeled I in Fig. 1). Rectangularly shaped areas are exposed silicon and the rest is polymer, (b) polymer pattern ($24 \times 80 \mu\text{m}$) on the PDMS side (II), (c) polymer pattern printed onto a device plate (III), (d) residue-free PDMS/Si plate after transfer (IV).

(label II in Fig. 1). In Fig. 3(a), the rectangularly shaped areas are the wells on the silicon stamp, which did not pick up polymer. The rest is coated with the polymer film that was picked up by the stamp. In Fig. 3(b), the small rectangles, with a size of $24 \times 80 \mu\text{m}$, are the polymer film, and the background is the PDMS substrate. Figure 3(c) is a micrograph of the polymer arrays after they have been transfer printed onto a device plate (silicon wafer used as a demo) (label III in Fig. 1). After the second transfer step, the PDMS/Si substrate is free of polymer films, as shown in Fig. 3(d) (label IV in Fig. 1).

The transfer-printing conditions used for the images shown in Fig. 3 are 110°C and 400 psi while a broad pressure (50–400 psi) and temperature ($50\text{--}150^\circ\text{C}$) range are able to achieve good pattern transfer qualities for the materials used in this study.

Figure 4 demonstrates the ability of the transfer-printing method to pattern active organic layers required for full-color display by repeating the transfer-printing steps with multilevel registration. Figure 4(a) is an optical micrograph

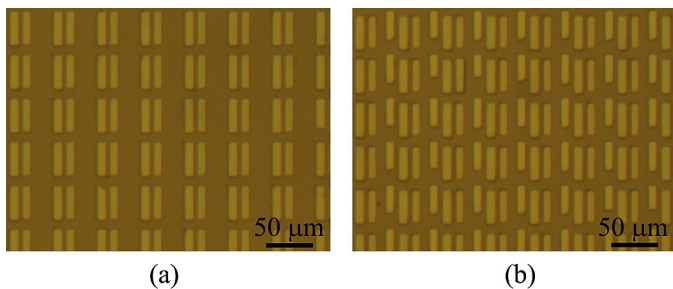


FIGURE 4 — Optical micrographs of printed polymer patterns. (a) After the green- and red-color subpixel arrays have been deposited. (b) After the green, red, and blue subpixel arrays have been deposited. The display resolution is 530 ppi.

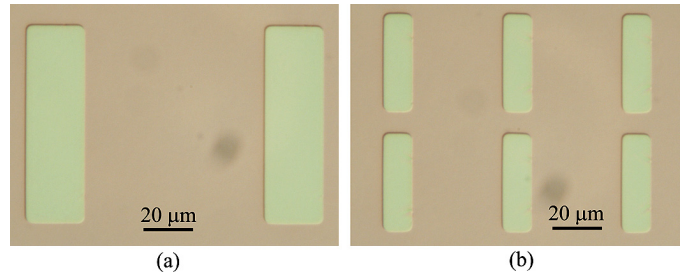


FIGURE 5 — Two optical micrographs of the printed polymer pattern at high magnification with feature sizes of (a) $24 \times 80 \mu\text{m}$ and (b) $12 \times 40 \mu\text{m}$. The edges of the printed polymer films are sharp and well-defined.

after the green and red (PVK + PBD + Nile red) light-emitting subpixel arrays have been deposited by the transfer-printing method. Figure 4(b) is an image after the green, red, and blue (PVK + PBD + C47) subpixel arrays have been transferred. The misalignment of the third layer was caused by poor manual alignment of the plates due to an equipment limitation. The dimension of the subpixels shown here is $12 \times 40 \mu\text{m}$, and the RGB combined pixel has a pitch of $48 \times 48 \mu\text{m}$ or a display resolution of 530 ppi. These results show that the method could be used to fabricate displays with a very high resolution. Results are similar for printing onto silicon (Fig. 3), glass (Fig. 4), or ITO-coated glass (used for our device performance test).

Figure 5 shows two high-magnification optical micrographs of the printed polymer pattern after the printing conditions have been optimized. The green-light-emitting blend films are patterned with two dimensions: $24 \times 80 \mu\text{m}$ [Fig. 5(a)] and $12 \times 40 \mu\text{m}$ [Fig. 5(b)]. As can be seen from Fig. 5, the edges of the patterned polymer films are very sharp, suggesting that it is possible to go with smaller feature sizes.

Figure 6 is a typical surface profile scan of a 75-nm transfer-printed polymer film. The rms roughness is calculated to be $\sim 1.2 \text{ nm}$ from multiple measurements. This thickness uniformity is critical for a uniform light emission. In contrast, solution-based printing techniques usually give

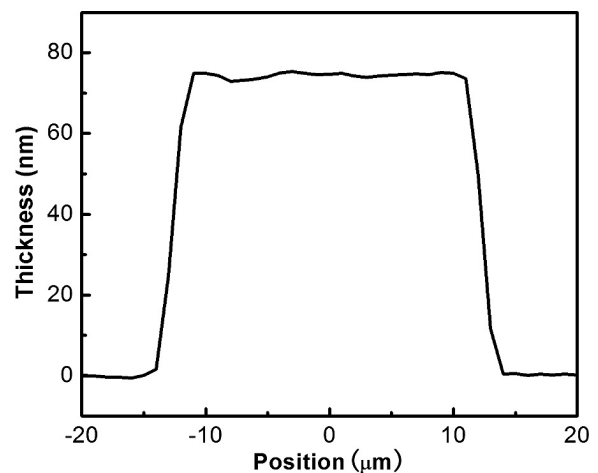


FIGURE 6 — Surface profile scan of a typical transfer-printed polymer film. The root-mean-square roughness is calculated to be $\sim 1.2 \text{ nm}$ from multiple measurements.

non-uniform layers which require further process steps for improved planarity.²⁻⁴

4 Device performance

Because active materials are patterned in this work, it is essential to study the electronic properties of the organic layers after processing and the interface between the printed material and the underlying layers. Several outcomes are possible as a result of the transfer-printing process. For example, the printed layer may not form intimate contact with the ITO target substrate, and thus may prevent hole injection into the polymer layers. Also, the polymer layers may degrade during the thermal and pressure cycles.

We have fabricated OLED devices where the green-light-emitting polymer-blend film was transfer printed onto an ITO-coated glass substrate followed by thermal evaporation of Mg:Ag (10:1) as the cathode. Control devices with the same structure are made with the light-emitting layers deposited by spin-coating. Figure 7 shows I - V curves and light emission-voltage curves from printed devices (closed symbols) and spin-coated control devices (open symbols). The printing condition used is 50°C and 50 psi. Both the I - V curves and the light emission from the two devices almost overlap with each other, meaning the devices printed under 50°C and 50 psi have similar performance compared to spin-coated controls. The results indicate that the interface between the printed layer and the ITO bottom electrode is of good quality. In addition, the printed layer itself must have retained its original electronic and optical properties after the transfer-printing process.

Because a broad range of temperature and pressure are used in our printing experiments, it is also worthwhile to study the effects of the printing condition on device performance. Figure 8 shows the external quantum efficiencies of devices prepared under a printing pressure range of

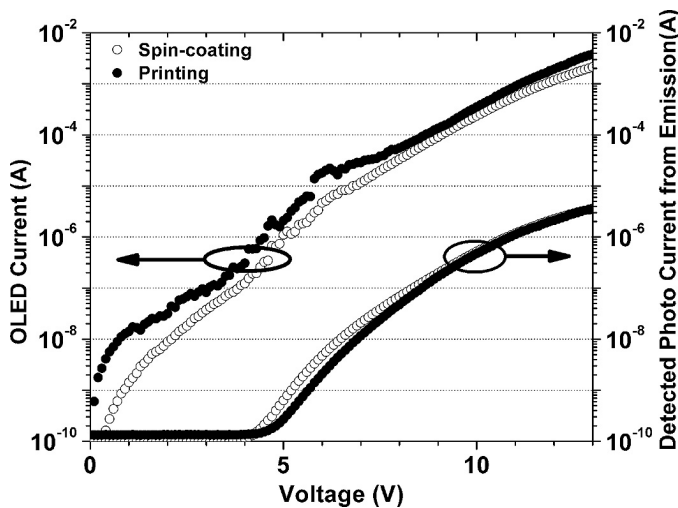


FIGURE 7 — Comparison of the I - V curves of OLEDs with polymer film deposited by transfer printing and spin-coating. The device area is 0.01 cm². Printing condition is 50 psi at 50°C.

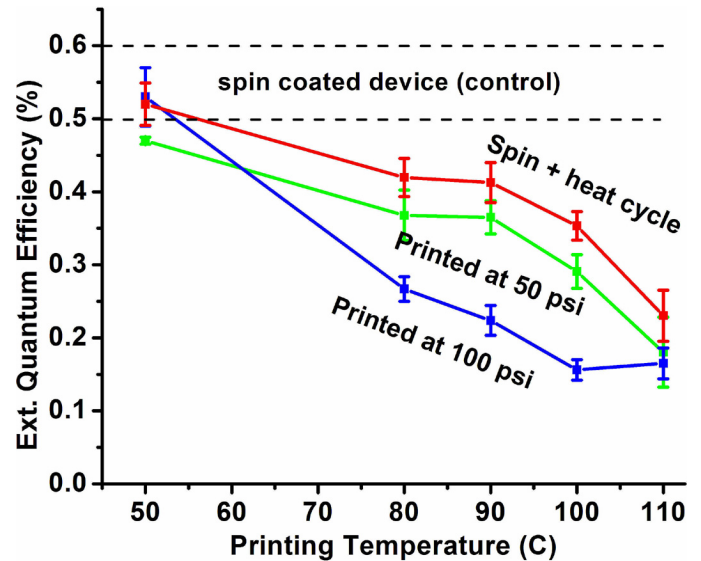


FIGURE 8 — Effect of printing pressure and temperature on device performance. Devices labeled with “spin + heat cycle” were prepared by spin-coating that had undergone the same thermal cycle as the printed devices.

50–100 psi and temperature range of 50–110°C. The spin-coated control devices have external quantum efficiencies in the range of about 0.5–0.6%, which are marked in the graph by the two dashed lines. Devices prepared at 50°C have identical performance compared to spin-coated control devices. However, higher temperature and higher pressure during the printing steps are harmful to device performance. Another set of devices were fabricated, which are labeled as “spin + heat cycle” in Fig. 8. In these devices, the ITO-coated glass substrates were spin-coated with the polymer layers and were inserted into the nano-imprinter to undergo the same thermal cycle as the printed polymer layer, except that no pressure was applied on the spin-coated layer. After the thermal cycle, the same Mg:Ag cathode was evaporated and the devices were tested. As shown in Fig. 8, these devices share a similar dependence of the device performance on temperature to the printed devices. Thus, we believe that thermal degradation is probably the most important factor that affects the device performance during the transfer-printing process.

5 Summary

In summary, a transfer-printing method to pattern active polymer layers used for OLED application is demonstrated. Red/green/blue light-emitting subpixel arrays have been patterned by this method by three successive steps with a three-color pixel resolution of 530 ppi. Films deposited by this method are uniform in thickness. OLEDs with a printed polymer layer show similar performance compared to spin-coated control devices. Due to the fact that the printing is a parallel process with high throughput, the transfer-printing technique may have a low-cost potential.

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