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NanoWestern

Research Western

Volume 4, Issue 4 Fall 2008

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Micro-scale surface Functionalization of Poly(dimethyl siloxane)

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Poly(dimethyl siloxane), (PDMS), is an optically transparent, biocompatible polymer which is permeable to both oxygen and carbon dioxide. Because of these unique properties, PDMS has captured the interest of many researchers in the development of microfluidic devices for various applications including DNA assays, immunoassays, cell culture studies and proteomics. These applications are, however, limited due to inert, hydrophobic methyl functionality located on the surface of the PDMS.
In a collaboration between Prof. Peter Norton and Prof. François Lagugné-Labarthet, the chemical reactivity of the polymer has been investigated to impose patterned chemical functionality within a microfluidic device. Of particular interest are the amine and thiol functionalities, for their use in protein and DNA assays, respectively.
The micron scale functionality is obtained by selectively exposing a physically masked PDMS sample (Figure 1a) to an argon plasma in the Edwards Auto 500 Magnetron Sputtering System. During the plasma treatment, the lower energy methyl groups are removed and restructuring of the inner silicon-oxygen bonds results in an oxygenated surface. Following plasma exposure, the surface is coated with a thin layer of aluminium to protect the oxidized surface and prevent hydrophobic recovery (Figure 1b).

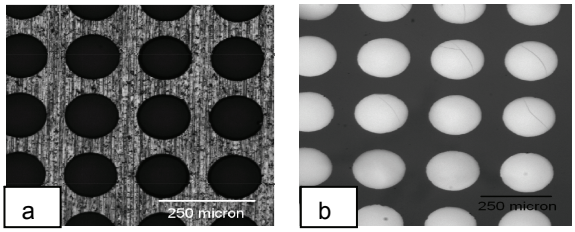

Figure 1 – (a) 180 µm stainless steel mask (b) 180 µm aluminium dots (white) on PDMS (grey)

When the aluminium is etched from the surface, a reactive hydroxyl surface is exposed, then, via silanization, the surface is altered to obtain amine and thiol functionalities.
The amine groups have been further functionalized using Fluorescein 5 (6) Isothiocyanate (FITC), a fluorescent dye which derivatizes primary amines. Using fluorescent confocal microscopy, the amine functionality of the modified regions was confirmed with very high contrast (Figure 2).

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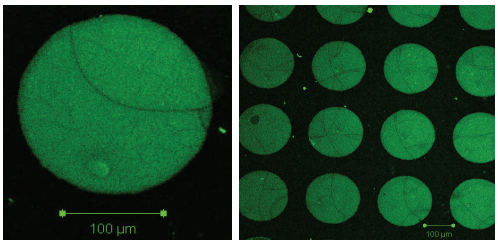

Figure 2 – Amine functionalized 180 µm diameter dots derivatized with FITC

Reservations for equipment use at the Nanofab can now be made online. Nanousers can go to uwo.ca/fab and click on the Online Reservations tab. Please contact Tim Goldhawk at nanofab@uwo.ca for login information and how to reserve equipment time.

Photonic Crystal Bio-Sensors

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Photonic crystals (PCs) are periodic arrangement of dielectric structures of two different refractive indices, generally possessing photonic band gaps - ranges of frequency in which light cannot propagate through the structure. One of the important properties of PCs, is their ability to localize light, which is achieved by introducing defects in a 2-D PC structure by either removing a single hole (point defect or micro-cavity) or a row of holes (line defect or PC waveguide). Light propagation modes in PC defects are highly sensitive to the refractive index in the vicinity of the PC[1]. When a bio-material is coated in or on a PC based sensor, it changes the effective refractive index of PC structure. This introduces a peak shift or change in the properties of the transmission. Using PCs, the size of the sensor can be dramatically reduced, less than commercial optical sensors. The nano-scale dimensions of these device allow for the fabrication of low-weight, compact and highly sensitivity parallel sensors.

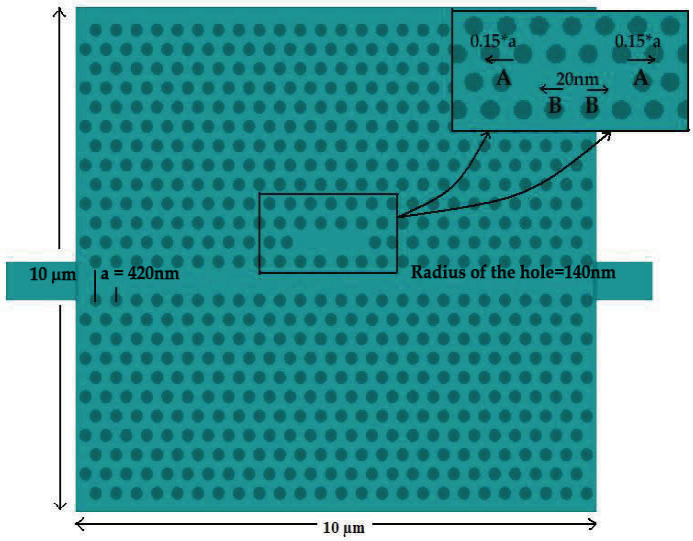

Fig. 1: PC micro-cavity sensor design

Figure 1 shows a 2D-PC micro-cavity design on a silicon-on-insulator slab designed in our group (Prof. Sabarinathan). Transmission spectrum of this device has a resonance dip at 1.555µm. The Q-factor of this device is 1000 (Q-factor is the measure of light confinement time in micro-cavity and therefore proportional to sensitivity). FDTD(finite difference time domain) techniques are used to simulate the effects on the transmission spectrum with change in thickness of bio-material coated on a PC micro-cavity. Figure 2 shows the linear shifts in transmission spectrum towards higher wavelengths with increase in bio-material coating thickness on a PC micro-cavity sensor. The PC micro-cavity sensor shows a change in transmission resonance dip of 4.57nm for a biomaterial thickness change of 2nm. If we define the sensitivity of the biosensor as the ratio of the shift in transmission resonance dip to the change in bio-material coating thickness, this sensor has a sensitivity of 2.285, which is very good for this type of sensor.

The PC structures are fabricated in the Nanofabrication lab on a silicon on insulator wafer using e-beam lithography. The patterned samples are then dry etched using the Alcatel 601E deep silicon etcher.

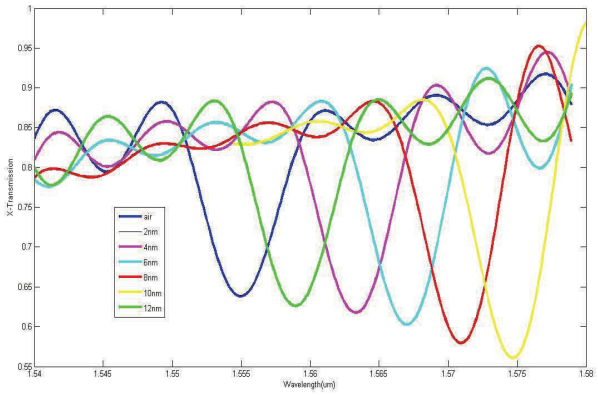

Fig. 2: The transmission data on this graph shows the shift of the micro-cavity resonance dip shifts to longer wavelength as thickness of the coating increased

The PC micro-cavity surface is then functionalized with proteins. A schematic diagram of proteins immobilization on silicon surface is shown in figure 3. The spectroscopic ellipsometer in nanofab lab was used to measure the coating thickness of the bio-material on a PC surface and was found to be 42.47±0.10 A° for our samples. The uniformity of bio-material coated on a PC sensor plays an important role in sensitivity. Non-uniform bio-material coating on a PC surface can introduce an error in measurements. Atomic Force Microscopy (AFM), in collaboration with Prof. Hutter's lab, was used to characterize the uniformity of the PC surface after coating with the bio-material.

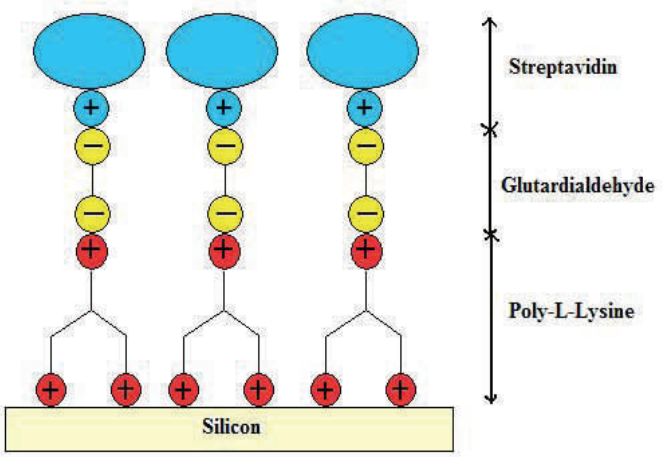

Fig. 3: Schematic diagram of immobilization of proteins on silicon surface used in this experiment

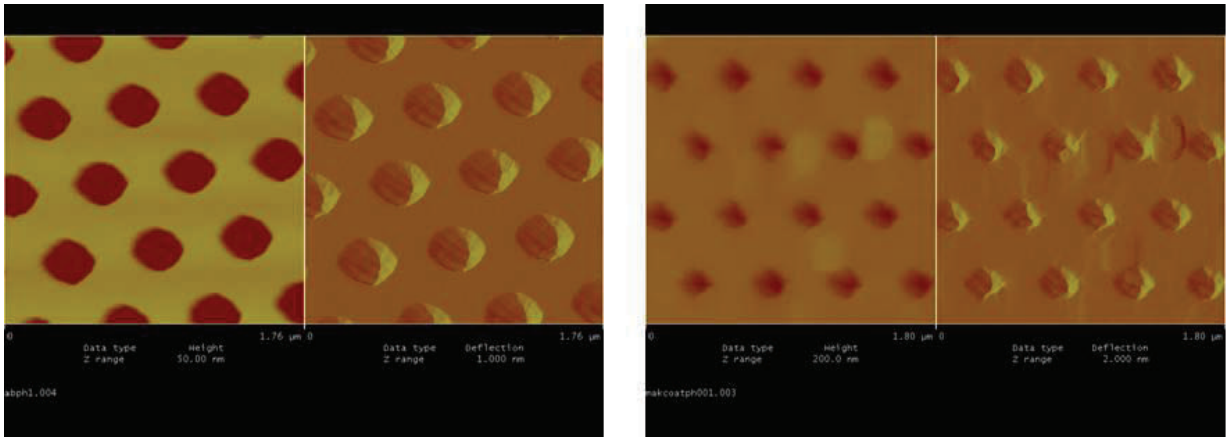

Fig. 4: AFM images of the surface of the PC, before and after bio-material coating is applied

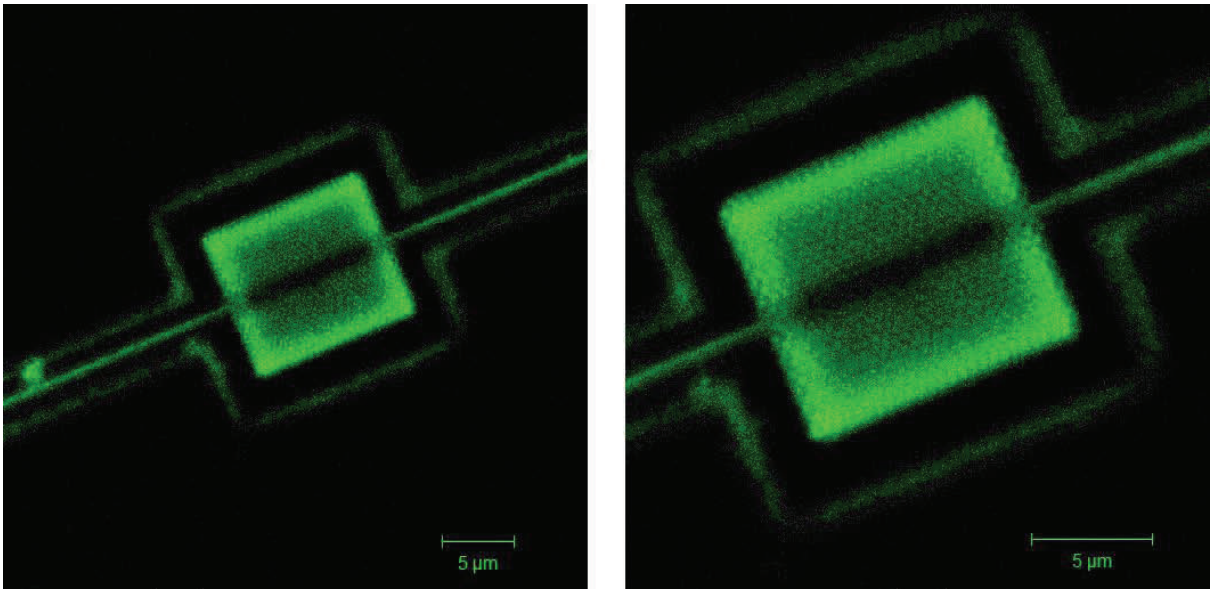

Fig. 5: Confocal images of streptavidin protein showing fluorescent signal

Figure 4 shows the AFM images of a PC, before and after bio-material coating on a PC surface. We found the surface is fairly uniform after the coating and conforms to the PC pattern. To locate where the proteins were immobilized on the PC surface, a confocal microscope was used (Bioscope Lab in collaboration with Prof. Labarthet.) to image the fluorescence signal from the proteins as shown in figure 5. The proteins were found to accumulate on the edges of the PC structure possibly due to the immobilization method used.

Immobilization of proteins on a PC device allows us to design a PC sensor which is both highly sensitive and highly selective. Immobilization of DNA on PC surface is also in progress, which enable us to detect DNA hybridization. Current work is in progress to measure the infrared optical response of the PC sensor in presence of analyte binding.

Acknowledgements: I would like to acknowledge Dr. Todd Simpson and Dr. Richard Glew for training and help on various instruments in Nanofab. I would like to thank Tim Goldhawk for his constant support in the Nanofab. I would also like to thank Jessica McLachlan for her help with confocal microscopy.

References:

Nina Skivesen, Amlie Ttu, and Martin Kristensen, "Photonic-crystal waveguide biosensor", OPTICS EXPRESS, Vol. 15, No. 6, 2007.

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Furthermore, our group has incorporated the chemical techniques inside a microfluidic channel and have achieved *in situ* functionalization of the micropatterned surface. Within the microfluidic device, the surface functionality has been investigated by studying the interaction of gold nanoparticles with the electron rich amine group (Figure 3). The amine functionality has also been exploited using the FITC dye (Figure 4).

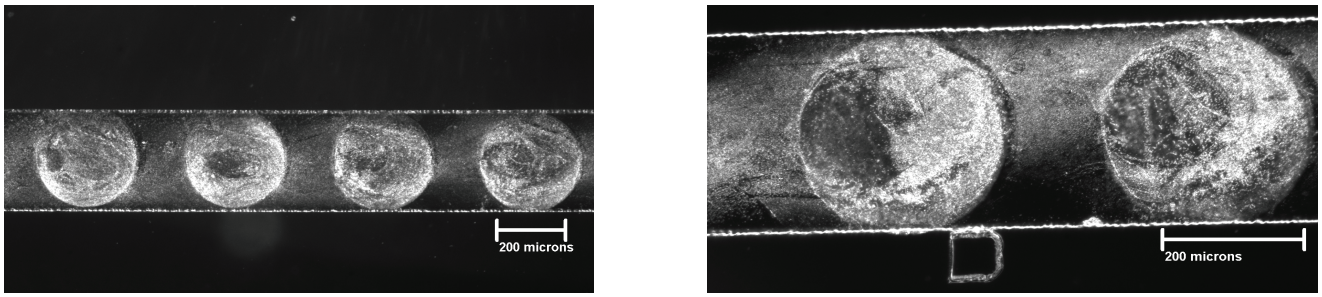

Figure 3 – 230 µm dots functionalized with gold nanoparticles inside a 300 µm channel

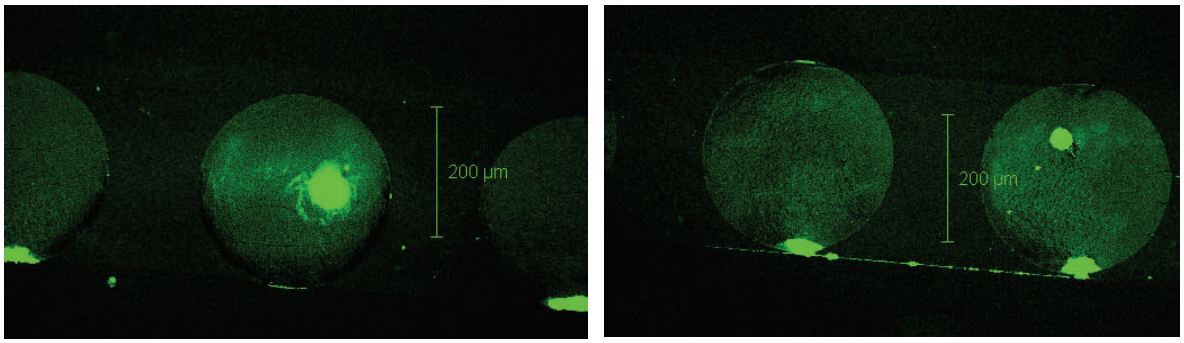

Figure 4 – 230 µm dots functionalized with FITC inside a 300 µm channel

Future studies will involve exploiting the surface functionality for protein assay applications. Using an amine reactive cross-linker, Protein A and subsequently, fluorescently labeled immunoglobulin molecules will be tethered to the patterned region.

Finally, our group will incorporate the chemical assay inside the microfluidic channel for *in situ* micron-scale protein assays.

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