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Nanotransfer Printing Using Plasma Etched Silicon Stamps and Mediated by in Situ Deposited Fluoropolymer

Deepak Bhandari,[†] Ivan I. Kravchenko,[‡] Nickolay V. Lavrik,[‡] and Michael J. Sepaniak*,[†]

[†]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

[‡]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

S Supporting Information

ABSTRACT: This communication describes a simple method that uses a thin film of octafluorocyclobutane (OFCB) polymer for efficient nanoscale transfer printing (nTP). Plasma polymerization of OFCB produces a Teflon-like fluoropolymer which strongly adheres and conformally covers a 3-D inorganic stamp. The inherently low surface energy of in situ deposited OFCB polymer on nanoscale silicon features is demonstrated as a unique nanocomposite stamp to fabricate various test structures with improved nTP feature resolution down to sub-100 nm.

The growing interest in nanoscience motivates researchers to develop new methods that can be employed for the fabrication of relevant test structures and functional devices. To date, microcontact printing and nanotransfer printing (nTP) are the most widely studied printing techniques. nTP is a high resolution (approximately 100 nm) and a purely additive printing technique[1] based on the principle that surface chemistries act as interfacial "glue" or "release" layers to control the transfer of nanoscale metal inks from relief features to a variety of substrates. Since its first implementation in 2002,[2,3] the technique has been used to create nanostructures for electronics,[4−7] spintronics,[8] and plasmonics/photonics.[9]

In this communication, we describe a new protocol of creating silicon stamps for highly efficient nTP that relies on in situ formation of a fluoropolymer release layer immediately following anisotropic plasma etching of silicon. We utilize plasma-assisted polymerization of octafluorocyclobutane (OFCB) to conveniently form an ultrathin (~10 nm) cross-linked Teflon-like[10,11] release layer on the surfaces of nanoscale silicon stamps created by a combination of electron beam lithography (EBL) and reactive ion etching (RIE) (see S3, SI). The effective coalescence of low surface energy ultrathin OFCB film and a high modulus silicon stamp in our study permits high fidelity transfer printing, thereby improving the feature resolution of nTP.

The nTP mechanism relies on two key parameters: (a) the preferential adhesion of the metal disk to the substrate, usually occurring due to the covalent interactions between metal—substrate and (b) easy release of metal-ink from the stamp, obtained by minimizing the work of adhesion between stamp and metal. Fluoro-compound coated surfaces are widely known for their low surface energy and have been widely explored in various soft lithographic applications.[12−17] However, a few nTP studies have been carried out using such promising surfaces. In 2002, Loo et. al used a wet chemical method to condense a self-assembled monolayer of tridecafluoro(1,1,2,2,tetrahydrooctyl)-1-trichlorosilane, the release layer, on the native SiO_2 surface of a silicon stamp.[2] Impressive high-resolution nanopatterns were created using this protocol. However, this wet chemical process may produce defects and promote the formation of unwanted residue. Moreover, it also requires recondensation of the release layer for subsequent stamping (i.e., stamp-and-repeat). Most recently, UV-cured perfluoropolyether-based stamps have been employed for the fabrication of various test structures.[8,17] Although the technique has potential, to our knowledge, the minimum feature size reported by this soft nTP technique is approximately 200 nm. On the other hand, polydimethylsiloxane (PDMS) elastomer-based nTP has been broadly studied in the past few years. PDMS stamps are easy to fabricate in a variety of features and do not require a release layer. A good deal of high-quality patterns have been successfully accomplished using this elastomeric patterned stamp.[2,6,18,19] Nevertheless, the low elastic modulus of a PDMS stamp is even more problematic as it limits the minimum size of the transferred feature and can collapse high-aspect-ratio features during transfer printing.

Plasma-assisted polymerization of fluorocarbons has several advantages compared to other fluoropolymer-mediated nTP protocols. The most obvious of these advantages is that it seamlessly integrates deposition of a release layer into the sequence based on dry etching of inorganic 3-D stamps (e.g., silicon, gallium arsenide). Adhesion of plasma polymers is superior to release layers that are physically deposited and have lower surface energy (~10 mJ/m^2, see S8, SI). In addition, the reported Si-OFCB nanocomposite stamps have unique advantages over widely used polymeric stamps: (i) much greater modulus of silicon (~100 GPa versus <1 GPa) provides excellent resolution and highest possible fidelity of transferred patterns; (ii) temperature stability makes them suitable for nTP of high-melting-temperature materials deposited on stamps by physical vapor deposition; (iii) reusability and durability is unsurpassed due to strong chemical resistance; and (iv) a variety of RIE protocols with precisely controlled etch rate and side wall profiles are available.

We first employed a top-down nanolithography approach (i.e., EBL) to create a variety of nanofeatures on positive e-beam resist (Zep520A) coated silicon wafer. Following Cr-mask deposition and lift-off procedures, extruded silicon nanofeatures were created using RIE. Created relief features were then plasma

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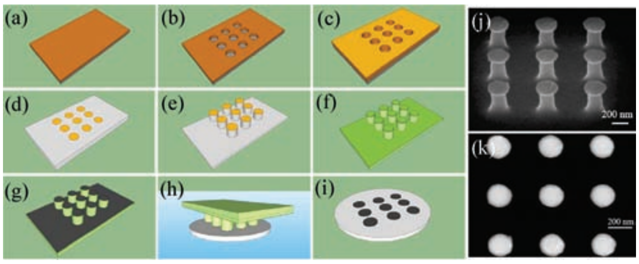

Figure 1. Step-by-step nanofabrication procedure: (a) Zep 520A spin-coated silicon substrate, (b) nanopattern developed on e-beam exposed resist, (c) Cr-mask deposition, (d) lift-off, (e) reactive ion etching, (f) in situ deposition of OFCB polymer film, (g) metal-ink deposition, (h) physical contact between stamp and a substrate of interest, (i) transfer printed pattern on a substrate. SEMs of nanopatterns: (j) 45° tilted view and (k) top view of OFCB-coated stamp.

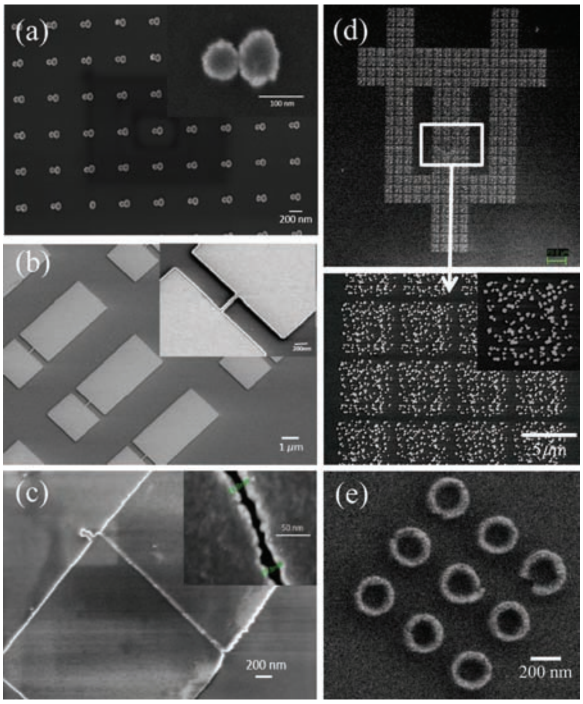

Figure 2. SEMs of various nanostructured devices fabricated via nTP: (a) Just-touching gold nanoparticle dimer array. (b) Gold nanowire—sensor array. (c) Planar nanogap gold electrode. (d) Nanoaggregates of random morphology silver nanoparticles cloned on large University of Tennessee emblem (i.e., UT) pattern.(e) Palladium nanoring array.

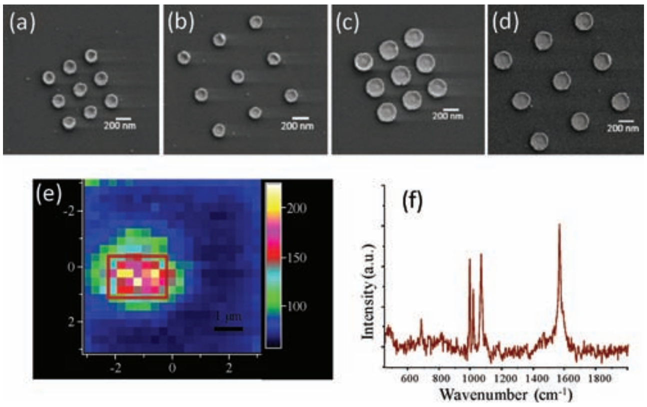

Figure 3. SEMs of 3 × 3 arrays of silver nanodiscs of different size and spacing: (a) 150 nm diameter, 300 nm spacing, (b) 150 nm diameter, 600 nm spacing, (c) 250 nm diameter, 300 nm spacing, (d) 250 nm diameter, 600 nm spacing. (e) SERS mapping of benzenethiol with respect to 1575 cm^{-1} peak on pattern "c" over 6 × 6 μm^2 area. Bright region represents nanostructured surfaces coated with benzenethiol. (f) Average SERS spectrum of benzenethiol taken from the bright region of a SERS map.

treated along with OFCB gas in a deposition reactor (Oxford Plasmalab Sytem100 ICP plasma etcher) to polymerize and deposit OFCB film, simultaneously, on a nanostructured surface (see S2, SI). Metal thin film was then vapor deposited onto OFCB coated relief nanofeatures prior to nTP. Figure 1 shows schematics of the detailed nanofabrication procedure.

The in situ OFCB deposition step is a fast process that yields ~10 nm films in <10 s. The substrate material and stamp do not require additional chemical modifications prior to nTP (see S6, SI). It can create sub-100 nm nTP features (limited by the size of the stamps) with interparticle spacing resolution down to sub-20 nm (see Figure 2a—c). Various complex nanostructures were created on silicon wafers and were replicated on quartz and silicon surfaces, i.e., hard substrates. Shown in Figure 2a is an array of circle-ellipse dimers of sub-100 nm silver particles which are of significant interest for surface-enhanced Raman spectroscopy (SERS)[20] (see S9, SI). Controlled synthesis of single-molecule SERS active hot spots should be facilitated by the significant improvement in resolution offered by the current printing approach. We further created connecting nanowires of approximately 50 nm width between two electrodes (Figure 2b; also see S10, SI). To our knowledge, this is the smallest particulate feature reported to date using a nanolithographically created printing stamp. Similarly, planar nanogap electrodes of ~15 nm spacing were created (Figure 2c; also see S10, SI). To further demonstrate the versatility of the approach, complex nanoaggregates of random shape and sizes were cloned together to create a relatively large (150 μm × 100 μm) University of Tennessee emblem (i.e., UT) and were successfully transfer printed onto various substrates (Figure 2d). In addition, palladium nanoring arrays were also successfully imprinted on the quartz surfaces (Figure 2e). Besides hard substrates, attempts were also made to imprint such nanofeatures onto soft polydimethylsiloxane (PDMS) surfaces. However, we constantly observed defects such as cracks and feature deformations on transfer printed sub-100 nm particles—perhaps, due to low elastic modulus of PDMS.

In our study, we have transfer printed various metals of different technological interest. Besides silver and gold, platinum and palladium patterns were imprinted on quartz and silicon surfaces (see S5, SI). Root mean square (rms) roughness of each metal thin film on OFCB-modified surfaces were characterized (see S7, SI). The rms values reported for OFCB polymer film, palladium, silver, gold, and platinum are respectively 0.543, 0.810, 1.568, 1.130, and 0.887 nm. Results showed that both plasma-polymerized OFCB and e-beam evaporated metal film form fairly smooth surfaces. Regardless of the slight variation in rms roughness, all metal-film under study were successfully integrated on a target substrate.

As stated earlier, the stamping/printing approach reported herein has broad technological significance. To demonstrate its quick application, nanostructures printed on quartz surfaces via our current approach were tested for SERS application. Panels a—d of Figure 3 show SEMs of 3 × 3 arrays of circular disk patterns having 150 and 250 nm diameters and 300 and 600 nm spacings. These plasmonic nanoparticles, similar to other transfer printed nanostructures, are characterized by having relatively rough/thick edges, as revealed by atomic force microscopy (see S11, SI). The SERS signature of benzenethiol was mapped over each pattern using 632.8 nm laser excitation. Results showed that 250-nm silver disk array with 300-nm spacing generates better signal compared to others. Panels e and f of Figure 3 show SERS profiles of benzenethiol harvested from pattern "c" with an average enhancement factor (EF) 2×10^7. SERS EF was estimated with respect to a 1575 cm^{-1} peak (see S12, SI). It should be noted that the array patterns used in our study were not optimized, as such a significant improvement in EF may be achieved with a rational design of nanoparticles or patterns on a suitable substrate.

In conclusion, we developed a simple and unique nTP approach to generate a range of test structures. Inherently low surface energy of a plasma polymerized OFCB forms an extremely smooth surface and hence acts as an efficient transfer media to imprint low nanometer features. This current approach provides new opportunity in routinely stamping out sub-100 nm functional devices, a significant improvement in comparison to other printing techniques.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental, empirical calculations, surface characterization, and additional information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

msepaniak@utk.edu

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