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# Carbon Nanotube-Based Membranes: A Platform for Studying Nanofluidics

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**Abstract** — A membrane of multiwalled carbon nanotubes embedded in a silicon nitride matrix was fabricated for use in studying fluid mechanics on the nanometer scale. Characterization by fluorescent tracer diffusion and scanning electron microscopy suggests that the membrane is void-free near the silicon substrate on which it rests, implying that the hollow core of the nanotube is the only conduction path for molecular transport. Nitrogen flow measurements of a nanoporous silicon nitride membrane, fabricated by sacrificial removal of carbon, give a flow rate of 0.086 cc/sec. Calculations of water flow across a nanotube membrane give a rate of  $2.1 \times 10^{-6}$  cc/sec (0.12  $\mu$ L/min).

**Index Terms** — carbon nanotubes, nanofluidics, membranes, microfabrication

## I. INTRODUCTION

Carbon nanotubes, with their unique mechanical, electrical, and chemical properties, have been used for a variety of applications, ranging from reinforced polymer composites [1] to field-emission devices [2] and DNA sensors [3]. Consideration of their hollow cores, ranging from  $\sim 1$  nm in the case of single wall nanotubes to  $\sim 10$  nm in the case of multiwall nanotubes, suggests they may also find applications in the area of molecular separations. This size scale is comparable to that of typical biological macromolecules, making these materials candidates for biosensing. On this size scale, however, little is known about the behavior of fluids; deviations from continuum transport are to be expected as the channel size becomes comparable to molecular diameters. Furthermore, questions arise as to the wetting properties of polar fluids like water in the hydrophobic channel of a carbon nanotube. In recent years, a number of molecular dynamics simulations have attempted to model this system. Many exotic predictions have been made, from the formation of novel phases of ice [4] and pulsed one-dimensional water transport [5], to the spontaneous insertion of ss-DNA into a single wall carbon nanotube [6]. What has been lacking, however, is a platform for experimentally verifying some of these predictions. To date, there has been just one experimental study [7] claiming to demonstrate gas and ionic transport through a polystyrene/nanotube membrane. Here we aim to

reproducibly produce a robust, nanoporous membrane in which the hollow cores of multiwall carbon nanotubes serve as the only conduit for molecular transport. Alternatively, these nanotubes would serve as a template for the production of nanoporous silicon nitride and silicon oxide, materials that would allow for relatively easy surface functionalization to permit chemically specific as well as size-based separations.

## II. EXPERIMENTAL FABRICATION

The starting material is single-side polished test grade Si(100). The catalyst used for nanotube growth is iron, deposited by electron beam evaporation to a thickness between 2.5-5.0 nm. The samples are oxidized shortly after the deposition of iron (500°C, 1 hour, 10 sccm O<sub>2</sub>) to stabilize the surface. Samples are next placed into an atmospheric pressure CVD system (1" diameter tube furnace) and initially exposed to a reducing environment of Ar/H<sub>2</sub> (600 sccm/400 sccm) as the temperature is ramped up to the growth temperature of 850°C. At this point, discrete iron nanoparticles of order 20-30 nm are formed which serve as the catalyst and nucleation sites for nanotube growth. After temperature stabilization, C<sub>2</sub>H<sub>4</sub> (1000 sccm) is introduced to initiate growth. Nanotube growth occurs typically for 20 minutes and results in a dense array ("forest") of multiwalled nanotubes of  $\sim 5$   $\mu$ m length and 20-50 nm diameter, as shown in Fig. 1a. As-grown carbon nanotubes poorly adhere to the silicon substrate and thus the spaces between them must be filled by a rigid, impermeable material that conforms to the nanotube, to enable further processing into a membrane. Silicon nitride was found to possess these desirable properties. Thus, after tube growth, the samples are placed into a low pressure CVD furnace to deposit a low-stress silicon nitride layer. A target film thickness of 800 nm was found sufficient to fill the bulk of the 5  $\mu$ m thick nanotube forest. The excellent coverage offered by this material can be seen in Fig. 1b, where the film is seen to completely encapsulate the nanotubes.

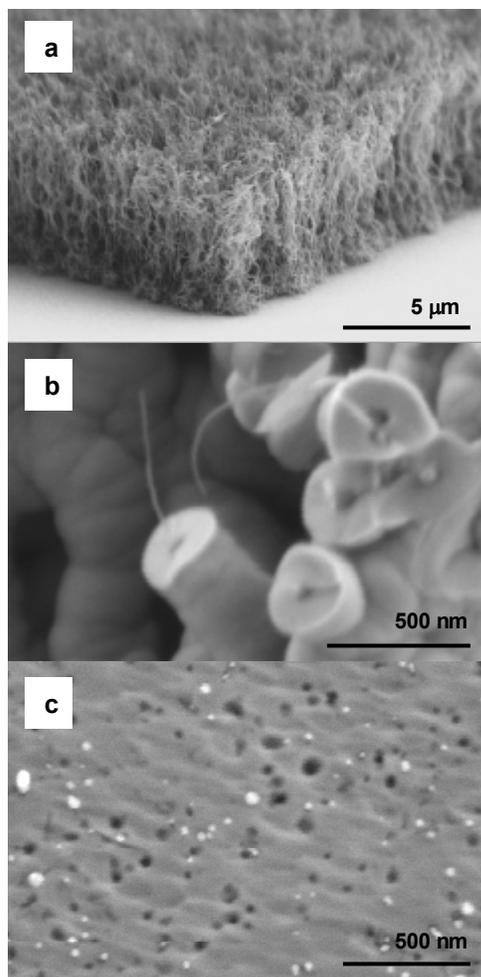


Fig. 1. (a) As-grown array of multiwalled carbon nanotubes, (b) carbon nanotubes encapsulated by a silicon nitride layer, (c) backside of membrane after KOH and HCl treatment; bright particles were confirmed by EDX to be residual iron not removed after the acid treatment.

A number of additional processing steps are required in order to produce continuous nanofluidic channels across this structure. Reactive ion etching (RIE) is used to open a window in the silicon nitride layer to expose the backside of the silicon substrate. This is followed by anisotropic KOH etching of silicon to expose the nanotube film. Energy Dispersive X-ray (EDX) analysis of this interface revealed that discrete iron nanoparticles remain, thus blocking access to the core of the nanotube. To remove these nanoparticles, the sample undergoes a brief RIE process to remove a few nm of silicon nitride and further expose the iron nanoparticle. This process also has the effect of oxidizing the nanoparticles, which are then dissolved by immersion of the sample in concentrated HCl for 24 hours. Subsequent EDX analysis confirmed the removal of a large fraction of the catalyst particles. Fig. 1c depicts the interface after this acid treat-

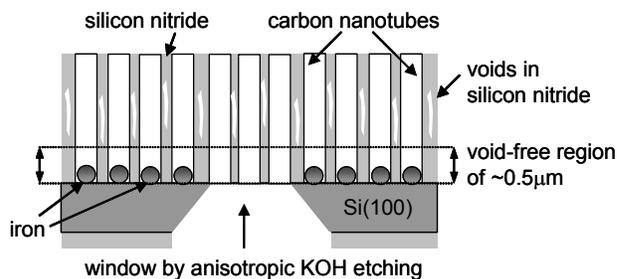


Fig. 2. Illustration of the completed carbon nanotube/silicon nitride membrane structure.

ment, with 20-50 nm pores clearly visible, comparable to the nanotube diameters. As a final processing step, excess silicon nitride on the opposite side of the sample is removed by RIE to expose the nanotubes and create a continuous nanofluidic channel. Fig. 2 is an illustration of the completed membrane structure.

### III. MEMBRANE CHARACTERIZATION

One of the principal concerns during the processing of these membranes is whether voids will be uncovered during etching of the silicon nitride. Cross-sectional micrographs of these membranes have shown a continuous, void-free region extending more than 0.5  $\mu\text{m}$  from the silicon interface (see Fig. 2 for an illustration). To further ensure that voids are not propagating through the membrane, fluorescent tracer experiments were conducted. Epoxy was used to bond the membrane to reservoirs on either side. In one side, pure water was used, while in the opposite, fluorescently-labeled polystyrene beads of first 100 nm, then 25 nm diameter were placed in solution. After a period of 48 hours, solution from the pure water reservoir was extracted and examined by fluorescence confocal microscopy. No evidence for diffusion of either labeled polystyrene was present, suggesting that voids, if present, are in the sub-25 nm regime. These measurements were followed by isotopic tracer measurements, where deuterated water was placed in one reservoir, with pure water in the other. After a period of 24 hours, a sample was extracted from the pure water reservoir and analyzed by stable isotope mass spectrometry. Again, there was no evidence for diffusion of the tracer ( $\text{D}_2\text{O}$ ) in this case. These results suggest that no voids were uncovered during processing of the membrane. It further suggests that the carbon nanotubes in the membrane are not hollow and indeed, transmission electron microscopy revealed that nanotubes grown under these conditions form a “bamboo” morphology, with periodically spaced chambers along their length.

In order to produce open, nanometer-scale channels through which molecular transport could be measured, an existing membrane was placed into an oxygen furnace (800°C, 1 hour, 10 sccm O<sub>2</sub>) to allow the nanotubes to combust. The resulting nanoporous silicon nitride membrane was then mounted in an O-ring sealed flow cell with a mass flow controller and pressure gauge upstream of the membrane. A pressurized nitrogen line was attached upstream, with the other end open to air. A control experiment utilizing a non-porous material of similar dimensions confirmed that all connections were leak tight such that the membrane would be the only gas transport path. By measuring the flow rate as a function of pressure drop, the permeance of the membrane could be determined. For pressure drops in the range from 70-2000 Pa (0.01-0.30 psi), a permeance of  $4.7 \times 10^{-4}$  mole/m<sup>2</sup> s Pa was determined. By comparing this value with that of a similar nanotube membrane of 7.5 nm diameter [7] ( $2.6 \times 10^{-6}$  mole/m<sup>2</sup> s Pa), an average pore size of 42 nm for the nanoporous silicon nitride membrane is inferred. This value is comparable to that of the multiwall nanotube outer diameter, which is to be expected since the nanotubes were used as a template for creating this membrane.

#### IV. PREDICTED TRANSPORT PROPERTIES

The behavior of fluids on the size scale of these membrane pores is expected to differ from that of bulk, continuum transport. In particular, a comparison of the mean free path at 1 atm for helium (100 nm) with that of the nitride pore size (20-50 nm) suggests that Knudsen diffusion is taking place. For modeling gas transport through the pores, sidewall collisions can be taken into account by means of the Clausing factor [8]. For a representative membrane of 5 μm thickness, with 42 nm pores, a pressure drop of 0.01 atm, and an estimated pore density of  $8.0 \times 10^{10}$  cm<sup>-2</sup> (based on the observed nanotube areal density), and an active membrane area of 0.08 cm<sup>2</sup>, a N<sub>2</sub> flow rate of 0.092 cc/sec is calculated. This compares well with the measured value of 0.086 cc/sec.

Also of interest is an estimate of the flow rate of water across the nanotube membrane. The method of van Rijn *et al.* [9] was used for this calculation, which assumes viscous, laminar flow and includes correction factors for frictional losses with the walls, interference effects of neighboring pores, and an additional pressure drop near the pore entrance. For 10 nm inner diameter nanotubes in a 10 μm thick membrane with a porosity fraction of 0.002 and a pressure drop of 1 atm, a water flow rate of  $2.1 \times 10^{-6}$  cc/sec (0.12 μL/min) is calculated. This value is considerably less than the  $1.3 \times 10^{-4}$  cc/sec (7.8 μL/min)

value determined by molecular dynamics calculations [5], which assumed frictionless transport through the nanotube. Nevertheless, the estimate obtained here suggests that liquid-based experiments should be possible with this structure.

#### V. CONCLUSION

A robust platform for the study of nanofluidics has been developed by standard microfabrication techniques. The gas permeability of a nanoporous silicon nitride membrane was confirmed and the nitrogen permeance determined. The calculated rate of water transport of order 0.1 μL/min through the smaller pore nanotube membrane suggests that the structure would be suitable for liquid-based experiments. The versatility to study nanometer-scale transport in both hydrophilic (silicon nitride or silicon oxide) and hydrophobic (carbon nanotube) versions of this membrane will bring new insights into the area of nanofluidics.

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