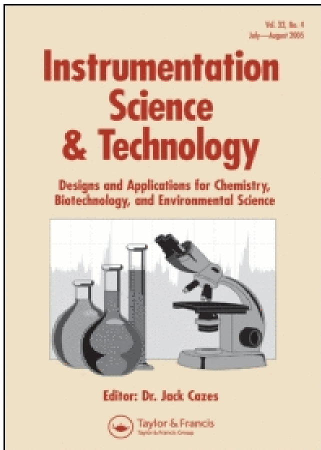

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A Simple Laboratory Method to Pattern Sub-Millimeter Features of Conductive Films of Gold and Indium Tin Oxide

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Abstract: A simple laboratory photolithography method for patterning 100 nm thick gold and indium tin oxide (ITO) films on glass slides with 100 μm resolution without the need of special equipment is described. During the procedure, the conductive films are coated with a commercial screen printing emulsion using a modified drill as spin-coater, then placed in contact with a negative photomask, and exposed to a 20 W light source for 30–60 min. The excess photoresist is washed off with water, and the glass slides are baked at 210°C to produce a mechanically and chemically resistant coating. The substrates are then etched in dilute aqueous HNO_3/HCl (gold) or 6 n HCl (ITO) to remove exposed gold and ITO films. After etching, the photoresist is removed by etching with peroxosulfuric acid (gold) or scraped off with a razor blade (ITO) leaving a conductive pattern. The procedure requires between 3 and 5 h of time, depending on experience.

Keywords: Patterning, Conductive films, Gold, Indium tin oxide, ITO

INTRODUCTION

Conductive films of gold and indium tin oxide (ITO) play a key role in advanced electroanalytical procedures,[1,2] for electrochemical syntheses,[3,4] in photochemical cells,[5] light emitting diodes,[6] and sensors[7] and in other areas of research.[8,9] For many of these applications, there is a need to pattern the films. Apart from microcontact printing[10,11] (which often requires lithographically fabricated masks), photolithography often remains

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the method of choice for patterning. However, photolithography has several drawbacks that make the method unattractive for users outside the electrical engineering field. The disadvantages include high costs of commercial photoresists, the requirement of a clean room facility, and the need to train personnel on the equipment and technique. Here, we present a laboratory version of the photolithography method that avoids these problems. The method allows the reproducible creation of 2D gold and indium tin oxide patterns with features as small as 100 μm. The method is inexpensive, it does not require specialized equipment or specific expertise, and it can be carried out in a standard wet laboratory. With 3–5 h production time for a single pattern, the method is also much faster than standard photolithography.

EXPERIMENTAL

Materials

ITO coated glass slides were purchased from Delta Technologies, Inc. The slides were made of 1.1 mm thick alumosilicate glass that was coated with a 120–160 nm thick layer of ITO and had a resistance of 5–15 Ω/cm. Glass slides (1 mm thickness) coated with a 100 nm layer of gold on a 10 nm layer of titanium were purchased from EMF Corporation. As photoresist, we used a commercial multi-purpose screen printing emulsion (Ulano RLX from Ulano Corporation) which is based on a diazo-acrylic photopolymer. Small batches of the sensitized photoresist emulsion were made in accordance with the manufacturer's guidelines by mixing 30 mL of the emulsion with 88 mg of sensitizer and 1.94 mL of water. The sensitized mixture can be stored in the dark for up to 1 month at room temperature. An electric drill (max speed 2750 rpm), equipped with a mandrel, was used as the spin coater (the mandrel serves to mount a hole saw blade to the drill). The drill was mounted in a vertical position using a steel clamp, and glass slides were glued to the mandrel using double adhesive tape. A standard desk light with a 20 W halogen light bulb served as exposure source. Inverse photomasks were produced using commercial drawing software, and either printed directly onto a transparency with an inkjet printer, or copied onto a transparency with a copier. The masks used for this work were printed with 1200 dpi resolution by a commercial printing service.

RESULTS AND DISCUSSION

The procedure for patterning gold and ITO films is shown in Figure 1. All steps were performed under ambient light conditions to avoid uncontrolled photopolymerization of the light sensitive emulsion. Prior to patterning, the slides were cleaned with soap and water, rinsed thoroughly with warm water followed by acetone, and dried in air. For spin-coating (step 1), the

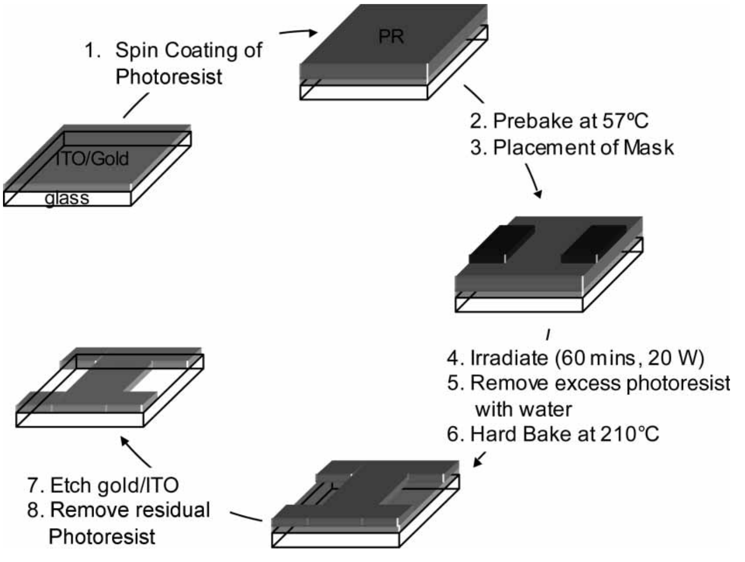

Figure 1. Procedure for patterning gold and ITO films on glass slides.

glass slides were glued to the even surface of the mandrel on the electric drill with double adhesive tape and 1–2 mL of the photoresist were then applied to the slide. The drill was operated for 30 s at 2750 rpm, after which the slide was evenly coated with a thin film of the polymer. The slides were removed and allowed to dry for 30 min at room temperature in a dark place, e.g., in a closed drawer. To strengthen the polymer, the slides were pre-baked (step 2) for 5–7 min by placing them on the surface of a hot plate at 57°C. During this time, the slides were covered with a home-built cardboard box set, which helped to control the temperature and which protected the slides from light. The pre-bake temperature was measured with a temperature gauge. In step 3, the mask with the desired negative pattern was placed onto the photopolymer-coated side of the glass slides, and the slides were then placed underneath a regular desk light with a 20 W halogen light bulb (step 4). For an illumination distance of 16.5 cm the photocuring time was 60 min. After photocuring, the mask was removed and the slide was briefly exposed to a stream of cold water (a few seconds, step 5) to expose the pattern. The unexposed, unpolymerized regions of the photoresist were then carefully removed with a wet paintbrush. This is the most delicate step in the procedure, and it requires a bit of practice. The pattern was then carefully washed with water and dried with a heat gun. To stabilize the photoresist, the pattern was then hard-baked (step 6) by placing the slide with the photoresist up onto a heating plate that had been preheated to 210°C. Heating was continued until the photoresist had a deep brown color. Because fumes are emitted in this process, this step must be performed in a fume hood or in a ventilated bake oven. The glass slides were then removed and allowed to cool to room temperature. For the etching (step 7), slides were exposed to a non-stirred etching solution at room temperature. Gold films were etched with a 1:2 (v:v) mixture of 6 M HCl and 6 M HNO_3 for 1−2 min. The progress of the etching was monitored visually and stopped when all unprotected gold patterns had disappeared. ITO coated slides were etched with 6 N HCl for 1 h. Slides were removed from the etching bath and rinsed with cold water to remove the acid. Excess photoresist on the ITO slides was scratched off with a fresh razor blade, and the slide was then rubbed clean with a paper tissue and acetone (step 8). Care had to be taken to avoid scratching the pattern. Gold slides were treated with a freshly prepared mixture of 30% H_2O_2 and concentrated H_2SO_4 1:3 (v:v) to remove the photoresist and residual titanium layer (10 nm). After about 20 s of etching, the acid was rinsed off with cold water. Excess contact with the etching solution needs to be avoided, since it can damage the pattern. The entire procedure requires between 3 and 5 h of time, depending on the level of experience.

Figure 2 shows examples of ITO films patterned with the described method. It can be seen that surface areas of several square centimeters in size can be reproduced reliably. The smallest reproducible features are on the 100 μm scale. Resistivity measurements showed that the conductivities of the patterns did not diminish upon patterning, which demonstrates that the indium tin oxide was effectively protected from the etching solution by the photoresist. As the feature sizes become smaller than 100 μm, problems with the pattern reproduction can be observed. These problems are caused, partially, by incomplete adhesion of the photoresist and partly by the etching process. The use of a desiccating primer might improve adhesion of

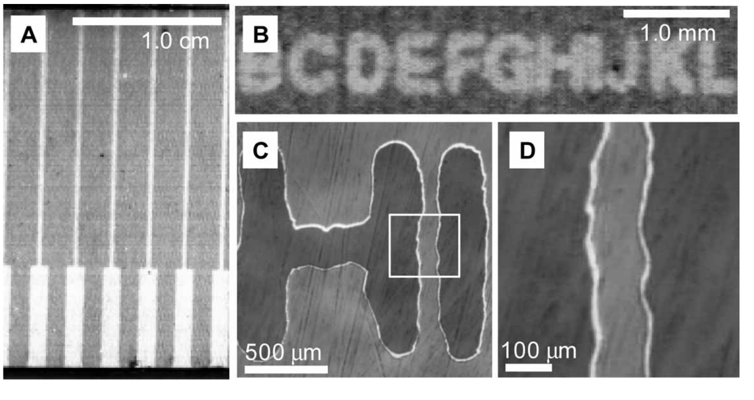

Figure 2. Patterned ITO films at variable magnifications. A) Electrode array, dark: ITO, light: glass, B) inverse letter sample (letter: glass, surroundings: ITO, C) inverse letter sample (magnified view), D) magnified section from c. The light border region corresponds to half-etched ITO.

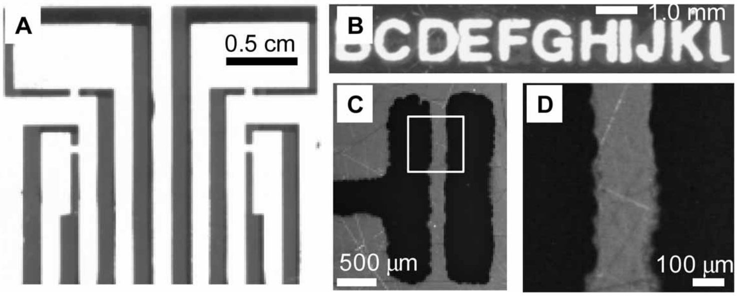

Figure 3. Patterned gold films at various magnifications. A) Electrode array, dark: gold, light: glass, B) inverse letter sample (letter: glass, background: gold). Here the doubling of the letter symbols is caused by internal reflection on the glass-air interface, C) magnified region in B, D) magnified region in c.

the photoresist and lead to better reproduction. The lighter edges in Figure 2(D) shows regions where the ITO has been partially etched by the acid mixture. This problem may be reduced by using less concentrated acid mixtures for etching and longer etching times.

The smallest achievable feature sizes on gold films (Figure 3) are similar to ITO. However, because the conditions for etching (HNO_3/HCl) are harsher than in the above case, etching artifacts can be seen in at the top and right side of Figure 3(C), where the acid has carved arc-like patterns into the protected gold substrate. The formation of these artifacts can be reduced by closely monitoring the etching time and by reducing the concentration of the acid. Overall, the gold films are more prone to be scratched (see Figure 3C) than the ITO. Resistance measurements of the patterned films showed, however, that neither scratches nor treatment with the photoresist reduced the conductive properties of the Au films.

CONCLUSION

In conclusion, we have presented a simple laboratory-scale photolithographic method that allows reliable and inexpensive patterning of indium tin oxide and gold coated glass slides. The procedure does not require special equipment or training, and it allows to reliably pattern film areas of several square centimeters with feature sizes as small as 100 μm. The patterning procedure does not interfere with the conductive properties of the protected area of the gold or ITO substrates and patterned films can therefore be used as electrodes in electrochemical or solid-state devices. The fact that it only takes about 5 h to complete a single pattern makes the described method particularly suitable for the fabrication of prototype devices that do not require microscale resolution. We anticipate that the described procedure will appeal to researchers outside the electrical engineering field, who do not have access to a clean room facility, and for instructors who want to make students familiar with the principles of photolithography.

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