Nanoscale Chemical Patterning for Layer-by-Layer Assembly of Conductive Polymers

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Abstract:

Surface chemical templates were created by microcontact printing 3-aminopropyltrimethoxysilane (APTMS) using a composite poly(dimethylsiloxane) (PDMS) stamp. The composite PDMS stamp with a hard PDMS patterned layer and a softer backing layer was required to produce line feature widths of 208 nm or 139 nm. The amino functional groups on APTMS were quaternized with iodomethane to give patterned positive charges on the surface, which could then be used in layer-by-layer (LbL) assembly. LbL assembly was used to create nanometer-sized conducting polymeric wires by the sequential electrostatic deposition of poly(styrene sulfonic acid) (PSS) and poly(aniline) (PANI) onto the quaternized patterns. The geometry of the patterns and wires were characterized with atomic force microscopy. Conductivity measurements were made on the wires, parallel and perpendicular to their long axis, after each successive layer of LbL.

Introduction:

Microcontact printing is a nanofabrication technique that uses a patterned polymer stamp upon which a chemical ink is deposited. Placing the inked stamp in contact with a flat substrate, such as a silicon wafer, creates a functional pattern that is determined by the initial polymer stamp dimensions. Layer-by-layer (LbL) assembly is the process of self-assembly to create multilayer films. LbL employs electrostatic interactions between polyelectrolytes of alternating charge to build up structures one layer at a time. Using this technique, characteristics such as total assembly thickness can be easily tailored. Additionally, polyelectrolytes with different properties, such as electrical conductivity, can be used to impart functionality to the layered assemblies.

Experimental:

Silicon diffraction gratings with periods of 416 and 278 nm were used as master templates for creating the h-PDMS composite stamp. The h-PDMS was spun cast on the templates, and Sylgard 184 PDMS solution was placed on top. Once both PDMS layers were cured for one hour at 70ºC, the stamps were peeled from the substrate, rinsed with ethanol, and dried to remove any debris. Silicon wafers were cleaned and exposed to oxygen plasma for ten minutes, with four minutes additional exposure of the cleaned stamps to increase their hydrophilicity. The stamps were inked for 30 seconds with 5% APTMS in a 95:5 ethanol-water solution and were then blown dry. The patterns were immediately printed onto the silicon wafers by placing the stamp on the wafer, waiting 30 seconds, then removing the stamp.

The APTMS functional wafer was quaternized in a 1 M solution of iodomethane, which converted the primary amines to quaternary ammonium groups. The quaternized print was immersed for 30 seconds in a 5 mM solution of poly(styrene sulfonate) (PSS) in water, which was acidified with two drops of H_2SO_4. The pattern was then rinsed in deionized water for 30 seconds to remove any debris, and dried. The print was then immersed in a 5 mM solution of poly(aniline) (PANI) in formic acid for 30 seconds, then immersed in formic acid for one second to remove any excess PANI. The print was rinsed in deionized water and dried. One layer of PSS and one layer of PANI constituted one layer pair.

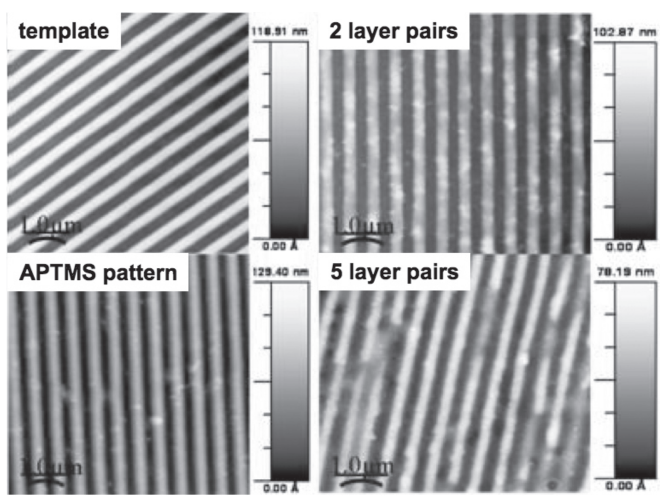

Figure 1: AFM of microcontact printing template, printed APTMS pattern, and one, two and five layer pair samples.

Conductivity was measured across the surface of the prints, both parallel to and perpendicular to the nanowires using a DC probe station. The tungsten probe tips were set directly on the surface of the pattern approximately 4 mm apart to measure DC current. A sweeping potential of -3 to 3 V was applied.

Results and Discussion:

Figure 1 shows atomic force microscope (AFM) images of 416 nm period prints with deposition of different numbers of layer pairs. Increasing line thickness, as evidenced by the bright features, was observed with increasing layer pairs. The AFM images confirmed that polymer deposition was only occurring on the patterned APTMS, not on the bare silicon substrate. The increasing thickness of the lines indicates that deposition did occur on the quaternized patterns and not on the unpatterned substrate.

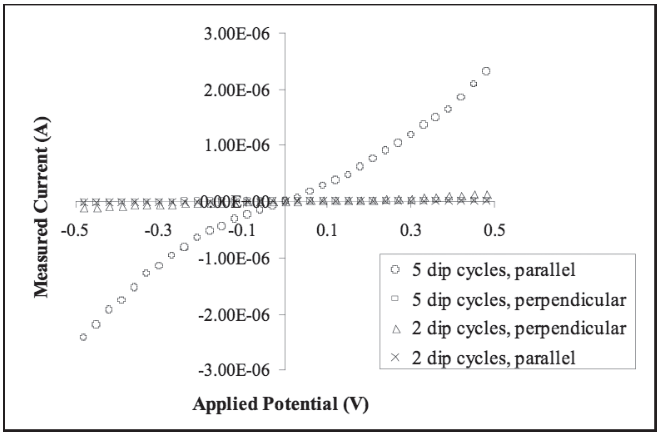

Figure 2: Current-Voltage curves parallel and perpendicular to two and five layer pair features

Figure 2 shows conductivity for 416 nm period prints with varying LbL layer pairs both parallel and perpendicular to the features. It was observed that the conductivity was greater when measured parallel to the nanowires as opposed to perpendicular, and that the conductivity increased with increasing layer pairs. The conductivity is greater across the five LBL layer pair sample than across the two LBL layer pair sample.

Ellipsometry was conducted in order to determine the thickness of the deposited polymer layers. Figure 3 illustrates the thickness of each adsorbed layer on an unpatterned sample. The exact refractive index was not known for the layers of polymer, so a value of 2.22 was selected to use as a baseline measurement. A built-in algorithm in the ellipsometer software was used to determine the refractive index, which was calculated from a two-angle measurement. A similar trend was observed for both cases. We found that the thickness of the sample increased as more LbL layer pairs were applied, and that this increase ranged from 2-5 nm.

Conclusions and Future Work:

Patterning of an amino functionalized silane was observed on small length scales, and LbL was successful for creating nanowires of conducting polymer. The conductivity increased with increasing LbL pairs, and the conductivity was greater parallel to the nanowires rather than perpendicular. These experiments demonstrated that asymmetric conducting structures can be formed in this manner. However, refinements to the printing process are needed to increase its robustness in varying relative humidity conditions and improve large-area patterning on the order of the size of an entire wafer. Future work will include using gold electrodes and measuring conductivity of the samples in 2-point and 4-point mode to gain a better understanding of the conductivity properties of the samples.

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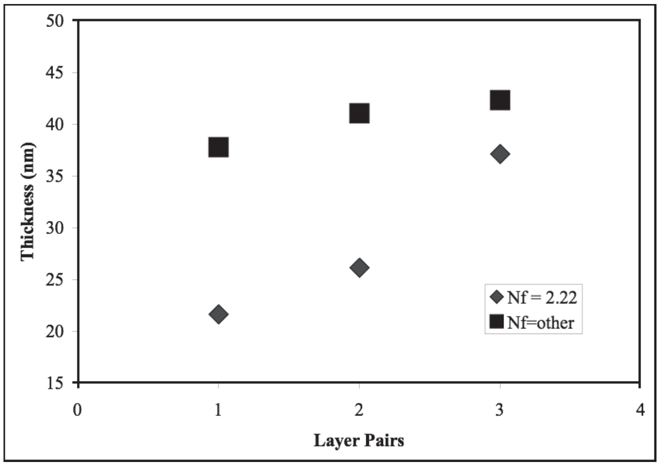

Figure 3: Thickness of layer pair deposition determined by ellipsometry.