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Patterning Indium Tin Oxide and Indium Zinc Oxide Using Microcontact Printing and Wet Etching

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We report a procedure that uses microcontact printing and wet chemical etching to fabricate patterned films of indium tin oxide (ITO) and indium zinc oxide (IZO). The procedure consists of three steps: (1) inking a patterned elastomeric stamp with an alkanephosphonic acid; (2) microcontact printing to form a patterned multilayer film of alkanephosphonic acid on the surface of an ITO or IZO film; (3) etching the unprotected regions of the ITO or IZO film using 0.05 M oxalic acid as the etchant. We demonstrate this procedure by fabricating patterned ITO and IZO films with areas as large as 15 cm² and minimum feature sizes of ~2 μm. The key step in this procedure is applying the alkanephosphonic acid ink to the surface of the stamp. We present two different inking methods to illustrate the impact of stamp inking on the quality of printed and etched ITO and IZO films.

Introduction

The microelectronics industry relies on photolithography as an all-purpose patterning method: it is used to fabricate submicrometer as well as micrometer-scale features. Although applications with submicrometer features require the high-resolution capabilities of photolithography and must tolerate the associated high cost, applications with micrometer-scale features would profit from alternative, low-cost patterning methods geared to micrometer-scale fabrication. Display fabrication is perhaps the most attractive of these applications, as falling liquid crystal display (LCD) prices drive industry demand for low-cost manufacturing methods. Others are using photolithography in innovative display fabrication approaches, such as fluidic self-assembly,^{1,2} to reduce manufacturing costs. Another approach is to replace photolithography with low-cost printing techniques, such as microcontact printing³ or inkjet printing.⁴ Here, we describe the use of microcontact printing and wet etching to pattern films of the transparent conductors indium tin oxide (ITO) and indium zinc oxide (IZO). These materials are essential to display technologies as pixel electrodes in devices such as LCDs, organic light-emitting diodes (OLEDs), and touch screens. This patterning method is a convenient, low-cost route to patterned transparent conducting oxide films, useful for the fabrication of devices in displays and in other technologies that use transparent conductors and do not require submicrometer-scale patterning. We demonstrate its usefulness by fabricating patterned ITO and IZO films with areas as large as 15 cm² and minimum feature sizes of ~2 μm.

Research on microcontact printing and wet etching has focused mainly on patterning coinage metal films (gold, silver, copper)^{5–7} using a printed thiol self-assembled

monolayer (SAM) as an etch resist. These are useful research models, but thiols have a low affinity for materials commonly used in the microelectronics industry, many of which have surfaces comprised of metal oxides with surface hydroxyl groups available for anchoring a SAM. There are only a few examples of printing etch-resistant organics on such surfaces: Printed organosilane SAMs have been used as etch resists to pattern Si/SiO₂, Al/Al₂O₃, and Ti/TiO₂,^{8,9} and alkanephosphonic acids have been used similarly to pattern Al/Al₂O₃.¹⁰ There are no reports to date of patterning ITO or IZO using microcontact printing and etching, although several materials form SAMs on ITO.^{11–24} Marks et al.²⁵ described “hot microcontact

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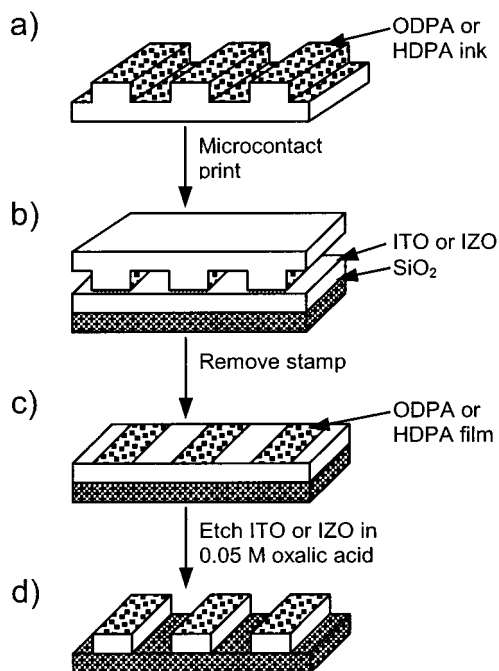


Figure 1. Schematic outline of the procedure to fabricate patterned films of ITO or IZO.

printing" to form patterned organosilane SAMs on ITO that modulate the luminescence of OLEDs. In this study, transfer of the organosilane "ink" from the stamp to the ITO surface required using rigorously anaerobic conditions and heating the substrate during stamping.

Selecting a chemical "ink" for its ease of use as well as for its performance as an etch resist is the first step to a microcontact printing and etching patterning method. First, the ink must be compatible with printing. The solvent used to dissolve the ink must not swell or distort the stamp. The ink itself should not react with the stamp surface, it must be convenient to apply to the stamp, and it must transfer effectively to the ITO or IZO surface. Second, the ink must perform well as an etch resist, which requires the ink to form a uniform coating on the ITO or IZO surface with minimal defects. Among the materials known to form SAMs on ITO—phosphonic acids,^{11,12} carboxylic acids,^{13–17} thiols,^{18,19} amines,²⁰ and silanes^{21–24}—phosphonic acids fulfill all of these requirements. They chemisorb to the ITO surface,¹¹ they are air-stable, commercially available, soluble in alcohols, and compatible with the stamp surface, and they have demonstrated their use as microcontact-printed etch resists.¹⁰ Carboxylic acids, thiols, and amines do not bind as strongly to oxide surfaces. Silanes are hydrolytically unstable and require handling in an inert atmosphere to prevent cross-linking on the surface of the stamp.

Figure 1 shows the steps for patterning ITO and IZO films: (a) inking an elastomeric stamp with either hexadecylphosphonic acid (HDPH) or octadecylphosphonic acid (ODPH); (b, c) microcontact printing to transfer a film of the alkanephosphonic acid to the ITO or IZO surface; (d) removing the unprotected areas of the ITO or IZO film with a wet etchant. The resistance of the printed alkanephosphonic acid film to the wet etchant is dictated by its uniformity and thickness; these properties are in turn dependent on the conditions used to apply the ODPH or HDPH ink to the stamp. Herein, we present two approaches for stamp inking and examine their impact on etch resistance.

Experimental Section

Materials. Octadecylphosphonic acid (ODPH) (Lancaster Synthesis, Inc., Windham, NH), hexadecylphosphonic acid (HDPH) (Oryza Laboratories, Inc., Chelmsford, MA), 2-propanol (Mallinckrodt Baker Inc., Phillipsburg, NJ), absolute ethanol (Aaper Alcohol and Chemical Co., Shelbyville, KY), oxalic acid (Aldrich, Milwaukee, WI), and poly(dimethylsiloxane) Sylgard 184 (PDMS) (Dow Corning Corp., Midland, MI) were used as received.

Substrate Preparation. Silicon wafers and glass substrates were cleaned for 10 min in Piranha solution (a 7:3 (v/v) mixture of 98% H_2SO_4 and 30% H_2O_2), followed by rinsing in deionized water and drying on a 120 °C hotplate. *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.* ITO and IZO films, with thicknesses ~ 500 Å, were deposited on the cleaned substrates using a conventional in-line sputter tool with alloy targets. Before microcontact printing, the ITO or IZO films were cleaned by UV ozone treatment (Jelight Inc. UVO cleaner, model 144) for 30 min.

Stamp Preparation. Stamps were fabricated using a photolithographically defined master, according to published literature procedures.⁸

Stamp Inking and Printing. A 5 mM solution of ODPH or HDPH in 2-propanol was filtered through a 0.2- μm PTFE Acrodisc syringe filter. PDMS stamps were inked in either of two ways: In the flooding method, the stamp surface was flooded with ink solution and left for 30 s. A stream of nitrogen was used to first blow off excess solution and then to thoroughly dry the stamp for 30 s, leaving a film of neat alkanephosphonic acid. In the spraying method, 0.25 mL (for 2 cm^2 stamps) or 5.0 mL (for 15 cm^2 stamps) of ink solution was loaded into an Olympos airbrush connected to a nitrogen line at 5 psi. The solution was sprayed onto the stamp surface with the airbrush set to the finest spray setting. The 2-propanol evaporated from the stamp surface as the ink was sprayed, leaving a film of neat alkanephosphonic acid. Inked stamps were placed on the surface of ITO or IZO films using tweezers, left for 1 min, and then removed.

Wet Etching. The printed samples were etched in an aqueous oxalic acid solution (0.05 M), with mild agitation. The end point was determined using a multimeter to test if the unstamped region of the surface was electrically conductive. A conductive surface indicates the presence of a layer of ITO or IZO, since the underlying substrate is an insulator. Typical etching times were ~ 5 min. for 500 Å films.

Characterization. Water contact angles were measured using the sessile drop method on an AST VCA-Optima 2500XE surface analysis system. Three readings from at least two samples were averaged. Optical inspection was performed using a Leitz Ergolux microscope. Scanning electron microscopy (SEM) images were obtained using a Hitachi S800 scanning electron microscope or a LEO 1560 digital scanning microscope.

Results and Discussion

Inking the Stamp. Using alkanephosphonic acids in microcontact printing differs from using thiols: alkanephosphonic acids form a film on the surface of the stamp rather than absorbing into the stamp as thiols do. With thiols, the stamp acts as an ink reservoir and a single inking may generate multiple prints; with phosphonic acids, the film of ink on the surface of the stamp transfers to the substrate and the stamp requires reinking between each print. Thiols can be applied to the stamp in a number of ways—flooding, immersing, spraying, or using an inked stamp pad—without variation in the printed pattern. The inking method with alkanephosphonic acids, however, determines the uniformity of the ink film on the stamp and, ultimately, the etch resistance of the printed film.

We used both flooding and spraying methods to ink 2- cm^2 PDMS stamps bearing an arbitrary pattern with features ranging from 200 to 2 μm . For larger stamps (15 cm^2), only the spray method of inking was used; flood inking usually resulted in large (millimeter scale) streaks of ink on the surface. Figure 2a shows an optical

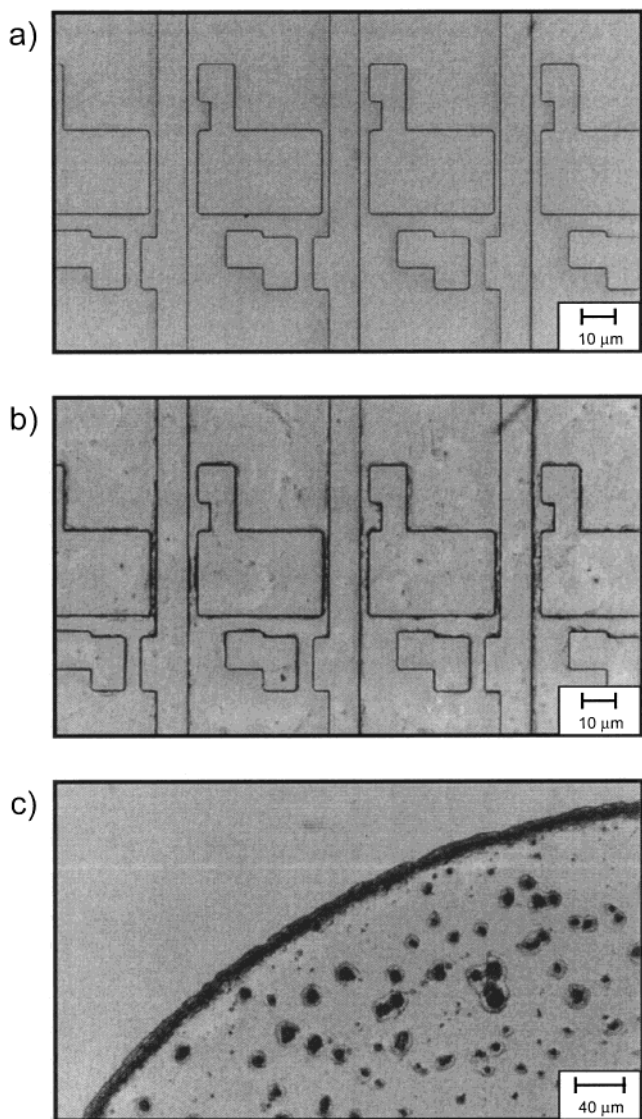


Figure 2. Optical micrographs of dried 5 mM hexadecylphosphonic acid ink: (a) the surface of a PDMS stamp inked by flooding; (b) the surface of a PDMS stamp inked by spraying with an airbrush; (c) 2- μ L drop of HDP A solution dried on the surface of a flat PDMS slab.

micrograph of a 2-cm² stamp inked by the flooding method. The surface of the stamp shows a barely visible, uniform film of HDP A ink. Figure 2b shows an optical micrograph of a stamp inked by the spraying method. The film on the surface of the stamp is composed of visible, overlapping drops of HDP A ink. The drops do not merge to form a uniform film of ink, regardless of solvent used (methanol, ethanol, or 2-propanol) or alkanephosphonic acid concentration. Varying the spraying conditions, for example with an ultrasonic sprayer²⁶ to achieve a soft, low-velocity spray, resulted in similar films. To better understand the formation of these films, we used an optical microscope to observe individual ink drops as they dried on flat slabs of PDMS. As the ink drop dries, irregularities of the surface cause pinning of the contact line; solvent evaporating from the edge is replenished by liquid from the interior and most of the HDP A ink deposits at the edge.²⁷ Figure 2c shows an optical micrograph of part of a dried 2- μ L drop of 5 mM HDP A on PDMS. The dark line is HDP A deposited

(26) Sono-Tek ultrasonic spray nozzle model 8700-60, operating at 60 kHz (Sono-Tek Corp., Milton, NY).

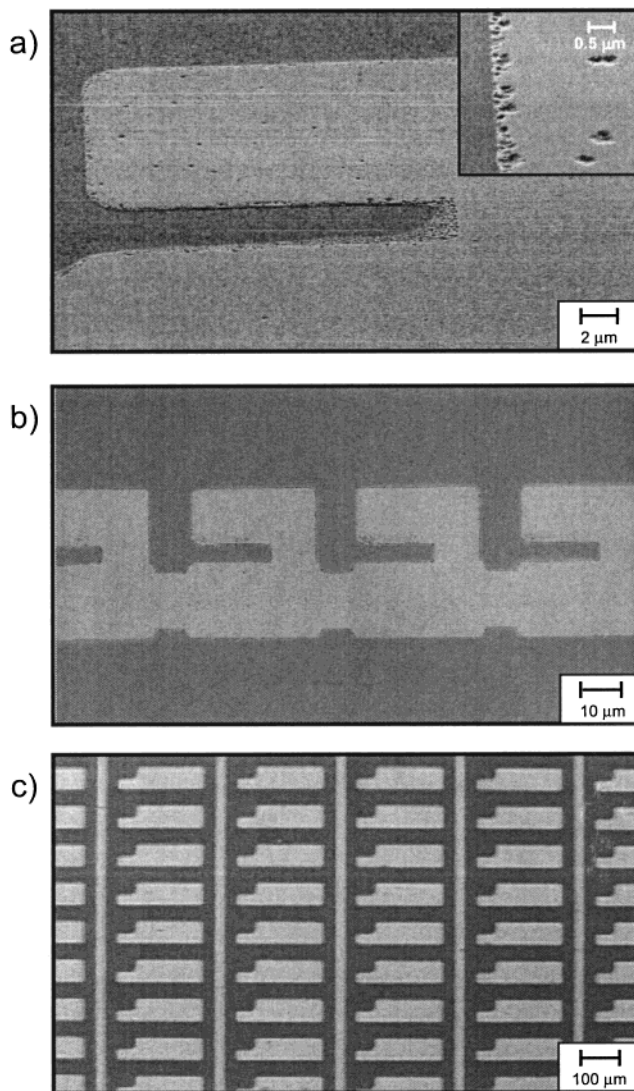


Figure 3. (a) SEM image of an IZO film patterned by printing ODPA and etching in 0.05 M oxalic acid. (b) SEM image of ODPA printed on an IZO film. Light regions are the ODPA film; dark regions are underivatized IZO. (c) Optical image of a portion of a patterned 15-cm² IZO film on a glass substrate, patterned by printing ODPA and etching in 0.05 M oxalic acid.

at the edge of the drop; there are also some small dark spots of HDP A scattered throughout the interior of the drop.

Microcontact Printing. Inked stamps were placed in contact with an ITO or IZO substrate for 1 min. and then removed, leaving behind a visible, multilayered film on the substrate similar to printed ODPA multilayers on Al/Al₂O₃.¹⁰ The multilayer can be removed by rinsing with 2-propanol, after which the patterned film is no longer visible. Alkanephosphonic acid does, however, remain on the surface: the contact angle of water on ODPA films on IZO printed using 2-cm² unpatterned PDMS stamps is 103° before rinsing and decreases only slightly (by ~5°) after rinsing. Nonetheless, we refrained from rinsing the multilayers because the rinsed films provided poor etch protection.

(27) As drops of a solution evaporate on a substrate, the solute tends to deposit along the perimeter if the drops meet the surface at a nonzero contact angle and the contact line is pinned to its initial position. The contact angle of 5 mM HDP A in 2-propanol on a PDMS slab is 15–20°. For an explanation of the formation of ring deposits, see: Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, 389, 827–829.

It is common for monolayers on oxide surfaces to require heating for dehydration, which facilitates bonding to the substrate surface and imparts etch resistance.^{10,28,29} With both ITO and IZO, heating the phosphonic acid films was not necessary and did not affect the etch resistance.

Wet Etching. Wet etching experiments revealed that the etch resistance of printed alkanephosphonic acid films is due to the formation of multilayers that are insoluble, hydrophobic barriers to the aqueous etchant. Poor etch resistance, resulting in visibly thinned ITO and IZO patterns, resulted when too little ink was used in printing or when printed ink films were rinsed with 2-propanol to remove multilayers before etching. Although it is difficult to control the amount of ink applied to the surface of the stamp with flood inking (most of the ink solution is blown off the surface of the stamp), we were able to vary the amount of ink left on the stamp surface by varying the concentration of the ink solution. We found that a minimum concentration of 5 mM was necessary to provide good etch resistance. We also attempted to control the amount of ink applied to the stamp by varying the volume of ink sprayed onto 15-cm² stamps. Spraying less than 5 mL of a 5 mM ODPA solution produced discontinuous ink films on the stamp consisting of partially overlapping, dried ink drops (see Figure 2b). After the stamping process, wet etching produced numerous large ($>2\ \mu\text{m}$) holes in the stamped regions of the ITO or IZO substrate. Increasing the volume of ink sprayed onto the stamp produced ink films printed on ITO or IZO that, although not uniform or smooth, were continuous and thus etch resistant.

With sufficient ink, printed ODPA or HDPA films provided excellent etch resistance. Figure 3a shows an SEM image of an etched IZO film patterned using a 2-cm² stamp flood inked with 5 mM ODPA in 2-propanol. For comparison, Figure 3b shows an SEM image of the printed multilayer before etching. After etching, the printed regions of the IZO surface are smooth, with few "pinhole"

defects. The inset in Figure 3a shows that these defects are circular, with diameters $\sim 300\ \text{nm}$, and that they dominate the edge of the pattern and form a border 100–400 nm wide.

Smaller features, such as the 2- μm -wide indentation in Figure 3a, have regions outside the pattern boundary with numerous defects. We believe that the inking process traps excess ink in these small, recessed crevices on the stamp. Some of this unwanted alkanephosphonic acid then transfers to the surface during stamping and partially protects the substrate during etching. Longer etch times may remove these unwanted areas.

The feature size requirements for ITO and IZO pixel electrodes are substantially relaxed for flat-panel display fabrication, but substrate sizes are generally larger than our 2-cm² test stamps. Figure 3c shows an optical micrograph of a printed and etched 15-cm² IZO film patterned with a pixel electrodes, using a 15-cm² stamp spray-inked with ODPA. With these large features, we obtained good pattern quality over the entire 15-cm² substrate, marred by large ($>2\ \mu\text{m}$) defects we attribute to bubbles or particles trapped between the stamp and the substrate.

Conclusions

We have demonstrated the convenient, low-cost patterning of ITO and IZO films using microcontact printing of alkanephosphonic acids and wet etching, in which etch resistance depends on the thickness and uniformity of printed alkanephosphonic multilayers. This method is effective for the fabrication of patterned ITO and IZO films with large ($>2\ \mu\text{m}$) feature sizes typically used in display fabrication.

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