Measuring the Thermodynamic Properties of Water at Negative Pressures in Synthetic Trees

Zachary Sonner
Microelectronic Engineering, Rochester Institute of Technology

NNIN REU Site: Cornell NanoScale Science and Technology Facility, Cornell University, Ithaca, NY
NNIN REU Principal Investigator: Abraham D. Stroock, Chemical and Biomolecular Engineering, Cornell University
NNIN REU Mentor: I-Tzu Chen, Chemical and Biomolecular Engineering, Cornell University
Contact: zcs7023@rit.edu, abe.stroock@cornell.edu, ic249@cornell.edu

Abstract:

Liquids at negative pressures are observed in nature as a means for liquid to travel through the xylem of a plant or tree. The mechanism by which this occurs is similar to an osmotic process whereby liquid within the xylem is placed in tension (negative pressure) through diffusion of water through an external membrane in the presence of sub-saturated air or soil. The focus of this project was the fabrication of a microfluidic device in silicon capable of holding water at these metastable, negative pressures. Bulk silicon bonded to glass was used to form holding vessels for the liquid water with a semi-permeable porous silicon membrane to couple to the outside environment. When subjected to reduced relative humidity, water vapor diffused through the porous silicon membrane placing the contained water in tension. Quantitatively, the amount of negative pressure presented from a change in relative humidity across the membrane is given by Equation 1 in Figure 1 where R is the gas constant (8.3145 J/mol·K), T is the temperature (K), V_{liq} is the molar volume of the liquid (m^3/mol) and a_v is the vapor activity, essentially the relative humidity divided by one hundred. In conjunction, the maximum amount of negative pressures able to be sustained across the membrane is described by the Young-Laplace equation as shown in Equation 2 from Figure 1 where γ is the surface tension of the water (J/m^2), θ is the contact angle made with the pore wall (°) and r_{max} is the largest pore size (m).

$$[1]\ \Delta P = \frac{RT}{\bar{V}_{liq}} \ln(a_v)$$

$$[2]\ \Delta P_{max} = -\frac{2\gamma \cos\theta}{r_{max}}$$

Figure 1: Pressure (1), and Young-Laplace (2) equations [1].

Experimental Procedure:

To create these devices 4-inch, 300 μm thick, 1-10 Ω-cm *p*-type silicon wafers were used and the corresponding process flow is shown in Figure 2. The first step involved the generation of masking layers of furnace grown silicon dioxide (SiO_2) and LPCVD silicon nitride (Si_3N_4) of 650 nm and 150 nm thicknesses, respectively. Contact photolithography was then used to generate two hundred 400 μm × 400 μm squares in two locations on the Si wafer. Using 33.3% KOH at 80°C as an Si etchant, the devices were then etched to form tetragonal pits of depth ~ 250 μm, and the nitride masking layer then removed. The backside of the wafer was coated with 350 nm of aluminum and then annealed as shown in Figure 2, Step 4.

Electrochemical (EC) porousification of the frontside then took place, which generated pores less than 10 nm in diameter for a depth of roughly 30 μm. The final step involved removal of remaining masking layers, silicon etching to open the pits to the porous silicon and anodic bonding of a borosilicate wafer to the backside. The stability limit provided by the membranes was tested by filling the cavities with liquid water and allowing it to come to equilibrium with sub-saturated vapors.

Results and Conclusions:

Figure 3 shows a scanning electron microscopy (SEM) image of the surface of the porous silicon membrane, noting all pores appeared to be less than 10 nm in diameter. This is an important factor within the membrane as this dictates the amount of negative pressure sustained as described by Equation 2 from Figure 1. Additionally, the development of these pores occurred at the propagation tip. This means that the pores will only grow to a certain size, which is dependent upon the silicon doping concentration and applied current density, and then become a self-limiting process fixing the diameters of the pores at a certain size.

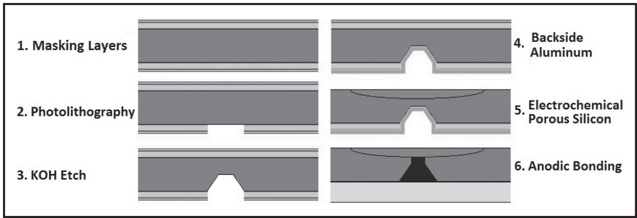

Figure 2: Process flow.

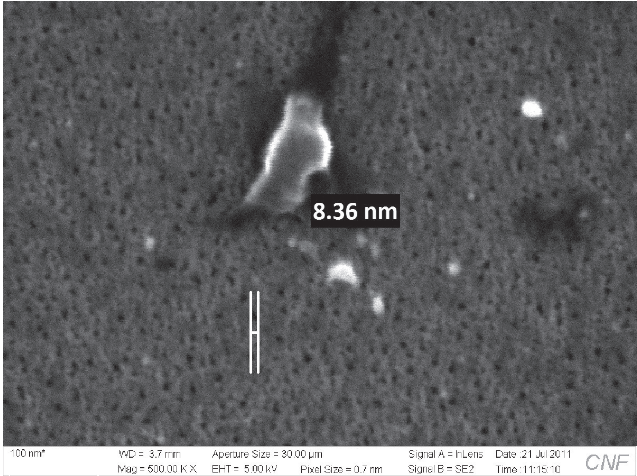

Figure 3: SEM image of pore size.

To simulate the capillary action as seen in nature, testing of the devices involved exposure to varying humidity levels. Figure 4 shows frames from a one-hundred minute timeline of one such device tested at 95% relative humidity; the backside of the device region with its many cavities is shown. Initially, all of the cavities were filled with water as explained by the ordered, lighter features highlighting the KOH cavities. When the holding vessels cavitated, the regions became dark as shown in Figure 4, where all vessels have cavitated. Cavitation at 95% relative humidity would suggest that the device withheld water just below -50 bars. However, in this short timescale, the devices did not equilibrate and were not stable at this humidity level.

Upon further inspection, the porous silicon membrane had disintegrated after testing due to instabilities related to micro-cracks within the surface of the membrane, which were created during the anodic bonding process when the devices are exposed to elevated temperatures (400°C). The fragility of the porous silicon to mechanical and thermal stresses evidently played a significant role in the quality of the membrane.

Future Work:

In addition to the brittle behavior of the porous silicon membrane, there was one main issue that arose during the development and fabrication of these devices. This problem was with leaking of hydrofluoric acid (HF) during the EC etch. The leakage occurred at the peak of the anisotropic cavities due to a stronger electric field at this location. The HF that leaked, reached the backside of the wafer; removing masking layers for the later silicon etch. With these masking layers removed by the HF, the silicon etch then roughened the surrounding surface, reducing bonding quality. A method currently being pursued is creating a deeper KOH cavity and carrying out a long (4-5 hour) EC etch. Using this method, one would perform a KOH etch for roughly 280 μm in depth and then execute a longer EC etch, which would ensure that the porous silicon reaches every cavity; also eliminating the afterward silicon etch step.

Acknowledgements:

National Science Foundation (NSF), National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, Cornell NanoScale and Technology Facility (CNF), Abraham D. Stroock, I-Tzu Chen, the Stroock Research Group, Rob Ilic, Melanie-Claire Mallison and all CNF staff.

References:

[1] Stroock, Abraham D.; "The transpiration of water at negative pressures in a synthetic tree"; Nature, 455, 208-12 (2008).

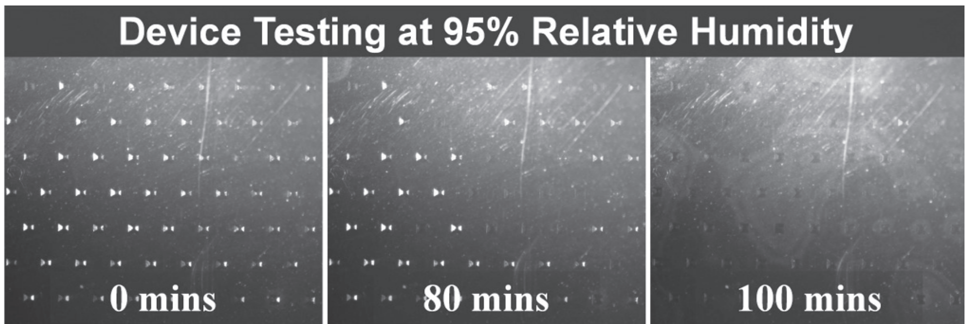

Figure 4: Device testing at 95% relative humidity.