ment with this interpretation the monolayers containing the thermally less stable tetrasulfide linkages react at moderate temperatures without the generation of gaseous decomposition products yielding again approximately the calculated fracture surface energy.

In conclusion it was shown that solid-phase reactions can be initiated between organic monolayers that are immobilized at smooth solid surfaces. Due to steric constraints, wafer bonding represents a novel environment for the study of chemical reactions.

The well-known ability of di- and polysulfides to react with carbon–carbon double bonds in olefins[14] gives rise to the expectation that other interface reactions can be carried out following the scheme presented here.

Experimental

Prime-grade polished silicon and quartz glass wafers were cleaned using a standard cleaning procedure: 1. $NH_4OH:H_2O_2:H_2O$ (1:1:6; 70°C; 10 min); 2. Rinse with ultra-pure water (10 min); 3. $HCl:H_2O_2:H_2O$ (1:1:5; 70°C; 10 min); 4. Rinse with ultra-pure water (10 min).

Monolayers of compound **1** and **2** (both compounds are commercially available) are deposited by exposing the freshly cleaned substrates to a solution of **1** or **2** in toluene ($c = 10^{-3}$ mol/L) for 4 h at room temperature in an inert atmosphere. After the deposition is complete unreacted compound is removed by extensive rinsing with toluene, acetone, *i*-propanol, and methanol. The wafers are spin-dried and contacted face to face under vacuum (4 mbar). The bonding of silicon wafers is monitored by illuminating the back of the wafer pair with IR light while observing the front with an IR-sensitive camera. For the detection of small particles and gas bubbles ultrasound microscopy is performed (Sonoscan-C-SAM 300 DX). The fracture surface energy is determined by inserting a wedge at the rim of the wafer pair (double cantilever method). The crack that opens up relates to the fracture surface energy [15–17]. A Woolham variable angle spectroscopic ellipsometer (WVASE 32) was used to measure the thickness of the monolayers. The surface roughness was determined using a large area atomic force microscope (Digital Instruments Dimension 5000). The contact angles were measured with a Krüss Contact Angle Measuring System G 10.

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Formation of Patterned Microstructures of Conducting Polymers by Soft Lithography, and Applications in Microelectronic Device Fabrication**

By *Weng Sing Beh, In Tae Kim, Dong Qin, Younan Xia,** and *George M. Whitesides*

This paper describes the use of one of the soft lithographic methods — micromolding in capillaries (MIMIC)[1] — in the fabrication of patterned microstructures of conducting polymers with feature sizes ranging from ~350 nm to ~50 μm. These electrically conductive microstructures were further used as patterned electrodes to fabricate flexible, all-plastic devices such as field effect transistors (FETs).

"Soft lithography" is the collective name for a group of non-photolithographic methods that are capable of generating patterned structures with feature sizes as small as ~30 nm.[2] Soft lithography offers immediate advantages over photolithography or other conventional lithographic techniques for a wide range of applications in which modification of surfaces, variation in materials, or patterning of non-planar substrates is the major concern. The initial success of soft lithography indicates that it has the potential to become an important addition to the field of micro- and nanofabrication.

Conducting polymers have been extensively explored as alternatives to metals or inorganic semiconductors in the fabrication of microelectronic, optoelectronic, and micro-electromechanical devices.[3] Functional components such as diodes,[4] transistors,[5] FETs,[6] light emitting diodes (LEDs),[7] mechanical actuators or transducers,[8] and optical modulators[9] have been successfully fabricated from conjugated organic polymers in prototype forms. Most of these applications require the formation of patterned microstructures of conducting polymers with feature sizes less than 100 μm. A number of methods have been investigated for this purpose; notable examples include photolithography,[10] e-beam writing,[11] surface-templated deposition,[12] screen printing,[13] and ink-jet printing.[14] In most cases, however, conducting polymers have to be modified to work

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effectively with these techniques. For example, photosensitizers have to be added into conducting polymers to make them patternable by UV photolithography.[10] The method we report here can be applied to most conducting polymers in their ordinary, as-synthesized forms. The only requirement is that the conducting polymer (or a precursor polymer) is soluble in a solvent that does not significantly swell poly(dimethylsiloxane) (PDMS), the elastomer used to fabricate the mold for MIMIC. We have focused on polyaniline (PANI) because this material is one of the most stable conducting polymers in air, and is relatively easy to synthesize.

Figure 1 shows the MIMIC procedure:[1] A PDMS mold having a patterned relief structure on its surface was placed on the surface of a substrate to form a network of channels between them. These channels were then rinsed with N-methyl-2-pyrrolidone (NMP). When a freshly prepared solution (~1 wt.%, filtered through a 0.2-µm membrane) of polyaniline emeraldine base (EB) in NMP was placed at the open ends of the channels, the liquid spontaneously filled the channels by capillary action. After the solvent had evaporated and the PDMS mold had been carefully removed, a network of polymeric material remained on the surface of the substrate. These patterned structures of PANI-EB were subsequently converted into the conductive, emeraldine salt (ES) form by doping in 1 M HCl for ~2 min. Although the PANI-EB solution was only ~1 % in concentration, the polyaniline structures generated by this method have approximately the same dimensions as those of the channels

in the PDMS mold. We believe the mechanism behind this process is similar to that responsible for the growth of patterned microstructures from polystyrene microspheres[15] or carbon paint[16] in PDMS channels: When the solvent evaporated slowly at room temperature, the polyaniline solution became a dispersion from which polymer chains precipitated out as very small particles. The attractive forces among these particles cause them to aggregate into nucleation sites. Because there was a large reservoir of dispersion fluid at the end where the polyaniline solution was placed, a fluid influx was induced towards the nucleation sites to compensate for the volume of solvent lost by evaporation. The transport of polyaniline particles towards the nucleation sites continued until the PDMS channels had been completely filled with aggregates of polyaniline.

Figure 2A shows a photograph of parallel lines (~2.5 cm in length, ~8 µm in thickness, ~50 µm in width and separated by ~50 µm) of PANI-ES on a polyester film. The lines were green in color, and they were electrically isolated from each other. A conductivity of ~5 S/cm was measured using the two-probe method. Figures 2(B-D) show SEM images of patterned microstructures of PANI-ES supported on Si/SiO₂ wafers. Because these polymeric microstructures of ES-HCl were electrically conductive, they did not have to be coated with thin films of gold before imaging by SEM. The edge roughness (=100 nm) of these patterned structures is mainly determined by that of the PDMS mold.

The smallest structures of polyaniline that we have fabricated using this procedure are ~350 nm in lateral dimension. Figure 3 shows the SEM (A) and AFM (B) images of these structures: parallel lines that are ~3 mm in length (as limited by the mold), ~750 nm in thickness, ~350 nm in width, and separated by ~2 µm. These lines were fabricated on a polyester film from PANI-EB, followed by doping in 1 M HCl aqueous solution for ~2 min.

Place PDMS mold on support

PDMS mold

Place a drop of polymer solution at one end

Fill channels by capillary action

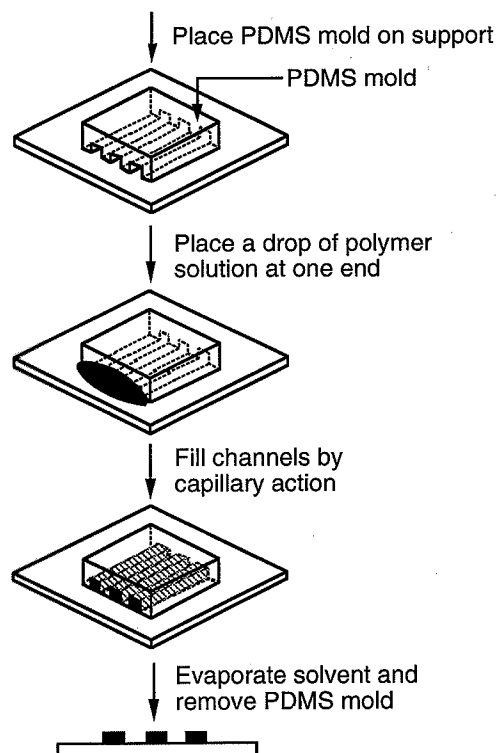Evaporate solvent and remove PDMS mold

Fig. 1. Schematic procedure for the formation of patterned microstructures of polyaniline EB by MIMIC.
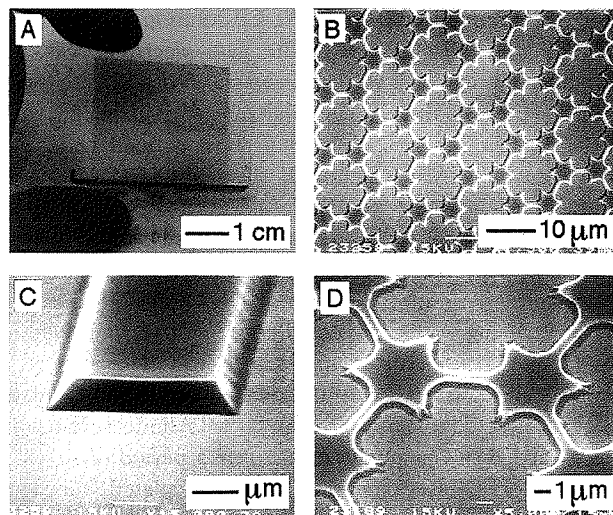

Fig. 2. (A) A photograph of parallel lines (along the vertical direction) of PANI-ES that were fabricated on a polyester film using MIMIC. (B, C, D) SEM images of test structures of PANI-ES that were formed on Si/SiO₂ using MIMIC.
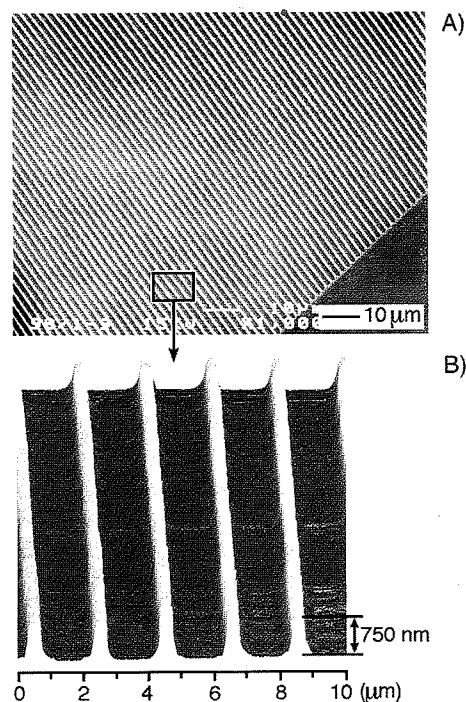
Fig. 3. (A) SEM and (B) AFM images of parallel lines of PANI-ES that were fabricated on a polyester film by MIMIC.
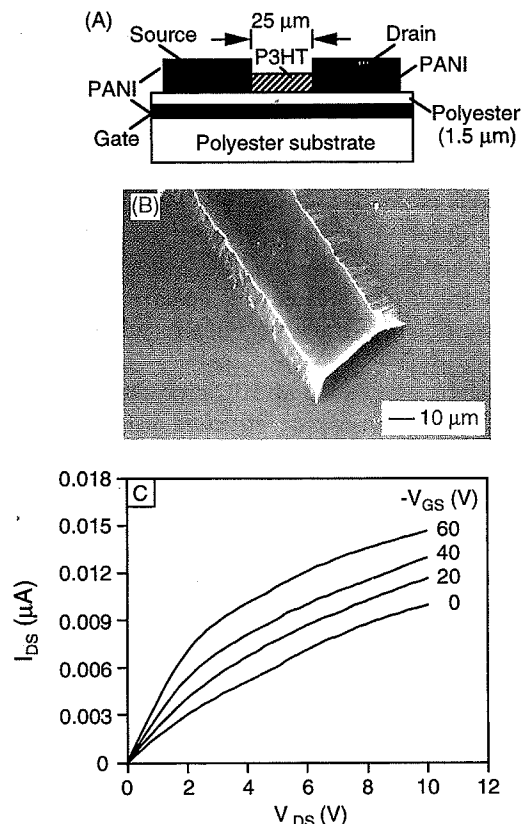

Fig. 4. (A) A cross-sectional illustration of the all-plastic FET that was fabricated in the present study. (B) An SEM image of the source (or drain) electrode that was fabricated from polyaniline using MIMIC. (C) I–V curves of an all-plastic FET as shown in (A).

The electrically conductive microstructures of PANI-ES can be used directly as arrays of electrodes to fabricate all-plastic FETs. The cross section of such a FET is shown schematically in Figure 4A. The insulating layer was an ~1.5-μm-thick polyester film (Goodfellow, Berwyn, PA) with a dielectric constant of ~3.0.[17] The semiconducting layer was a thin film cast from a solution of poly(3-hexylthiophene) (P3HT) or poly(3-dodecylthiophene) (P3DT) in chloroform; both polymers were regioregular, and were obtained from Aldrich (used as received). All the electrodes were prepared from PANI-EB solution in NMP, and then doped with 1 M HCl. The gate electrode was an ~1-μm-thick film of PANI spin-coated on a polyester substrate (~200 μm thick). The source and drain electrodes were parallel lines of PANI that were defined and patterned using MIMIC. Figure 4B shows an SEM image of the source electrode. The pattern was generated using a rapid prototyping procedure described previously.[18] Figure 4C shows the current–voltage (I_{DS}–V_{DS}) curves at various values of gate bias (V_{GS}) for a FET with P3HT as the semiconducting layer. The channel length (L) and width (W) were ~25 μm and ~1 mm, respectively. These characteristics are consistent with those of all-organic FETs with electrodes made of carbon pastes.[13,16,17] All measurements were carried out manually in air over a period of several days. The field-effect mobility (μ_{FET}) calculated from the linear region of the I–V curves is ~10^{-3} and ~10^{-7} cm^{2}V^{-1}s^{-1} for P3HT and P3DT, respectively. These values are roughly of the same order of magnitude as those measured on polymeric FETs fabricated from P3HT or P3DT using other

techniques.[19] The high "Ohmic" current at $V_{GS} = 0$ V suggests that the polythiophenes might have been doped by mobile impurities such as oxygen; a similar phenomenon has also been observed by other groups.[20]

In summary, we have demonstrated a non-photolithographic method for patterning conducting polymers into sub-half-micrometer features on *insulating* substrates. This method is simple, convenient, and potentially low-cost. The only requirement is that the conductive polymer can be dissolved or dispersed in a solvent that does not significantly swell the PDMS mold. The electrically conductive structures patterned using this method can be used directly as electrodes in fabricating microelectronic devices and sensors. We expect these patterned microstructures fabricated from conducting polymers to be useful in other areas: for example, as active elements to construct microelectromechanical systems (MEMS),[8] as diffractive components to fabricate electrochemically controllable optical modulators,[9] and as templates in electrolytic or electroless plating to deposit patterned structures of metals.[21]

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