Fabrication of Nanoporous Ultrananocrystalline Diamond Membranes

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ABSTRACT

Nanoporous membranes have a wide range of applications in many fields, including medical diagnostics, drug delivery, and hemodialysis. Ultrananocrystalline diamond (UNCD®) coatings are becoming more and more significant in medical applications because of the highest degree of biocompatibility, unmatched by other materials. The 100-nm- and 200-nm-diameter pores have been fabricated in 1-µm-thick UNCD film on silicon wafers using e-beam lithography, reactive ion etching and laser writing.

Keywords: ultrananocrystalline diamond, RIE, e-beam lithography, nanonporous diamond membrane

1 INTRODUCTION

Nanoporous membranes engineered to mimic natural filtration systems can be used in smart implantable drug delivery systems, bioartificial organs, and other novel nano-enabled medical devices [1]. Some of the key properties required by these membranes are narrow and controlled pore size distribution, high pores density and low thickness to enable high flux, as well as mechanical and chemical stability. Nanoporous silicon [2] and silicon nitride membranes [3] have been used in drug delivery systems [4]; silicon nanopillars [5] were used for capturing circulating tumor cells in blood. Interestingly, irrespective of the regular nature of pore geometry, blocking of pores by proteins or cell debris is still a major problem. Biocompatibility and anti-biofouling are central issues when membranes are used as interfaces in implantable devices.

Ultrananocrystalline diamond films are becoming more and more significant in medical applications because of the highest degree of biocompatibility and anti-biofouling, unmatched by other materials [6]. The porous diamond membranes may open new opportunities in implant medicine.

Here we report results on high porosity, high-aspect-ratio ultrananocrystalline membranes fabricated using e-beam lithography, reactive ion etching and optical lithography.

2 EXPERIMENTAL

The nanoporous membranes were fabricated from 1-µm-thick UNCD films (Aqua 25 UNCD®, Advanced Diamond Technologies). These UNCD films have the hardness, Young's modulus, and other extreme properties of natural diamond, as well as smooth (~7 nm rms) surface, and a very low internal stress, which is essential for membrane fabrication [7]. The nanoporous UNCD membrane fabrication followed the sequence shown in Figure 1, as detailed in the following subsections. The optical masks for alignment marks and membrane were fabricated with a LW405 MicroTech laser writer system, and the array of holes was patterned with a Raith 150 e-beam lithography equipment.

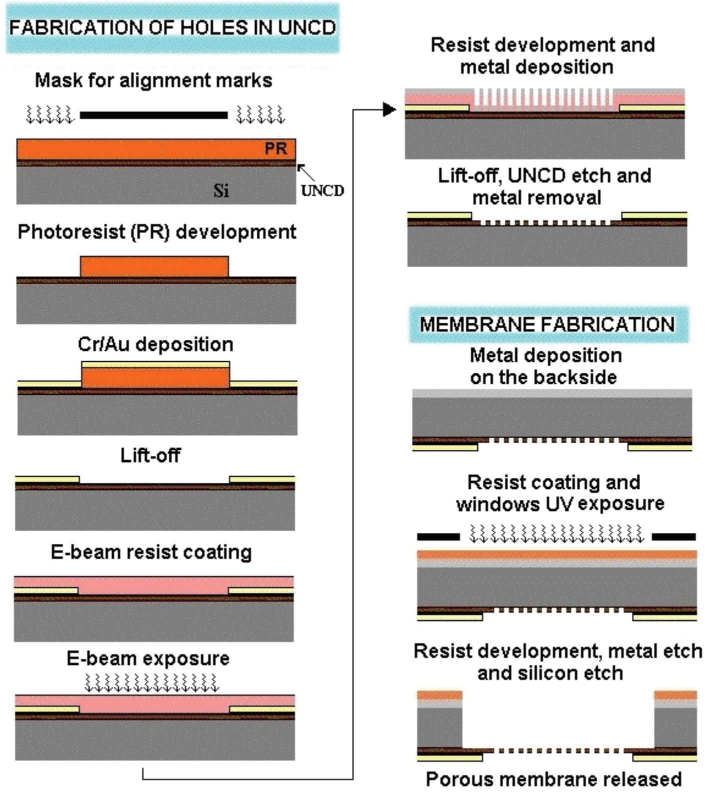


Figure 1. Illustration of the fabrication of holes and UNCD membrane.

The front-to-back side alignment and optical lithography were performed with a Karl Suss MA6 aligner. Metal depositions were performed with a Lesker PVD-250 electron-beam evaporator with a Sigma deposition controller.

2.1 Fabrication of holes in UNCD

The UNCD surface was treated prior to resist coating with hexamethyldisilazane vapors for 20 min in a YES-3/5TA priming oven (Yield Engineering Systems) at temperature of 150°C and 1Torr. This step improved the resist adhesion significantly.

The alignment marks were patterned separate from the main arrays of holes by direct write optical lithography, to avoid time-consuming large area exposures with the e-beam lithography tool. 0.5-μm-thick positive resist (S1805) was used (spin coated at 3000 rpm and baked on a hot plate at 115°C for 1 min). The alignment marks were fabricated by lift off, using a Cr/Au (5 nm/20 nm) layer, providing good contrast in scanning electron microscopy (SEM) mode for alignment in the e-beam lithography tool. These marks allowed a 3-points alignment in the e-beam writer and for backside optical lithography alignment.

The 25 nm films were evaporated at room temperature, with a base pressure of 2 x 10^{-8} Torr at a deposition rate of 2 Å/s. The lift-off step was performed in 1165 remover (Rohm and Haas) at 70°C for 30 min.

After cleaning with piranha solution for 10 min the samples were treated again in the priming oven. Negative e-beam resist ma-N 2405 (Micro Resist Technology GmbH, Germany) diluted 1:1 in anisole was spin coated at 3000 rpm to obtain ~200 nm-thick layer, followed by baking on a hot plate at 100°C for 90 sec, e-beam exposure, and then development in ma-D 533S developer (Micro Resist Technology GmbH, Germany) for 12 s. Resist exposure was performed using a Raith 150 e-beam system, an acceleration voltage of 20 keV, a beam current of 250 pA, and a dose of 300 mC/cm^2. The pattern consisted of arrays of 100- and 200-nm-diameter circles with a separation distance of 400 nm between the circle centers. The usage of negative resist for this process is essential in reducing the exposure time and the negative side wall angle after development facilitates the lift-off task.

To obtain a hard mask for pattern transfer in UNCD, after resist development, a ~5-nm-Ti and ~55-nm-thick Ni layers were e-beam evaporated using the Leskar system at a deposition rate of 3 Å/s. The proper choice of the metal for the lift-off mask is very important. It was shown [8] that Al can be used as hard mask for etching UNCD, but the sputtering yield of Al is high and metal re-deposition on UNCD surfaces can lead to a significant slow-down of the etching process and roughing of the etched surfaces. For this reason, and because Ni was shown to be a durable mask in inductively coupled plasma reactive ion etching (ICP-RIE) of nanometer size holes in GaN [9], it has been chosen as a hard mask for UNCD etch. Lift-off of the Ni was done at 100°C in 1165 Remover for 3 hours, and an ultrasonic agitation was used for 90 s at the end of this step.

The UNCD layer was etched by ICP- RIE using oxygen plasma in a PlasmaLab 100 System (Oxford Instruments). The etching recipe used O_2 =50 sccm (sccm denotes standard cubic centimeter per minute at standard temperature and pressure, STP), SF_6 = 0.5 sccm, pressure 9 mTorr, temperature 20°C, ICP power 2700 W, and RIE power 300 W [10]. At these parameters, UNCD etching rate on large open surfaces was found to be ~500 nm/min and Ni etching rate was ~ 20 nm/min. After UNCD etching, the hard mask was removed in Cr etch solution (Transene). One wafer was cut at 90° angle using a dicing saw (Thermocarbon TCAR 864-1 Programmable Dicing Saw), and the cross-section of the UNCD was examined using SEM of an FEI Nova NanoLab microscope, to certify the complete through-etching.

2.2 Membrane fabrication

A 5-nm-thick Ti and 250-nm-thick Ni layers were deposited on the back side of the silicon wafers with patterned UNCD layer. Positive resist S1818 of 1.5-μm-thick layer was spin coated at 3000 rpm and baked on a hot plate at 115°C for 1 min. The resist was exposed with the second optical mask for window fabrication using backside alignment method with MA6 mask aligner. After development for 30 s in 351 developer, diluted 1 to 3, the metals were wet etched. The Si etching for membrane fabrication was done in PlasmaLab 100 System ICP chamber using: 50 sccm CHF_3, 7 sccm SF_6, pressure 15 mTorr, RF power 30W, ICP power 1200W at 20°C.

The UNCD membranes contain 100-nm- and 200-nm-diameter pores forming arrays stretching over a 5 mm x 5 mm area, with a silicon frame of 15 mm x 15 mm (Figure 2).

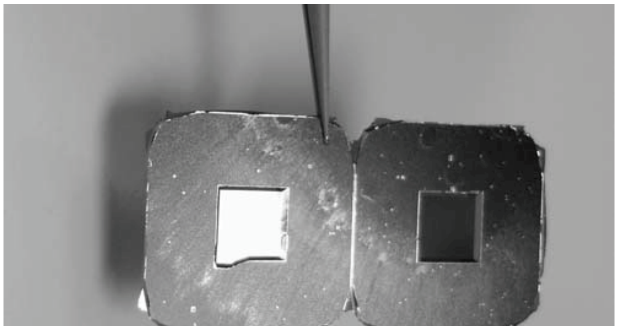


Figure 2. Photograph of the UNCD membranes on Si wafer.

3 RESULTS AND DISSCUSSION

A micrograph of the sample after lift-off with 100-nm-diameter openings in Ni layer is shown in Figure 3.

We noticed some residual spots on the metal layer, which could be attributed to resist residue or to non-uniformity of metal coating. They didn't affect on performing the next step of UNCD etching.

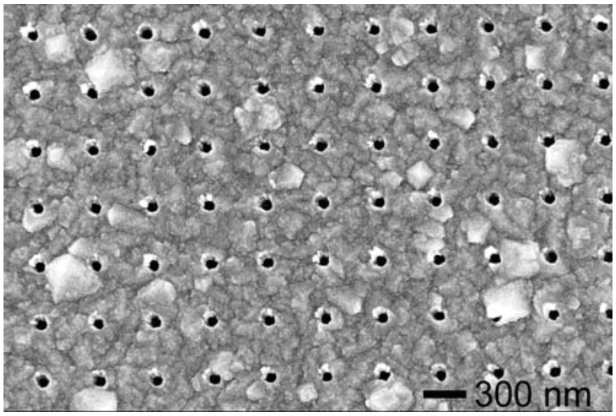


Figure 3. SEM image of the sample after lift-off.

For the used etching parameters, the etching rate of Ni was found to be ~ 12 nm/min, so 4 min is a max possible etching time for using ~ 55- nm-thick Ni mask. The thickness of Ni layer was limited by e-beam resist thickness in order to obtain ~ 100-nm-diameter circles and perform then lift-off.

Using 200-nm-diameter openings in Ni mask, ~ 1 µm-deep pores have been obtained in UNCD after 4 min-etching (Figure 4).

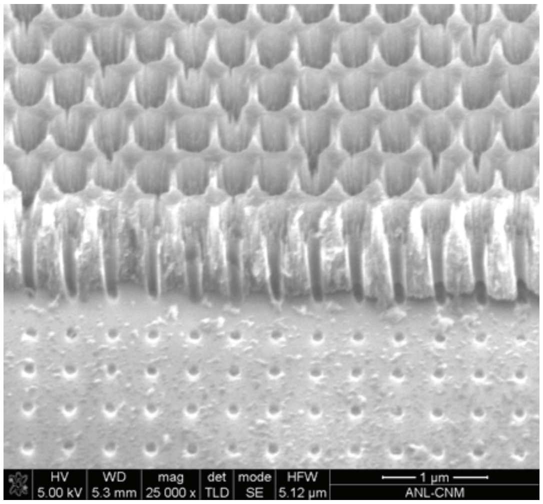


Figure 4 Cross-sectional SEM image of UNCD film that was etched using ~200-nm-diameter openings in Ni mask.

The Ni mask was completely etched in 4 min and this caused an increase in pore sizes at the surface. The holes were etched through, down to the Si surface where the hole pattern was slightly transferred into the Si due to the fluorine content of the plasma mixture. For the same etching time the 100-nm-diameter openings were not etched through, as shown in Figure 5.

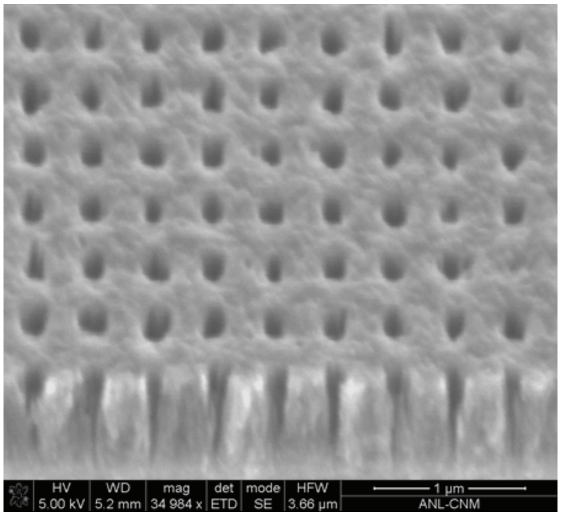
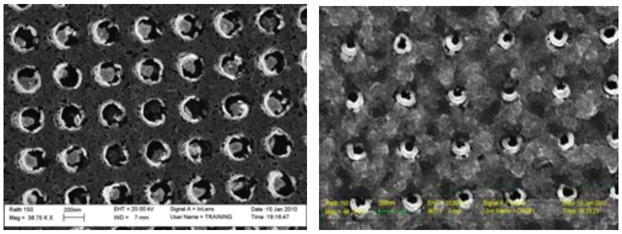


Figure 5. Cross-sectional SEM image of UNCD film with 100-nm-diameter pores, which were not etched completely. through openings in Ni mask.

A longer etching time is required to obtain etched through ~100-nm-diamter pores but thicker layer of Ni is needed. Based on these results, we did similar experiments with a thicker Ni layer (80 nm) pushing the limits of the lift-off step for a 200-nm-thick resist layer. With this Ni thickness it was possible to etch through ~100-nm and ~200-nm-diameter holes in ~1-µm UNCD layer. In Figure 6 SEM images of the membrane with 200-nm (left) and 100-nm-diameter (right) pores are shown.



(A)/ (B)

Figure 6. SEM image of the membrane with 200-nm (A) and 100-nm-diameter (B) pores.

Thin UNCD membrane has very low conductivity, and we could perform SEM metrology only after coating the membrane with a conductive polymer ESPACER 300 (Showa Denko, Japan). Even with ESPACER the sample was charging a lot, and it is likely that the residue-like features around the holes in the SEM images can be attributed to the low conductivity of UNCD thin film because the cleaning with piranha solution didn't change the quality of the images.

4 CONCLUSION

High porosity (~ 50%), high-aspect-ratio (up to 10:1) UNCD membranes with 100-nm and 200-nm-diameter pores were fabricated using e-beam lithography, reactive ion etching and optical lithography. Ni mask showed good durability in the RIE-ICP etching of diamond film. Pore diameters were limited by the thickness of the Ni mask. Further experiments will investigate the usage of SiO_2 as hard mask for UNCD pore etching.

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