

## Interfacial Chemistries for Nanoscale Transfer Printing

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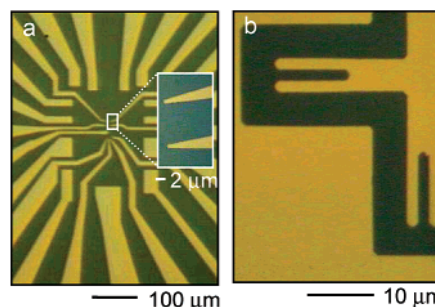
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Advanced techniques for nanofabrication are now essential for progress in many areas of science and technology. Substantial research focuses on surface chemistries and materials that can extend the resolution of printing and writing techniques into the submicron regime.<sup>1</sup> One goal of these efforts is to establish nanofabrication techniques that have capabilities which can complement the strengths of methods designed for semiconductor manufacturing (e.g. electron beam lithography, photolithography, etc.). For example, microcontact printing<sup>2</sup> ( $\mu$ CP) and dip pen nanolithography<sup>3</sup> (DPN) represent two relatively new methods that combine high resolution “stamps” and “pens” with self-assembled monolayer (SAM)<sup>4</sup> “inks” for high-resolution patterning. These and other emerging techniques are rapidly becoming important for a range of applications.<sup>5</sup>

This paper introduces the use of SAMs as covalent “glues” and “release” layers for transferring material from relief features on a stamp to a substrate. This approach, which we refer to as nanotransfer printing (nTP), is a purely additive technique that can generate complex patterns of single or multiple layers of functional materials with nanometer resolution over large areas in a single process step. Unlike  $\mu$ CP, nTP does not suffer from surface diffusion or edge disorder in patterned SAM “inks” nor does it require post-printing etching or deposition steps to produce structures of functional materials. We demonstrate the versatility of nTP with SAMs by forming patterns with a range of geometries on flexible and rigid substrates using both hard inorganic and soft polymer stamps.

Scheme 1 illustrates the use of SAMs and nTP for forming patterns of Au on a silicon wafer. The process begins by soaking the wafer in a 6:1:1 volumetric mixture of distilled water, H<sub>2</sub>O<sub>2</sub>, and HCl for 10 min at 75 °C, rinsing it with deionized water, and then drying it under a stream of nitrogen. This procedure generates surface hydroxyl (–OH) groups on the native SiO<sub>2</sub> layer. Placing the wafer and a small amount of 3-mercaptopropyltrimethoxysilane (MPTMS; Aldrich Chemical Co.) in a vacuum chamber for ~3 h at room temperature leads to co-condensation of the methoxy groups of the MPTMS with the hydroxyl groups on the surface of the wafer. Infrared spectroscopy, contact angle, and ellipsometry measurements all indicate the formation of a SAM of MPTMS with the thiol groups oriented upward.<sup>6</sup> Immersing the wafer in a ~0.005 M solution of MPTMS in benzene or toluene provides another route to forming this SAM.<sup>7</sup>

To print on this reactive surface, we use high-resolution elastomeric poly(dimethylsiloxane) (PDMS) stamps coated with Au. Casting and curing a prepolymer (Sylgard 184; Dow Chemical Co.) of PDMS against a pattern of photoresist produce the stamps.<sup>1,2</sup> The depth of relief was ~2  $\mu$ m; the sidewalls were vertical to within ~5°. Depositing 20 nm of Au on the stamp by thermal evaporation (1.0 nm/s; ~10<sup>–7</sup> Torr base pressure) yields a macroscopically



**Figure 1.** Optical micrographs of patterns of gold formed by nTP on (a) a silicon wafer and (b) a sheet of PET.

smooth and continuous coating. A collimated flux of Au normal to the surface of the stamp ensures deposition only on the raised and recessed regions of relief and not on the sidewalls. Bringing this coated stamp into contact with the MPTMS SAM leads to the formation of sulfur–gold bonds in the regions of contact. Removing the stamp after a few seconds efficiently transfers the gold from the raised regions of the stamp (Au does not adhere to PDMS) to the substrate. Covalent bonding of the SAM “glue” to both the substrate and the gold ensures good adhesion of the printed patterns: they easily pass Scotch tape adhesion tests. Based on preliminary experiments, we speculate that more than 15% of the treated surface is involved in the bonding. Figure 1a shows an optical micrograph of a pattern that illustrates the type of high-resolution printing that is possible.

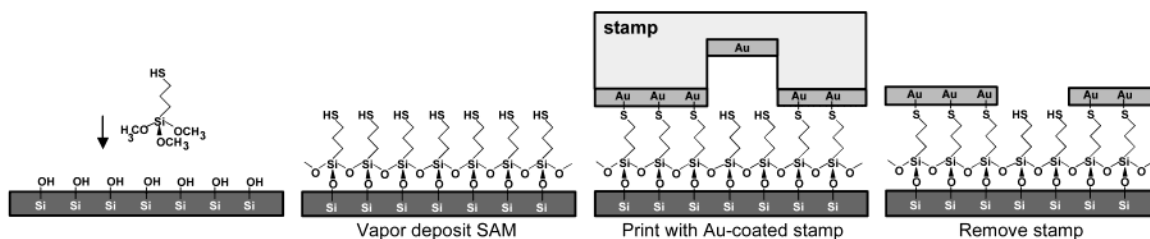
Similar results can be obtained with other substrates containing surface –OH groups. For example, we printed Au patterns onto ~250  $\mu$ m thick sheets of poly(ethylene terephthalate) (PET; Southwall Technologies) by first spin casting and curing (130 °C for 24 h) a thin film of an organosilsesquioxane (GR720P in propoxypropanol; Techneglass, Inc.) on the PET. Exposing the cured film (~1  $\mu$ m thick) to an oxygen plasma (reactive ion etching with an O<sub>2</sub> flow rate of 30 cm<sup>3</sup>/min and a pressure of 30 mTorr at 100 V for 30 s) and then air produces surface (–OH) groups. Patterns of Au were printed on these glass resin/PET substrates with nTP procedures developed for silicon substrates. Figure 1b shows a typical pattern. The resolution and adhesion of structures printed on plastic sheets are as good as those on silicon wafers.

The use of PDMS stamps limits the minimum feature sizes in Figure 1. To demonstrate the nanometer resolution, we used GaAs stamps fabricated by electron beam lithography and etching. These stamps contain features with lateral dimensions as small as ~75 nm and relief depths of ~0.5  $\mu$ m. The substrates in this case consisted of films (~50  $\mu$ m thickness) of PDMS on sheets of PET. The elastomeric PDMS layer ensures atomic-scale physical contact to the hard GaAs stamp without the need to apply pressure. Plasma oxidizing the PDMS for ~5 s with conditions described above produces surface (–OH) groups.<sup>8</sup> Figure 2 shows a printed pattern in the geometry of a two-dimensional photonic crystal waveguide.

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Scheme 1

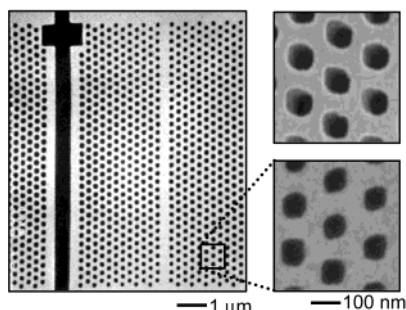


The edge resolution is remarkably high (5–15 nm); it is comparable to the grain size of the gold and the resolution of the stamp itself. This high level of fidelity in pattern transfer can also be achieved with non-SAM based surface chemistries. The pattern shown in Figure 2, for example, was transferred by a condensation reaction between surface silanols (Si–OH) on the PDMS and titanols (Ti–OH) on a plasma oxidized (similar conditions; 4 min of exposure), thin (5 nm) film of Ti on the Au (50 nm) coated stamp. In this case, a condensation reaction produces bridging –Ti–O–Si– bonds that facilitate the transfer. The titanol chemistry is similar to that used in titania-based antifogging lenses.<sup>10</sup> The condensation bonding is similar to the –Si–O–Si– chemistry that can be used to seal PDMS-based microfluidic systems.<sup>8,11</sup>

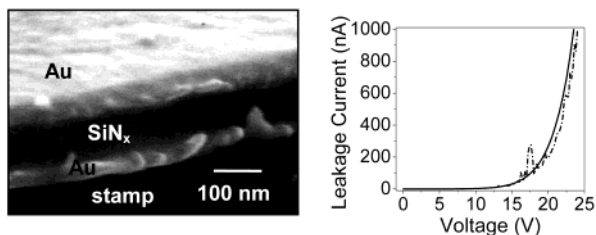
Flexible electronic systems represent a promising potential application for nTP. To demonstrate its utility in this area, and to illustrate its ability to print complex multilayer structures, we fabricated metal-insulator-metal capacitors on plastic substrates by nTP. We used silicon stamps formed by photolithography and etching. A “nonstick” SAM of tridecafluoro(1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (UCT, Inc.) is first condensed on the native SiO<sub>2</sub> surface of the stamp (conditions similar to those used for the MPTMS SAMs). This fluorinated SAM ensures weak adhesion between the deposited multilayer and the stamp. The multilayer stack consisted of sequentially deposited coatings of Au (50 nm), SiN<sub>x</sub> (100 nm; by plasma enhanced vapor deposition, PECVD, at

130 °C with a N<sub>2</sub> flow rate of 900 cm<sup>3</sup>/min, SiH<sub>4</sub> of 200 cm<sup>3</sup>/min, NH<sub>3</sub> of 2.3 cm<sup>3</sup>/min, and a total pressure of 900 mTorr at 25 W for 15 min), Ti (5 nm), and Au (50 nm). Unlike thermal evaporation, which is a directional deposition method, the PECVD process yields a conformal SiN<sub>x</sub> coating on the sidewalls as well as raised and recessed regions of the stamp. A short reactive ion etch (with a CF<sub>4</sub> flow rate of 50 cm<sup>3</sup>/min and a pressure of 50 mTorr at 100 V for 7 min) is thus necessary after the second Au deposition to remove the SiN<sub>x</sub> from the sidewalls (see Figure 3). These layers were printed onto a substrate of Au(15 nm)/Ti(1 nm)-coated PDMS-(50 μm)/PET(250 μm) substrate. Interfacial cold welding<sup>12</sup> between the Au on the surfaces of the stamp and substrate bonds the multilayers to the substrate. The fluorinated SAM ensures efficient release of the Au pattern when the stamp is removed. Figure 3 shows the characteristics of a typical printed capacitor (lateral dimensions of 250 μm × 250 μm, for ease of electrical probing); its performance is similar to devices fabricated on silicon wafers by photolithography and lift-off.

Nanotransfer printing with SAM “glues” and “release” layers represents a useful approach to nanofabrication. Its versatility was demonstrated by forming patterns and functional structures with several different transfer chemistries; with hard inorganic and soft polymeric stamps; with rigid and flexible substrates; and with single and multiple layers of metals and dielectrics. Although we have not yet quantified the accuracy in multilevel registration that is possible with nTP, we expect its performance to be similar to that of embossing techniques when rigid stamps are used.<sup>13</sup> The flexibility provided by the SAM chemistries suggests that nTP will be suitable for high-resolution patterning with a wide range of other stamps, substrates, and materials. It also points to the potential use of nTP for building molecular scale electronic devices that use SAMs as semiconductor and dielectric layers.



**Figure 2.** Scanning electron micrographs of a Ti–Au (bright regions) pattern in the geometry of a 2D photonic waveguide. Micrographs on the right display magnified views of the coated stamp before transfer (top right frame; angled view) and the printed pattern (bottom right frame).



**Figure 3.** Left: Cross-sectional scanning electron micrograph of a multilayer stack on Si stamp. Right: Current–voltage characteristics of a printed capacitor (dashed) on PET and a capacitor of the same size fabricated by photolithography on a Si wafer (solid).

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