Novel Platform for Characterization of Nanostructured Polymer Brushes

Principal Investigator: Christopher Kemper Ober[2]

User: Wei-Liang Chen[1,2]

Affiliations: 1. School of Chemical and Biomolecular Engineering,
2. Department of Materials Science and Engineering; Cornell University

Abstract:

For further characterization of polymer brushes by neutron and laser scattering, a specific platform was fabricated. The platform allows the anchoring of the polymer brushes on the sidewall of the trenches only, which makes the scattering signals responsive to the change of the polymer brush morphologies. Such methods could increase the sensitivity of the characterization and make probing of more complicated structures possible. Poly(2-(dimethylamino)ethyl methacrylate) brushes were synthesized by atom transfer radical polymerization on the grating. The polymer brushes grown on the sidewall have gradient profiles with a maximum thickness at the bottom of the grating, which is due to the lack of confinement on the top. Such a platform lays down the foundation for the future characterization.

Summary of Research:

Polymer brushes have already demonstrated their application in many fields and their structures have been studied widely in different conditions as described [1]. However, studies focusing on the more complicated structures of polymer brushes, such as molecular brushes, are still in need. It is critical to characterize the polymer brushes in wet state since the tension applied on them is amplified and thus forms more ordered structures. This requirement inspires us to develop a platform, which has polymer brushes anchored on the sidewall of the grating only. When having such platforms in the wet medium, the morphological change of the polymer brushes then controls the opening of the grating which could subsequently be captured by laser and neutron scattering [2]. By using the grating, the response of the polymer brushes would be amplified and allow us to reveal more details in polymer brush structures.

To have a single crystalline silicon (Si)-based grating, a top-down process had to be developed to fabricate the platform. On the other hand, since there is no method to perfectly deposit thin films on top and bottom of the trenches, a sacrificial layer based on silicon dioxide (SiO_2) is needed on the sidewall of the trenches to make sure the sidewalls are free of any residual chromium. The developed process is shown in Figure 1.
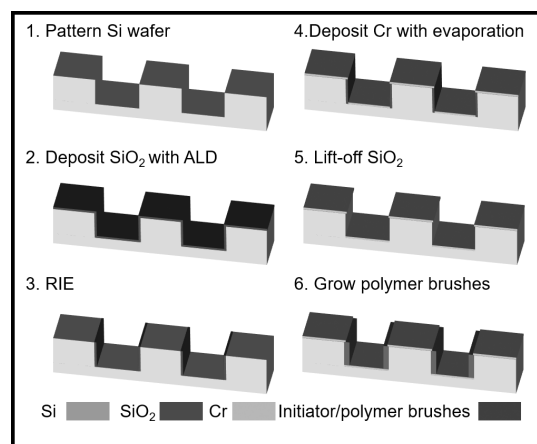

Figure 1: Fabrication process of grafting platform.

Atomic layer deposition (ALD) technique is selected for its layer-by-layer depositing mechanism allowing it to create precise, conformal layer on the grating. After deposition of thin silicon dioxide on the grating, the reactive ion etching process (RIE) is selected to remove only the top and bottom materials to achieve selectivity between sidewall and flat surface on the grating. After depositing thin chromium layers, the lift-off process with
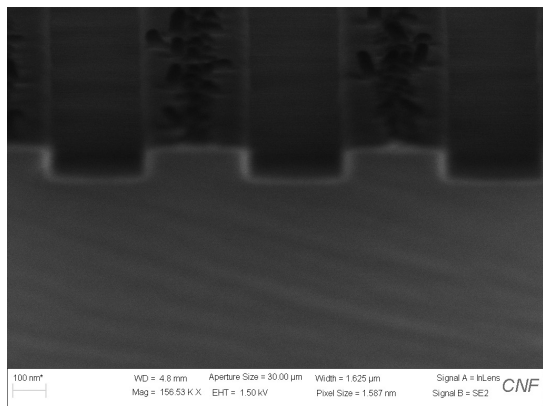
Figure 2: SEM cross-sectional image of grafting after ALD SiO$_2$ deposition.
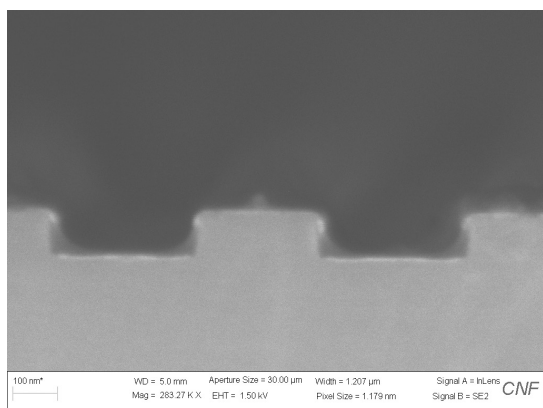

Figure 3: SEM cross-sectional image of grating with PDMAEMA brushes anchoring on sidewall.

hydrofluoric acid could remove undesired chromium on the sidewall and the required grating is obtained for the growth of sidewall-only polymer brushes.

The ALD formed SiO$_2$ is tuned to have a low density that facilitates the lift-off. The target chromium film thickness is still 5 nm for preservation of the grating original dimension.

Poly(dimethyl aminoethylmethacrylate) (PDMAEMA) brushes were then synthesized on the grating after lift-off BOE immersion. The cross-sectional scanning electron microscope (SEM) images are shown in Figure 2. It is shown that ALD successfully deposited SiO$_2$ conformally on the grating and subsequently both the top and bottom SiO$_2$ layers were removed by anisotropic RIE treatment. It was found out that the few dirt-like materials aggregated to the top of the grating are residues of the lithographic materials. Those residues could be removed with longer RIE treatment. The grating was then used to synthesize PDMAEMA brushes and the result is shown in Figure 3.

It could be observed that the PDMAEMA only anchored on the sidewall of the grating and have the maximum thickness at the bottom of the grating. This is reasonable for the fact that the confinement is no longer existing on the top of the polymer brushes, which makes them like the patterned polymer brushes as studied in the literature [4]. Without the lateral confinement (on the top of the grating in this case) the polymer chains feel no steric repulsion and therefore the stretching level of the polymer chains decreases from the bottom to top of the grating so as the thickness of the polymer brushes.

In conclusion, here we demonstrated the successful fabrication of reflective grating with polymer brushes anchored on the sidewall only. These gratings would make it possible for the neutron/laser scattering characterization responding to the change of the brush in a liquid environment and reveal further details in the structure/dynamic of polymer brushes. It is then expected that not only cationic, but also anionic/zwitterionic polymer brush characterization will soon become available after the preliminary characterization, which is still required to finalize the setup of the experiment instruments.

The synthesis of the polymer brushes with ATRP and characterization of the grafting density has been also explored and this will help fabrication of the well characterized samples. In the future, this will be used to reveal the structure of grafted molecular brushes that have more delicate 3D structures.

References:

[1] Macromolecules 2017, 50 (11), 4089-4113.

[2] ACS Appl. Mater. Interfaces 2015, 7 (22), 11857-11862.

[3] IEEE Sens. J. 2012, 12 (7), 2374-2379.

[4] Macromolecules 2017, 50 (12), 4715-4724.

Materials