Self-assembly of Functional Groups Inside High Aspect Ratio Silicon Nanopores

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ABSTRACT

In this study, development of a technique for self-assembly of molecules with functional end groups inside high aspect ratio silicon nanopores is reported. A 20-μm thick porous silicon membrane with pore sizes of 5-7 nm was fabricated. The structure was then hydroxylated to enable silane-based self-assembly. A setup was fabricated to hold the membrane die between two chambers charged with dry helium. A 1 mM solution of 3-mercaptopropyl-trimethoxysilane (MPTMS) in benzene was supplied to the top side of the membrane. A constant flow of helium over the bottom of the membrane allowed continuous evaporation of the solvent from the bottom of the pores, so that the fresh solution could get into the pores from top. The pores were charged with solvent approximately 10000 times, to supply enough MPTMS molecules to fill the estimated OH sites within the pores. Penetration of the MPTMS molecules down to the bottom of the pores was verified by measuring sulfur variation through the membrane thickness using Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) technique.

Keywords: self-assembly, nanoporous silicon, functionalization, biosensing, proton exchange membrane

1 INTRODUCTION

In recent years, functionalization of porous structures has garnered intense interest. In biosensing technology, interaction between biomolecules and materials through an intermediate layer commonly with amines, carboxylic acids, and thiol functional groups is required. Porous structures provide a great advantage over flat surfaces because they provide significantly higher binding capacity (i.e. number of sites for capturing molecules) due to their high specific surface area [1]. Functionalized porous membranes can also greatly advance the fuel cell technology. Development of mechanically and thermally stable proton exchange membranes (PEMs) through assembly of functional groups within a porous solid structure enables development of the next generation membrane electrode assembly (MEAs) with enhanced performance, lifetime, and reliability.

Functionalizing porous materials has been actively researched. For example, sulfonic-functionalized porous structures were made through co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in presence of tri-block copolymer Pluronic 123 [2] or porous particles (Si-MCM-41 or Si-SBA-15 powder) were functionalized with MPTMS [3]. The common approach in self-assembly of monolayers (SAMs) inside pores of a membrane (e.g. porous silicon membrane in [4]) has been to soak the membrane in a solution containing SAMs, but poor results has been achieved since diffusion is relied upon to deliver molecules through torturous nanopores with high aspect ratios.

A simple estimation suggests that one pore volume of a 1 mM solution contains 3-4 orders of magnitude fewer molecules than necessary for complete coverage of all hydroxylated sites on the wall of a long (several microns) nanopore. Therefore, high aspect ratio nanopores should be filled with solution thousands of times to supply enough solute molecules to the pores. Increasing the solution concentration to reduce the number of filling times is not an option, since it leads to self-polymerization of the solute molecules. The approach taken in this study has been to extract the depleted solvent from the bottom of the membrane pores continuously while the solute-rich solvent is supplied to the top of the membrane.

An experimental apparatus has been fabricated for this purpose and a set of recipes has been developed to assemble MPTMS molecules fairly uniformly throughout a 20-nm thick silicon membrane. Details of the developed processes are described in the following sections.

2 FABRICATION PROCESS

A 20-μm thick silicon membrane was fabricated through KOH etching of a p-doped silicon wafer. The membrane was anodized in HF electrolyte in a standard two-chamber bath. Details about the apparatus and the process could be found in [5]. Since the primary goal for this effort was to develop a PEM in which a pore size of several nanometers is necessary to maintain a low fuel crossover level, 5-7 nm in diameter pores (cf. Fig. 1) were produced inside the membrane. This was achieved by varying several parameters including concentration of the HF electrolyte, anodization current density, and silicon doping level. The pores grew through the entire membrane thickness, except through an approximately 50-nm thick layer at the backside of the membrane that was later etched...
using reactive ion etching process. The anodization process and subsequent back etching of the membrane with SF₆ plasma rendered the porous membrane surface hydrophobic due to high concentration of fluorine on the surface and inside the pores. The surface of the pores was cleaned and hydroxylated. This process left the pores slightly wider (7-10 nm) than their original size (cf. Fig. 2).

Figure 1: SEM view of the cross section of the middle of the anodized membrane with 5-7 nm in diameter pores. Anodization was conducted in 25% HF electrolyte at a current density of about 20 mA/cm². The silicon wafer used was p-doped with a resistivity of 0.01-0.02 Ω-cm.

In a preliminary test, self-assembly of MPTMS molecules on a hydroxylated silicon surface was conducted. Results of X-ray Photoelectron Spectroscopy (XPS) confirmed presence of thiol groups on the surface. In addition, Angular Resolved XPS (ARXPS) was conducted to ensure that the MPTMS reacted with the surface through its silane end (i.e. the outermost layer on the surface is thiol).

Figure 3: Sulfur 2s binding energy of thiol (SH) terminated surface. Peak at 226.7 eV corresponds to SH. Peak at 230.5 eV corresponds to sulfonate (SO₃H) group. Some of the thiol groups were oxidized in ambient.

2.1 Functionalization Apparatus

As mentioned earlier, one pore volume of the solvent contains orders of magnitude less solute molecules necessary for all OH sites inside a long pore. For example, one volume of a 5-nm diameter, 20-µm long pore only contains 232 MPTMS molecules, when filled with a 1 mM solution, while the number of potential OH sites on the pore wall is close to 2 million. A relatively dilute solution of 1 mM was selected to avoid self-polymerization of the MPTMS molecules. Therefore, the pores should be filled thousands of times to supply the number of molecules needed in the pores. In order to achieve this goal, a setup was fabricated to allow holding the porous membrane die between top and bottom compartments of a chamber and flow the solution through the pores. Figure 4 shows a top view of the setup during operation.

Immediately after the hydroxylation process, the membrane die was placed within a fixture designed for holding the membrane between the two compartments of the setup main chamber. The chamber was put under vacuum and purged with helium multiple times to minimize water vapor presence inside the chamber. Then, the MPTMS in benzene solution was supplied to the solution reservoir on top of the
main chamber of the setup

Solution reservoir filled with liquid

Figure 4: Top view of the main chamber of the nanopore self-assembly setup and close view of the sample holder and solution supply line during operation.

membrane. While the top chamber was charged with helium and the vacuum and helium lines connected to it were closed, the lines connected to the bottom compartment were slightly open to maintain a slow flow of dry helium. The process was continued for up to 2 days to complete (i.e. supply approximately 10000 pore volumes of solution to the pores). The estimated liquid velocity inside the pore during the process was on the order of 1 μm/s.

3 VERIFICATION

Penetration depth of the functional group inside the membrane was verified using Time of Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) with depth profiling. As can be seen in Figure 5, the sulfur penetrated through the entire membrane thickness. Results show a higher count for all elements at both top and bottom of the membrane. This is counterintuitive, considering the fact that the anodization process left the pores larger at the top of the membrane than its middle. Also, the hydroxylation process enlarged the pores at the bottom of the membrane and made it more porous than its middle. Thus, silicon count should have been the lowest at both sides of the membrane. We speculate that higher count at both sides of the membrane is an artifact of the technique employed. Generally, more surface area near the beam results in generation of more secondary ions. Hence, a higher number of counts could result from a more porous surface. If this argument is true, variation of the elements count could also represent a change in the pore size. Interestingly, it appears that the silicon, oxygen, and fluorine count curves, which represent the initial construct of the porous membrane (i.e. before functionalization), have a relatively similar slope.

Also, the variations in the count curves for sulfur and hydrogen (and to some extent carbon at the first half of the curve) that represent the MPTMS presence in the pores follow a similar slope. These curves have a noticeably steeper slope than that of silicon. This suggests that the higher sulfur count up to a certain depth might not be due only to the surface effect described above, but perhaps suggests sulfur concentration is higher close to the top surface. It is not clear, however, whether this higher concentration is due to the higher surface area of the more porous structure at the top of the membrane or the presence of physisorbed molecules on the monolayer.

4 CONCLUSIONS

A nanoporous silicon membrane with pore aspect ratio of several thousands was successfully functionalized. This was achieved through development of a set of recipes for fabrication of a porous silicon membrane, its hydroxylation,
and development of a new technique for supplying the necessary number of molecules deep inside the nanopores. The results were verified using ToF-SIMS with depth profiling.

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