Abstract:
Polyelectrolyte brushes are a special class of polymer brushes with charges present along the backbone. They have unique properties and promising applications as stimuli responsive smart surfaces for numerous areas [1]. However, a greater fundamental understanding of the behavior and stability of these brush systems in different environments is still needed. Advanced characterization tools such as neutron scattering are helpful for this purpose. Here we report the development of a novel platform that has been used in neutron scattering studies of polyelectrolyte brushes. This design enabled the growth of brushes laterally from sidewalls of trenches of patterned silica surfaces and helped us to gain insight on the relationship between the backbone and charged group on polyelectrolyte brushes.

Summary of Research:
We employed a top-down process starting with patterning a silicon wafer. In order to prevent polymer brush growth from the top and bottom of the trenches, we decided to cover those parts with chromium film (about 5 nm thickness). However, since we don’t want to have chromium residue on the sidewalls, we first deposited a sacrificial SiO$_2$ layer on the grating with atomic layer deposition (ALD). Then this layer is selectively removed from only the top and bottom of the trenches by reactive ion etching (RIE) followed by the deposition of chromium layers on these flat surfaces with atomic layer deposition. Potential chromium residue on the sidewalls is removed by hydrofluoric acid, which results in the desired grating design where the flat surfaces are covered with chromium to prevent polymerization, whereas sidewalls are covered with SiO$_2$ to be ready for lateral brush growth. Figure 1 summarizes the fabrication process.

After finishing the fabrication, poly(dimethyl aminoethylmethacrylate) (PDMAEMA) brushes with different thickness were grown from the sidewalls of the grating. Since the top of the brushes do not feel steric repulsion due to the lack of confinement [2], the polymer chain stretching is the highest at the bottom of the grating and thickness decreases towards the top. A schematic of the platform design with the polymer brush is shown in Figure 2. The neutron scattering studies that have been done with the help of our collaborators at the University of Sheffield showed good fit between the model and experimental specular data. Using these fits as input, we will further investigate brush profile by using off-specular data.

We are also planning to use the Cornell NanoScale Science and Technology Facility (CNF) for our new polyelectrolyte brush architecture that incorporates well defined charged side groups via peptoid structures. We are studying these brushes to see the effect of charge type and proximity to the backbone on brush behavior. We will use nanopatterning through CNF as a tool for controlling the geometric confinement and we will continue to fabricate the advanced platforms for further characterization of these new brush types.

References:
Figure 1, left: Fabrication process for advanced characterization platform.

Figure 2, above: Design details schematic of the platform showing polymer brush growth form sidewalls.