Characterization of Polymer Films on Silicon Photonics Devices for Blood Analysis

Alexandra S. Benson
Chemistry, Hope College

NNIN REU Site: NanoTech User Facility, University of Washington, Seattle, WA
NNIN REU Principal Investigator: Daniel M. Ratner, Ph.D., Bioengineering, University of Washington
NNIN REU Mentor: James T. Kirk, Bioengineering, University of Washington
Contact: alexandra.benson@hope.edu, dratner@uw.edu, jtk8@u.washington.edu

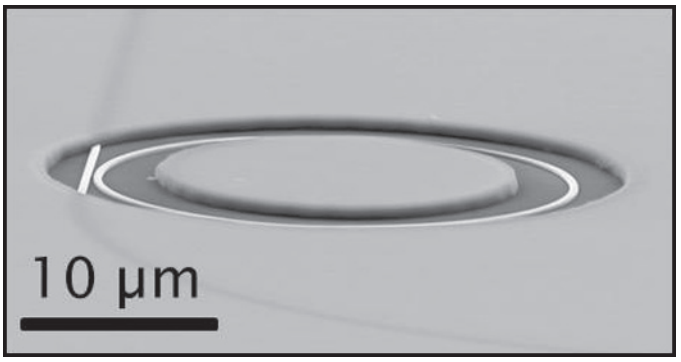


Figure 1: Silicon microring resonator on insulating oxide with fluoropolymer coating.

Introduction:

Silicon photonic devices employ nano- and microscale silicon features as optical guides to direct light in applications such as high-speed telecommunications and biosensing. The microring resonator, an archetypal silicon photonic device, consists of an optical waveguide fabricated in close proximity to a silicon ring (see Figure 1) [1]. Light at a resonant wavelength dependent on ring dimensions and effective refractive index couples into the ring; in biosensing applications, waveguides are modified using surface chemistry to facilitate selective binding of biomaterials from complex media such as blood. With any biological binding event, a shift in resonant wavelength is detected due to a change in the local refractive index at the waveguide surface. Surface protein fouling of these biosensors has been observed upon use in clinical samples, but growth of zwitterionic polymer films through atom-transfer radical polymerization (ATRP) minimizes non-specific binding events while enabling chemical immobilization of capture elements for biosensing [2].

Here, we developed a reliable protocol for the characterization of these polymer films using atomic force microscopy (AFM) to correlate topographical film quality and surface roughness with the ability of modified sensors to inhibit protein fouling. The reproducibility of the polymer film quality was essential for the potential use of these devices in clinical applications, particularly in antibody/antigen binding for performing serologic and phenotypic analysis of biologic samples.

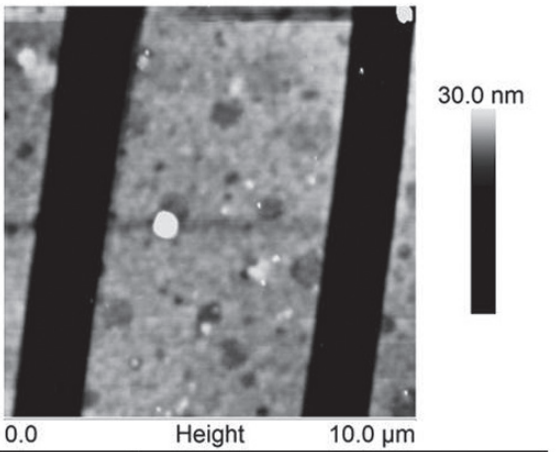
Experimental Procedure:

Silicon microring resonators fabricated by Genalyte in arrays on chips on insulating oxide were piranha-cleaned using a 50:50 solution of 30% H_2O_2 and concentrated H_2SO_4. The chips were oven-dried for several hours prior to overnight solution functionalization with a silane initiator in toluene. Using carboxybetaine methacrylate (CBMA) as the monomer for ATRP, a batch polymerization scheme was employed to produce thin polymer films. Characterization of the polymer film was performed on several chips from different polymerization batches using AFM. Both 5 μm and 3 μm scans were obtained of the waveguide and cladding to measure the average height and large-scale topography of the features on substrates both with and without polymer. Small-scale scans were also obtained in regions near the waveguide at a size scale of 1 μm in order to compare surface roughness and morphology among the bare chips and various batches of polymerization. Polymer film thickness measurements were also deduced from bare silicon substrates used as control surfaces. This was done by scanning regions in which the polymer film had been scratched away down to the silicon surface. All of these measurements were obtained in tapping mode with an OTESPA tip in air or a FESP tip in water.

Results and Conclusions:

AFM was used to measure the polymer film thickness in a scratched region of an unpatterned silicon substrate (see Figure 2). While the numbers obtained via AFM were comparable to those determined using ellipsometry, the data was not within error. Therefore, it is necessary to further develop the protocol for determining film thickness using AFM before it can be used exclusively for this characterization on the microring resonator chips. Something besides ellipsometry is necessary to determine film thickness on the chips due to the complicated architecture and small sample size of the microrings.

Further characterization of the polymer film was performed using AFM in order to correlate topographical data with quantitative data regarding protein fouling. In Figures 3 and 4, images of the topography of the polymer film from two identical batches of polymerization are juxtaposed with graphs



Method	Average Polymer Film Thickness (nm)
AFM	23.1 ± 1.3
Ellipsometry	26.74 ± 0.25

Figure 2: AFM image of scratched region of silicon substrate after first polymerization batch.

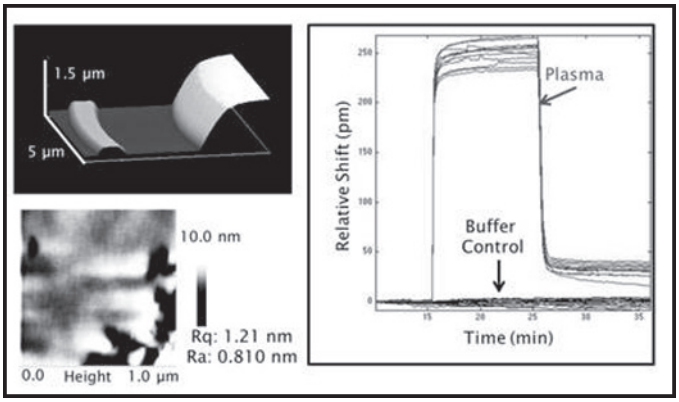


Figure 3: AFM and protein fouling data from first polymerization batch.

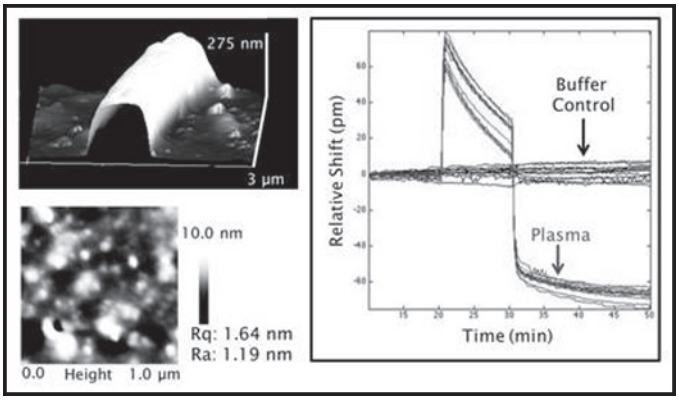


Figure 4: AFM and protein fouling data from second polymerization batch.

concerning the quantity of protein fouling. In Figure 3, the AFM image of the topography of the surface shows that it is smooth with some defects indicated by darker regions. This correlates with the graph that shows that the surface is not to non-fouling standards but does show a lower amount of protein fouling than a bare silicon substrate. In Figure 4, however, the graph shows unexpected results that could be due to a loss of polymer from the surface upon flowing plasma over the chips. This is supported by the AFM data showing that there are large features on the surface of the chip. AFM has been useful to relate the small-scale surface features to the quantitative protein fouling data and will be useful in the further optimization of the batch polymerization process.

Future Work:

The goal is to further optimize the procedure for the characterization of chips with polymer coating using AFM in order to use it more exclusively as a technique for determining polymer thickness on the microring chips for which ellipsometry is not possible. AFM will also be used in a characterization protocol to assist in the optimization of polymer film growth for minimizing protein fouling on the chips. Further, functionalization of the terminal ends of the polymer film will allow for specific immobilization of elements in complex media for detecting biological analytes.

Acknowledgements:

I would like to thank the Ratner lab, especially Dr. Dan Ratner and Jim Kirk, for their support and guidance contributing to my learning throughout my time on the project. My thanks also go out to Dr. Shaoyi Jiang's lab for assistance with the batch polymerization and the Nanotech User Facility at the University of Washington for instrumentation use. Gratitude must also be given to the site coordinator at the University of Washington, Mack Carter. Funding sources included the NSF-funded National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, and NSF Biophotonics Grant Nos. 0930411 and 1264174.

References:

[1] Iqbal, M., et al.; IEEE Journal of Selected Topics in Quantum Electronics, 16, 654 (2010).

[2] Kirk, J.T.; Brault, N.D.; Baehr-Jones, T.; Hochberg, M.; Jiang, S.; Ratner, D.M.; Biosensors and Bioelectronics, 42, 100 (2013).