

Micropatterning metal electrode of organic light emitting devices using rapid polydimethylsiloxane lift-off

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The authors demonstrate a subtractive stamping technique for patterning metal electrodes of organic light emitting devices. Patterning is achieved by placing a relief patterned polydimethylsiloxane stamp in contact with a planar metal electrode film and subsequently peeling off the stamp. A fast peel rate increases the weak adhesion energy of the stamp to the metal so that no surface treatment, pressure, or temperature control is necessary to lift-off the metal film in contact with the stamp. Patterning is dependent on metal film thickness, geometry of the features, and peel direction of stamp release. The minimum feature size patterned is 13 μm wide stripes within $<1 \mu\text{m}$ in-plane edge roughness and 0.1 μm height transition region of the patterned edge. © 2007 American Institute of Physics. [DOI: 10.1063/1.2759466]

Fabrication of high resolution arrays of organic electronic devices, in particular, organic light emitting devices (OLEDs), would benefit from the ability to pattern micron sized features of top array electrodes. Presently, the dominant commercial technique for patterning top electrodes is a low-pressure physical deposition of metal vapor through a shadow-mask stencil, a technique which is, unfortunately, limited in resolution and scalability. The thickness of the stencil and the control of the stencil proximity to the substrate set the pattern quality, where for the highest resolution thin shadow masks are needed, but these are susceptible to warping and distortion under their own weight, limiting the ability to scale shadow-mask processing to large array areas. Although it is possible to implement a scalable shifting shadow mask to pattern minimum feature sizes of 30 μm , as needed for a subpixel in a high resolution display, it is not without added complexity and cost.^{1,2} In addition, rigid masks are hard to adapt to patterning of curved substrate, as might be needed for roll-to-roll fabrication of structures on flexible substrates. Some alternative techniques for patterning the top electrode of OLEDs include pixel patterning through laser ablation,³ electrode lift-off,⁴ integrated shadow mask,⁵ and epoxy mold release.⁶ Each of these methods exhibits some shortcomings: the serial process of laser ablation is not readily scalable to large areas, electrode lift-off requires a wet etch that is potentially damaging to the organic layers, the integrated shadow mask relies on a geometry primarily used for patterning passive matrix displays, and epoxy mold release requires temperature and pressure control.

It has consequently been suggested that for a scalable electrode patterning solution one can use contact-stamping techniques where a relief stamp patterns the electrode on the raised features of the stamp.⁷ For example, in one proven contact-stamping method, cold-welding mechanism was used to promote adhesion of an unpatterned silver film to the rigid silver-coated silicon relief stamps under high contact pressures (290 MPa). The high pressure was required for fracturing the metal film at the pattern edges and for obtain-

ing intimate contact of a rigid stamp to the electrode surface in the presence of impurities.⁷ To reduce required pressures (to 190 MPa) and to eliminate the need to fracture the metal electrode during patterning, an additive stamping method was also demonstrated with a rigid gold-coated stamp and applied to patterning organic field effect transistors (OFETs).⁸ Improvement on this technique used a flexible stamp made of polydimethylsiloxane (PDMS), a two-part silicone elastomer with a low Young modulus, to dramatically lower the pressure required to make conformal contact with the electrode (to 180 kPa).⁹ Finally, additive transfer of OFET electrodes relying on temperature controlled adhesion has been demonstrated but without the release layer for the relief PDMS stamp because of the poor adhesion of the metal to the PDMS.¹⁰

Simplifying further the earlier contact-stamping techniques, the present work demonstrates subtractive contact stamping for patterning OLED electrodes using a relief PDMS stamp and, in contrast to earlier studies, requiring no applied pressure, temperature control, or stamp surface modification.¹¹ The patterning is enabled by the kinetically controlled adhesion of the PDMS relief stamp to the surface to be patterned. For example, patterning of a planar metal film coating a substrate is accomplished by forming a mechanical contact with the PDMS relief stamp, where the strength of the PDMS/metal film bond is controlled by the rate of peel of PDMS away from the substrate. When PDMS stamp is rapidly separated from the substrate, the energy release rate of PDMS can increase by an order of magnitude, ensuring strong PDMS/metal adhesion, and portion of the metal film in contact with PDMS will be pulled away from the substrate forming a pattern. It has already been demonstrated that the adhesion to the stamp can be sufficiently strong to enable removal of planar structures that are even ionically bonded to the donor substrate.¹² A subtractive patterning technique which relies on the same adhesion mechanism has been recently developed for patterning organic layers of an OFET.¹³

Our subtractive electrode stamping technique is applied

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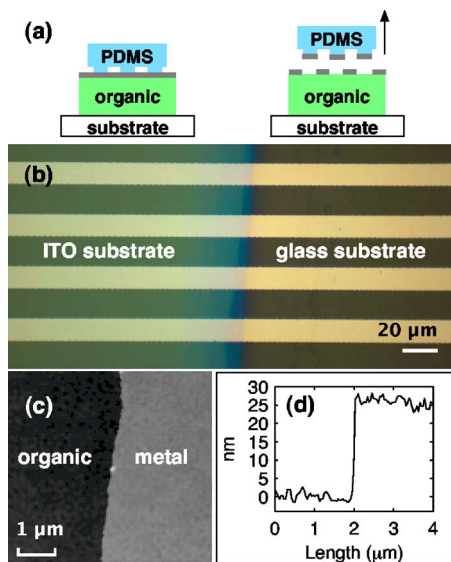


FIG. 1. (Color online) Schematic depiction of PDMS lift-off technique for patterning metal electrodes in organic devices. Metal layer deposited on top of organic substrate is detached from the substrate surface when (a) patterned PDMS relief stamp makes conformal contact with the surface and is followed with a rapid peel off. (b) 13 μm wide lines of patterned 20 nm thick Mg:Ag on top of 50 nm thick Tris-(8-hydroxyquinoline)aluminum (Alq_3)/50 nm thick *N,N'*-Bis(3-methylphenyl)*N,N'*-bis(phenyl)-benzidine (TPD)/poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS)/ITO/glass on left and on top of glass substrate on right (c) atomic force microscope (AFM) image of a sample similar to that in (b) with a corresponding AFM cross section shown in (d).

in ambient conditions to patterning a metal electrode in an OLED stack (Fig. 1). We first form the PDMS stamp by mixing a 1:10 weight ratio of PDMS (Dow Corning Sylgard® 184 silicone elastomer) curing agent to base. This mixture is then poured into a petri dish containing the silicon masters with a relief pattern of 2 μm depth, placed under low vacuum until no bubbles are observed escaping out of the viscous PDMS mixture, and baked at 60 $^\circ\text{C}$ for at least 5 h. The cured stamp is then released from the petri dish and silicon masters and sectioned into 1 cm^3 cubes. For peel direction experiments, the stamp thickness was reduced to 0.2 cm. The PDMS relief stamp is then placed in a mechanical contact with the metal electrode of the OLED thin film stack, with the raised features of the stamp establishing a conformal contact with the metal electrode, without any applied pressure. The conformal contact occurs even on surfaces that are not flat, such as a glass/indium tin oxide (ITO) step.

With a slow peel rate of the PDMS stamp away from the substrate (~ 10 mm/s), the metal film remains intact and is not lifted off, which is consistent with static interfacial adhesion analysis, since the static PDMS-metal work of adhesion ($W_{\text{PDMS,Mg:Ag}} = 16\text{--}18$ mJ/m^2) is smaller than metal-organic ($W_{\text{Mg:Ag,Alq}_3} = 65\text{--}96$ mJ/m^2), organic-organic ($W_{\text{Alq}_3,\text{TPD}} = 43\text{--}54$ mJ/m^2), or organic-substrate work of adhesion ($W_{\text{TPD,ITO}} = 36\text{--}42$ mJ/m^2).¹¹ However, with a rapid peel rate of the PDMS stamp away from the substrate (≥ 10 mm/s), the adhesion between the PDMS and metal interface increases due to the kinetic increase in the adhesion strength, and is able to overcome adhesion between the metal or organic interfaces, allowing lift-off of the metal film from the substrate. Besides our work,¹¹ the same adhesion analysis

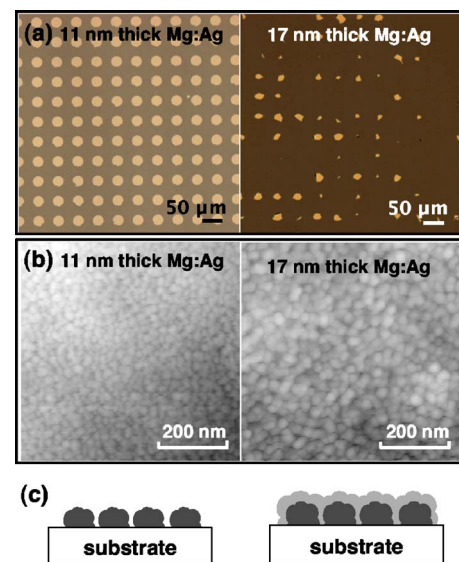


FIG. 2. (Color online) (a) Optical micrograph of 25 μm diameter circles patterned from Mg:Ag on top of 50 nm thick Alq_3 /40 nm thick *N,N'*-Bis(3-methylphenyl)-*N,N'*-bis(phenyl)-9,9-spirobifluorene/PEDOT:PSS/glass with metal thickness indicated in the figure. For a given pattern, increasing metal film thickness results in lift-off but not patterning of the metal film. (b) Corresponding AFM images of metal electrode surface indicate larger grain size for thicker film. (c) Cartoon depiction of the difficulty in patterning thicker films due to the increased grain size and continuous nature of the film.

has recently been applied to quantifying pattern formation in pentacene OFET films.¹³ Note that our work of adhesion calculation is based on contact angle measurements¹⁴ using ethylene glycol and water on various surfaces. Maximum and minimum contact angles were used in the work of adhesion calculation, resulting in the above stated range of values.

To generate a pattern with this subtractive contact-stamp patterning method, metal film fracture must occur at the edges of the stamp relief features, similar to the cold-welding process.⁷ Externally applied pressure across the PDMS stamp is ineffective in forming the metal layer fracture, as it simply leads to the distortion of the flexible stamp. Consequently, in our demonstrations we use thin layers of metal which are easy to fracture in a lift-off process because of reduced cross sectional area of the film, less continuity in the film, and smaller grain sizes of the metal that constitutes the film. We find that the ability to pattern a metal film is also dependent on the geometry of the pattern. As an example in Fig. 2, we show good pattern transfer in metal films with layer thickness of 11 nm for 25 μm diameter circle pattern. Increasing metal film thickness leads to complete metal electrode removal instead of patterned removal of the film during the PDMS lift-off process (Fig. 2). We find that in transfer of line patterns, better quality image transfer occurs when the peel direction of separating the PDMS stamp away from the substrate is aligned with the relief line pattern. Peeling along the line pattern direction assists propagation of the metal film fracture. In contrast, peeling in the direction perpendicular to the relief stamp line pattern leads to poor pattern definition, since the breakage and release of the metal film must repeatedly occur in a discontinuous fashion. Examples of the peel-dependent pattern transfer quality are shown in Fig. 3. We note that the metal films become increasingly difficult to lift-off as the film thickness is decreased below 10 nm.

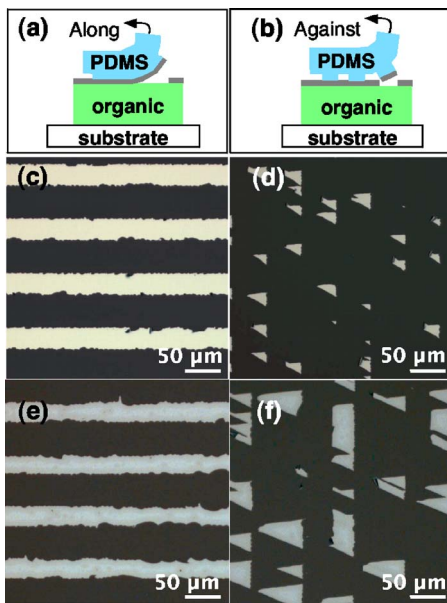


FIG. 3. (Color online) Peel direction along (a) or perpendicularly against (b) line pattern of the relief stamp affects patterning lift-off of 20 nm thick Ag [(c) and (d)] or 12.5 nm thick Mg:Ag [(e) and (f)] film on top of 50 nm thick Alq₃/50 nm thick TPD/ITO/glass. Optical micrographs show that peel along [(c) and (e)] the line pattern results in patterning of 30 μm wide lines with edge roughness of up to ±5 μm, while peel against [(d) and (f)] the line pattern does not result in good pattern transfer.

Using the PDMS lift-off process, we patterned the top electrode of an OLED and compared the operating characteristics to an OLED whose top electrode is patterned by shadow masking. The two devices are grown on the same 1 × 1 in.² substrate using shadow-mask patterning on half of the substrate. After device growth, half of the substrate is patterned using PDMS lift-off technique. Figure 4 shows nearly identical current density versus voltage and electroluminescence quantum efficiency characteristics for the two devices, indicating equivalent quality of the PDMS lift-off and shadow-masked structures.

In summary, we demonstrated a simple and scalable method for patterning thin Mg:Ag or Ag electrodes using a PDMS stamp and no externally applied pressure or chemical surface treatment. Unlike previous demonstrations of subtractive patterning of electrodes, this technique does not rely on cold welding or pressure-induced electrode fracture. We applied the relief stamp peel-off method in patterning OLED electrodes, demonstrating equivalent performance to the OLEDs patterned by shadow masking.

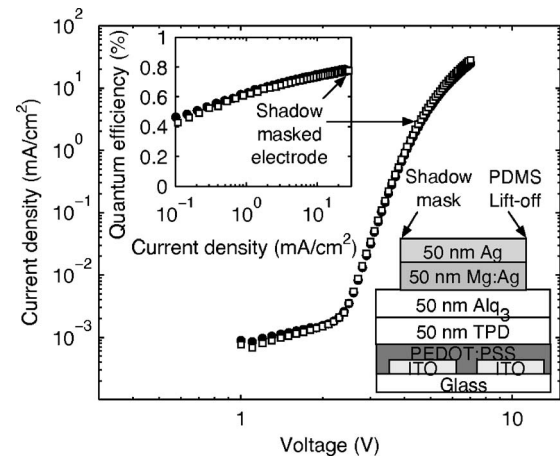


FIG. 4. Current density vs voltage characteristics of a 2.81 mm² area organic light emitting device (OLED) patterned by PDMS lift-off. The completed device consists of 50 nm thick Mg:Ag/50 nm thick Ag on top of 50 nm thick Alq₃/50 nm thick TPD/PEDOT:PSS/ITO/glass. Also shown are current density vs voltage characteristics of a 4.34 mm² area OLED patterned by conventional shadow-mask method. (Inset) External electroluminescence quantum efficiency vs current density for the same devices. Device structure is shown on the bottom right.

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