Biomineralized Nanopore Membranes on Silicon for Nanoparticle Translocation

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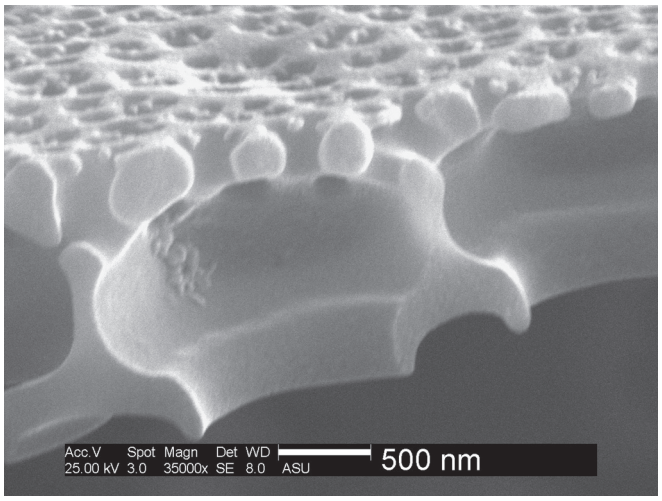

Figure 1: Scanning electron micrograph of the cross section of a diatom showing the different pore sizes.

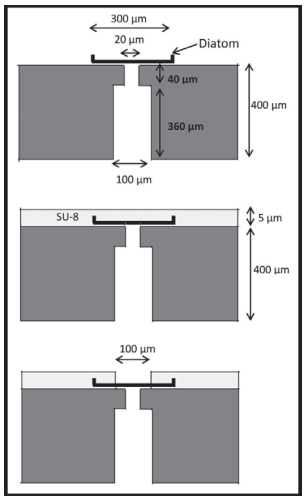

Figure 2: Schematic diagram of fabrication process.

Abstract and Introduction:

Nanopores have many biological applications. They can be used as single molecule detectors, deoxyribonucleic acid (DNA) sequencing, and potentially be functionalized to simulate lipid bilayers or nuclear pore complexes. However, these nanopores are expensive and time consuming to make using conventional microfabrication techniques. An alternative to these top-down processed nanopores is diatoms. Diatoms are a major group of algae that synthesize a three-tier network of silica pores for their cell wall, which can be seen in Figure 1. They can grow up to 300 μm in diameter, yet the smallest pores are approximately 40 nm wide. In order to have access to these nanopores, the diatoms need to be positioned and immobilized over 20 μm pores etched through silicon wafers.

Currently, the diatoms are manually placed over the pores and a UV curable epoxy, Norland optical adhesive-60 (NOA-60), is manually dispensed around the diatom. In order to create a more efficient process with a higher yield, standard contact lithography was explored to immobilize the diatoms over the micropore. The criteria used to determine the effectiveness of the process was to check for absence of leakages, breaking of the diatom or clogging of the nanopores.

Two photoresists were tested, SU-8 and NOA-60. SU-8 is a negative UV-curable photoresist that is well established in contact lithography. NOA-60 is polyurethane-based resin that adheres to glass. Therefore, it requires an anti-adhesion layer to enable release from the glass mask and the sample. Polydimethylsiloxane (PDMS) was used as the anti-adhesion layer as suggested in [1].

However, our experiments proved that the PDMS layer was ineffective in enabling separation of photomask and substrate after UV exposure. SU-8 proved to be successful in meeting the criteria in combination with a sulfuric-peroxide mixture (SPM) treatment.

Fabrication Process:

Oxidized silicon wafers with through-wafer pores were used as substrates. The pore diameter on the back side of the wafer was 100 μm and the pore diameter on the front side was 20 μm. Details on the fabrication process of the silicon micropores can be found in [2].

Diatoms were deposited on the wafer from a 1:1 water:ethanol solution and positioned over the silicon the micropore using a micromanipulator. Subsequently, positively charged poly-L-lysine was used to form a temporary bond between the negatively charged diatom and the oxidized silicon wafer. After poly-L-lysine was deposited on the chip, SU-8 3005 was spun on at 3,000 rpm for 30 seconds. Once the post-exposure bake was completed, the mask consisting of a 100 μm dot was aligned over the 20 μm through-wafer pore. Exposure was completed on an EVG-620 with a dose of 350 mJ.

After the post-exposure bake, the chip was developed in SU-8 developer for two minutes and rinsed with isopropyl alcohol. A schematic of the process can be seen in Figure 2. The SPM treatment was completed using a 3:1 ratio of sulfuric acid to

peroxide. The diatom chip was placed in the mixture for two minutes.

Results and Discussion:

Indication of open pores was found by testing for nanoparticle translocations using the setup in Figure 3. The diatom chip was placed between two chambers containing a nanoparticle solution of 100 nm polystyrene beads. Silver chloride-coated silver (Ag/AgCl) electrodes were inserted in each chamber and a constant voltage of 400 mV was applied. When a particle passed through a diatom nanopore, it changed the electrical resistance. Using the equation V = IR, a resistance increase lead to a decrease in current at a constant voltage. Therefore, a nanoparticle passing event resulted in a quick dip in ionic current.

Figure 3 shows the graph of multiple 100 nm polystyrene bead translocation events through diatom pores. The negative value of the current is due to an offset caused by the Ag/AgCl electrodes that have to pass the current. This also leads to the drift in baseline current.

One of the major concerns of using SU-8 was the possible stress it could put on the diatom during the baking process, which could cause cracking and breaking of the diatom. It can be seen in Figure 4 that SU-8 does not exert any excessive stress on the diatom. The SU-8 layer also formed a clean, complete seal around the diatom.

Conclusions:

The process described proved to be successful in immobilizing the diatoms without any leaks, breaking, and clogging the diatom's nanopores. It was found that NOA-60 was problematic to use via contact lithography, because its strong adhesion to glass, and even PDMS, prevented clean separation of the substrate from the photomask. The SPM treatment was effective in removing residual SU-8. However it is still unclear how much the cleaning step affects the pore size of the nanopores, because the size of the pores varies with each diatom.

Future Work:

Future work includes testing to determine the effect of the SPM treatment on the diatom membrane as well as a process for positioning and securing multiple diatoms over the micropores without using a micromanipulator.

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References:

[1] E. Sollier, C. Murray, P. Maoddi and D. Di Carlo, Lab Chip, 11, 3752-3765 (2011).

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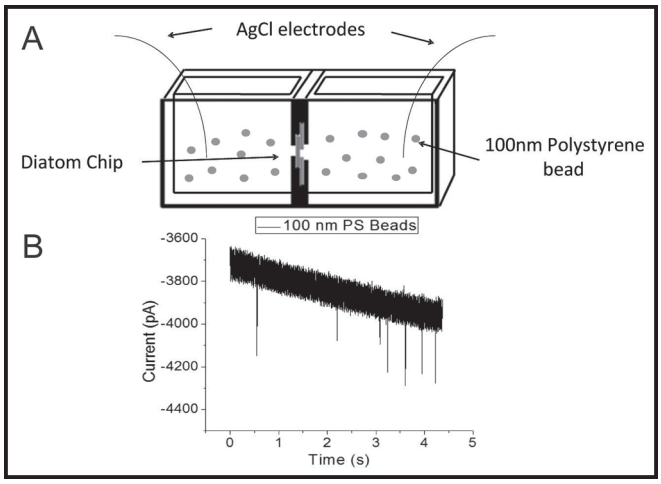

Figure 3: (a) Nanoparticle translocation setup. (b) Graph of multiple 100 nm polystyrene bead translocation events through open pores.

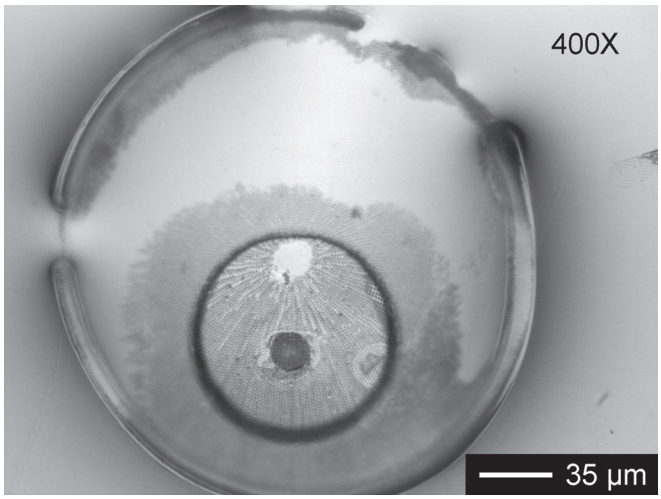

Figure 4: Optical micrograph of diatom after SU-8 coating and exposure.