Flexible and Stretchable Networks of Metals

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Abstract:

Flexible and stretchable networks of metals were pursued, with a vision for their application in flexible electronics. This project aimed to develop: 1) methods for the nanofabrication of these networks with ~ 25 nm dimensions, and 2) processes for the transfer of these structures to elastomeric substrates. Block copolymers were used as a unique method of lithography for patterning the networks [1]. Lamellar nanostructures of unique connectivity were fabricated using polymers of varying compositions of polystyrene (PS) and poly(methyl methacrylate) (PMMA). The selective removal of the PMMA domains followed by metal deposition and liftoff processes enabled the production of interconnected metal networks that could subsequently be isolated and transferred to a flexible substrate.

Introduction:

Electronics have traditionally been limited to rigid and planar surfaces. However, many applications—from computing and energy to sensing and biomedical technology—would be vastly enhanced if electronic materials could be fabricated upon flexible substrates that can undergo mechanical deformation [2]. The fabrication of interconnected metal networks consisting of thin nanowires is thought to provide the flexibility needed while maintaining conductive properties.

Thermodynamically controlled, self-assembling morphologies of block copolymer systems provide a reproducible method of lithography for the production of these networks. Poly(styrene-*block*-methyl methacrylate)—PS-*b*-PMMA—assembly of specific molecular weight ratios result in lamellar, or "fingerprint," patterns, shown in Figures 1a and b, respectively. These patterns are ideal as masks.

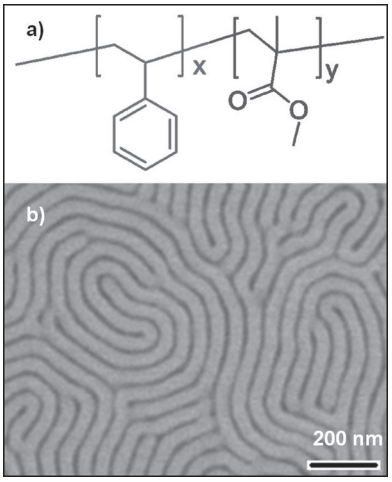

Figure 1: (a) Molecular structure of PS-b-PMMA. b) FESEM image of the PS-b-PMMA assembly, where the lighter regions are the PS domains.

Experimental Procedure:

Clean silicon wafers with 289 nm thick, thermally grown silicon dioxide layers were treated by a polymer brush layer with ~ 59 mol % of PS and ~ 41 mol % of PMMA. On top, a blend of copolymer (53 kg/mol PS and 54 kg/mol PMMA) with PMMA homopolymer (20 kg/mol) was spin-coated on the substrates and thermally annealed in vacuum at 180°C for 1200 minutes. The PMMA domain was removed by exposure to 254 nm ultraviolet radiation for 60 seconds, followed by development in acetic acid for 120 seconds. Subsequently, samples were treated with oxygen plasma (40 W, 150 mtorr, 5 sccm O_2) for 20 seconds. Via thermal evaporation, 2 nm of titanium was deposited as an adhesion layer followed by 5 nm of gold. After cooling, the samples were sonicated in toluene for 90 minutes at about 50°C. The progress of each step in the network fabrication process was confirmed by a JEOL JSM-7401F field-emission scanning electron microscope.

A patterned support layer can aid the lift off of the metal network from the oxide surface [3]. A layer of PMMA (950 kg/mol, 5.5 wt % solids in anisole) was spin-cast at 1500 RPM and baked at 180°C to yield an approximately 500 nm thick polymer layer. On top, a layer of positive photoresist, AZ P4210, was applied and patterned with 2 μm diameter holes. The samples were overexposed under 320 nm UV radiation and overdeveloped with AZ 400K solution to ensure complete development through the resist to the

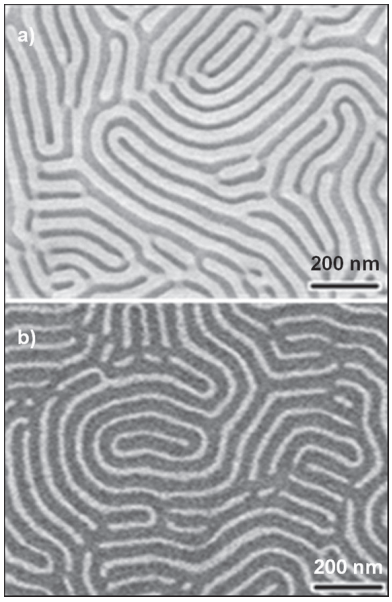

Figure 2: (a) PS mask after PMMA removal, and the b) gold network after PS removal.

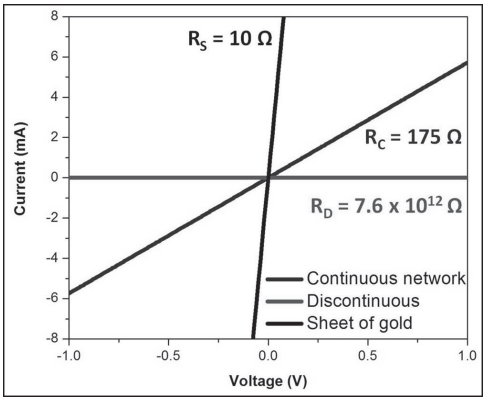

Figure 3: IV curve showing unique resistance values for three different conditions.

underlying PMMA layer. Oxygen plasma etching (10 sccm O_2, 150 W, 200 mtorr) for 170 seconds selectively removed the exposed PMMA regions all the way to the oxide surface. After removal of the photoresist layer by exposing and developing entire surfaces, the samples were immersed in 49% hydroflouric acid (HF) solution. After 200 minutes, the patterned PMMA layer delaminated from the surface. Samples were lightly dried with nitrogen after being rinsed in water. A PDMS (Dow Corning Sylgard 184, 10:1 silicone elastomer base: curing agent) stamp was laminated onto the PMMA layer and slowly peeled away.

To confirm the interconnectedness of the metal network, gold contacts were deposited on the metal network on silicon oxide surfaces using a shadow mask. A two point probe was used to measure conductivity between the gold contacts.

Results and Discussion:

The addition of the 20 kg/mol PMMA homopolymer successfully shifted polymer connectivity to the PMMA domain over the PS domain, which leads to better connected metal networks after deposition and liftoff. The UV/acetic acid development process effectively removes the PMMA domain, leaving the PS domain intact, as shown in Figure 2a. The short oxygen plasma etch step shows some promise, but some brush layer or polymer residue may remain, indicated by disconnected islands of metal after deposition. Figure 2b shows that toluene sonication proved to be effective at removing the PS domain without affecting the quality of the metal on the oxide surface.

Two point probe testing provided enough data to confirm the lateral connectivity of networks greater than 50 μm. IV curves in Figure 3 reveal obvious variance among the recorded resistances of a continuous network, a continuous sheet of gold of the same thickness, and a discontinuous network. Immersion in HF successfully etched away the sacrificial oxide layer through the patterned holes. Figure 4 illustrates the successful transfer of the support layer to a PDMS stamp via preferential van der Waals forces [4] and the deformation of the metal network.

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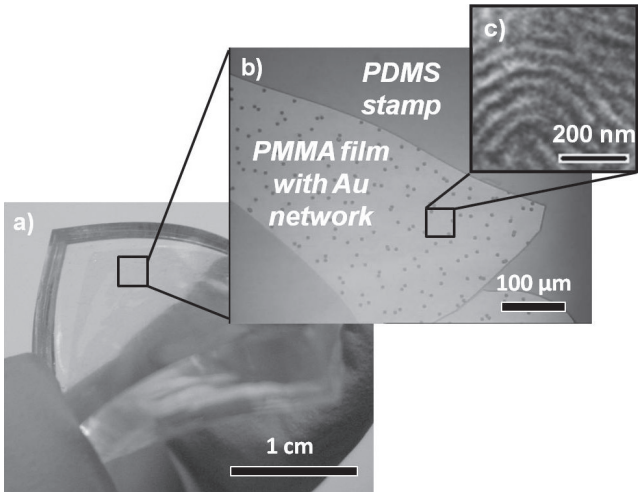

Figure 4: (a) Polymer support layer laminated on PDMS, (b) Optical micrograph, and (c) FESEM image show the patterned layer and network.