Formation of Nanopore-Arrays by Plasma-based Thin Film Deposition

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The ability to fabricate membranes with arrays of apertures only a few nanometers in diameter are important to many fields of research, including ion beam lithography[1], DNA sequencing[2], single ion implantations[3], and single molecule studies. Because even the state-of-the-art lithography tools are limited in their ability to produce nanoscale features, alternative methods of fabricating single pores of nanometer scale have been developed, using ion-beam sculpting[2] and focused-ion-beam assisted deposition[4]. However, these methods cannot simultaneously produce multiple holes of nanometer dimension. Here we report a means of forming arrays of nanopores simultaneously on a thin, solid-state membrane using plasma-based thin-film deposition. By depositing layers of metallic thin films, the aperture sizes of pores in a pre-fabricated membrane can be reduced from a couple of micrometers down to tens of nanometers and even smaller. The technique offers a way to reduce the sizes of aperture of any shape in a variety of substrate materials, both conducting and insulating. Such arrays of nanopores can serve as membrane channels for DNA sequencing, as masks in ion-beam imprinters, for the fabrication of quantum dots, and in other applications.

Currently methods of producing nanoscale pores in membranes have important limitations. One method of fabricating holes with dimension of tens of nanometers is to use electron-beam lithography, followed by reactive-ion etching. But achieving smaller feature sizes is difficult, and because the process includes resist exposure and etching it is slow. Holes directly milled by focused ion beam (FIB) are limited in dimension to the beam diameter, which is about 10 nm, and arrays of apertures must be drilled one aperture at a time. Molecular-scale nanopores in silicon nitride (Si_3N_4) films have been reported using the technique of ion-beam scuplting[2]: apertures with an initial diameter of 100 nm were fabricated in a free-standing Si_3N_4 membrane supported on a silicon frame. Irradiating the holes with a 3-keV argon ion (Ar^+) beam caused them to close rather than open up, resulting in nanopores 2 to 3 nm in diameter, as controlled by a feedback monitoring circuit. However, this technique can only be applied to insulating membrane, such as Si_3N_4 and silicon dioxide (SiO_2), and multiple simultaneous nanopores have not been reported using ion-beam sculpting. Another method of fabricating nanopores is to use a dual beam system employing an FIB and a scanning electron microscope (SEM)[4]. Apertures ranging from 50 nm to 600 nm in diameter are premachined using an FIB, followed by gas-assisted deposition using an FIB/SEM dual beam. Depositing a film of metal like platinum around the edges of the aperture makes them smaller and smaller. Like the ion-beam sculpting technique, forming multiple nanopore arrays with FIB/SEM is very slow.

In this letter, we describe a simple method of forming nanopore arrays by simultaneously shrinking apertures of micrometer dimensions using plasma-based thin-film deposition.

As shown in Figure 1, a metallic thin film such as copper or nickel is deposited on a substrate placed in a plasma. Over time, the size of an aperture in the substrate gradually

shrinks due to the buildi-up material deposited on the surface and sidewalls. By carefully controlling deposition time, nanopores of any size can be obtained. In the case of copper, plasma is generated by a radiofrequency-driven multicusp source with a copper antenna; argon is introduced into the source chamber to generate the plasma. Neutral copper atoms are first sputtered from the antenna by the background Ar^+ ions. These atoms are subsequently ionized by the plasma electrons.[5-6] Copper thin films steadily grow on the substrate placed in the plasma. The growth rate can be adjusted by varying the plasma operation condition. A deposition rate as high as 130 nm/min has been achieved.

The plasma-based thin-film deposition technique has two significant advantages. First, there is no restriction on the material that can be used for membranes. The presence of a plasma eliminates any charging problem, allowing uniform thin-film coating on either conducting or insulating samples. In the experiment reported here, a membrane was prepared as a pattern generator for an ion-projection lithography system.[7] Starting with a bare 4”-diameter silicon wafer, boron dopants were diffused into the front side of the substrate from a solid source at 1100 ^{0}C for 7 hours. By this means a boron concentration higher than 10^{20} cm^{-3} can be obtained in the top 5-_m layer of silicon; this silicon layer heavily doped with boron was used as an etch stop in a later wet-etch step employing potassium hydroxide (KOH). After boron diffusion, 30 mins of wet oxidation was performed at 850 ^{0}C, followed by 150-nm-thick low stress nitride (LSN) deposition on both sides of the wafer. LSN was used as a mask during KOH wet etching in order to pattern 1-mm^2 windows on the backside of the wafer. After the KOH etch, a silicon membrane approximately 4 _m thick remained. A focused gallium ion (Ga^+) beam was then used to drill apertures of different dimensions in the membrane.

A second advantage of this technique is that there is no restriction on the initial dimension of the premachined apertures. Starting with a silicon membrane with an array of 5-μm-diameter apertures, as shown in Figure 2 (A), the apertures become smaller after nickel deposition for 30 min (Figure 2B). The shrinkage of the multiple apertures was achieved by depositing thin films on the substrate surface and sidewalls. The SEM micrographs in Figure 2(B) and 2(C) show that the diameter of each hole was uniformly reduced to approximately 2 μm. The picture of the back of the hole in Figure 2(D) indicates that the shrunken apertures are cone-shaped; with conformal plasma deposition, apertures with straight sidewalls can be obtained. By controlling deposition time, aperture sizes of tens of nanometers have been achieved from initial hole sizes of several micrometers. Figure 3 shows a series of apertures before and after copper deposition. After 2.5 hours of coating, the diameter of a circular hole was reduced from 1.7 μm (Fig. 3A) to approximately 1 μm (Fig. 3B). Varying the plasma conditions results in different thin-film growth rate; by this means the diameters of the holes shown were reduced from 1 μm (Fig. 3C) to 750 nm (Fig. 3D) and from 630 nm (Fig. 3E) to 200 nm (Fig. 3F), respectively.

There is no limit to how small the aperture will shrink before it is fully closed up. By depositing layer after layer of copper film the size of an aperture continues to shrink, as shown in Figure 4. During subsequent copper depositions, the width of a nanoscale slit was continually reduced, from 250 nm (Fig. 4A), to 190 nm (Fig. 4B), to 75 nm (Fig. 4C), to 55 nm (Fig. 4D). Finally, after approximately four hours of copper ion deposition, the size of the aperture was reduced to approximately 20 nm. Presently the dimension of nanopores is gauged only by the deposition time. Accurate control of the

final aperture size can be achieved by monitoring the ion current that passes through the aperture.

This method is useful for fabricating a variety of nano-structures. Similar shrinkage was observed for several different geometries besides round holes, including rectangular slits. The oval feature shown in Figure 4A maintained the same oval shape after the shrinkage, as illustrated in Fig. 4D.

Formation of nanopore arrays using plasma-based thin-film deposition offers a promising new approach for achieving feature sizes of nanometer scale with high throughput. The technique will find many applications, including fabrication of masks for ion-beam imprinter, implantation of quantum dots and wires, and the production of multiple channels for DNA sequencing.

Acknowledgments

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Figure Captions:

Figure 1: Schematic diagram of forming nanopores using plasma-based thin-film deposition. The aperture size gradually shrinks due to the copper deposited on the surface and sidewalls.

Figure 2: (A) Premachined silicon membrane with an array of 5-μm-diameter apertures. (B) After nickel deposition for 30 min, the diameter of each hole was uniformly reduced to approximately 2 μm. (C) Front of the aperture. (D) Back of the aperture.

Figure 3: A series of apertures before and after copper deposition. Aperture I: (A) before and (B) after the deposition. Aperture II: (C) before and (D) after the deposition. Aperture III: (E) before and (F) after the deposition.

Figure 4: SEM micrographs of an aperture after each subsequent copper depositions. The size of the aperture continues to reduce from (A) 250 nm, to (B) 190 nm, then to (C) 75 nm, and finally (D) reaches 55 nm.

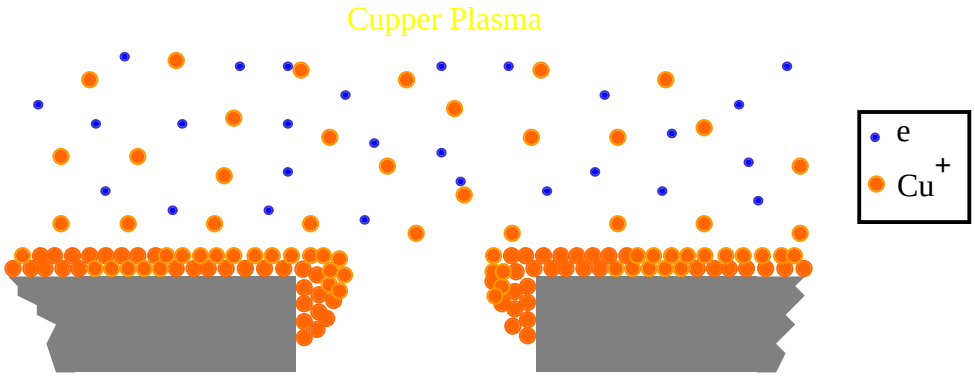


Figure 1

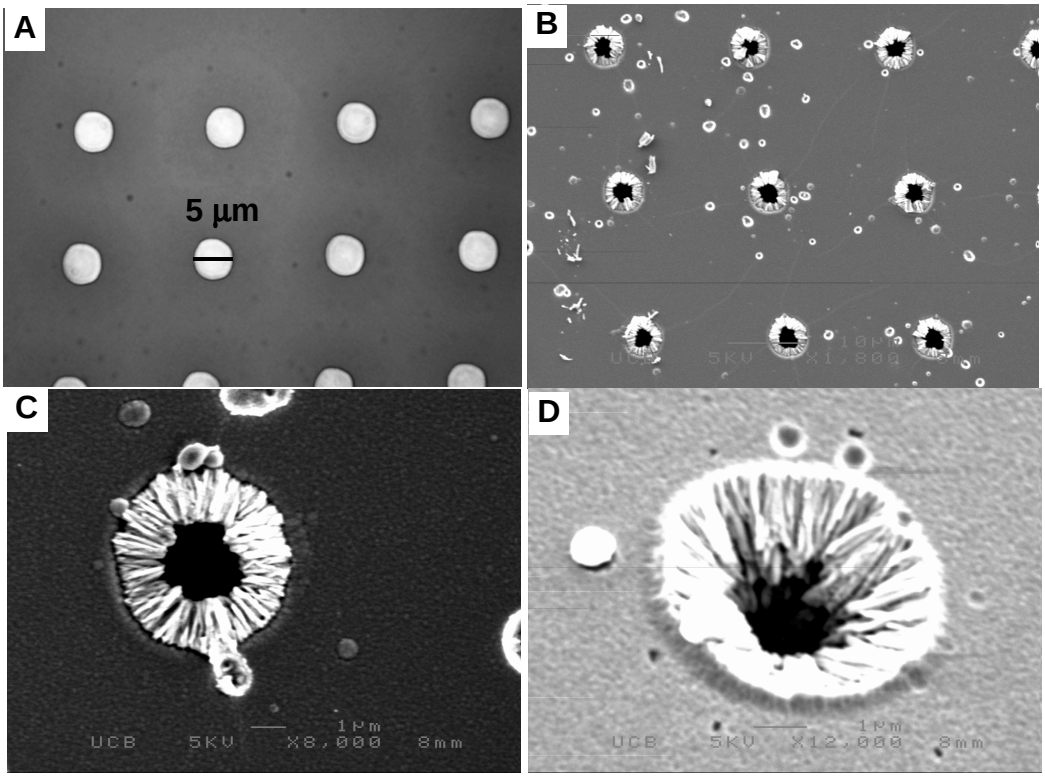
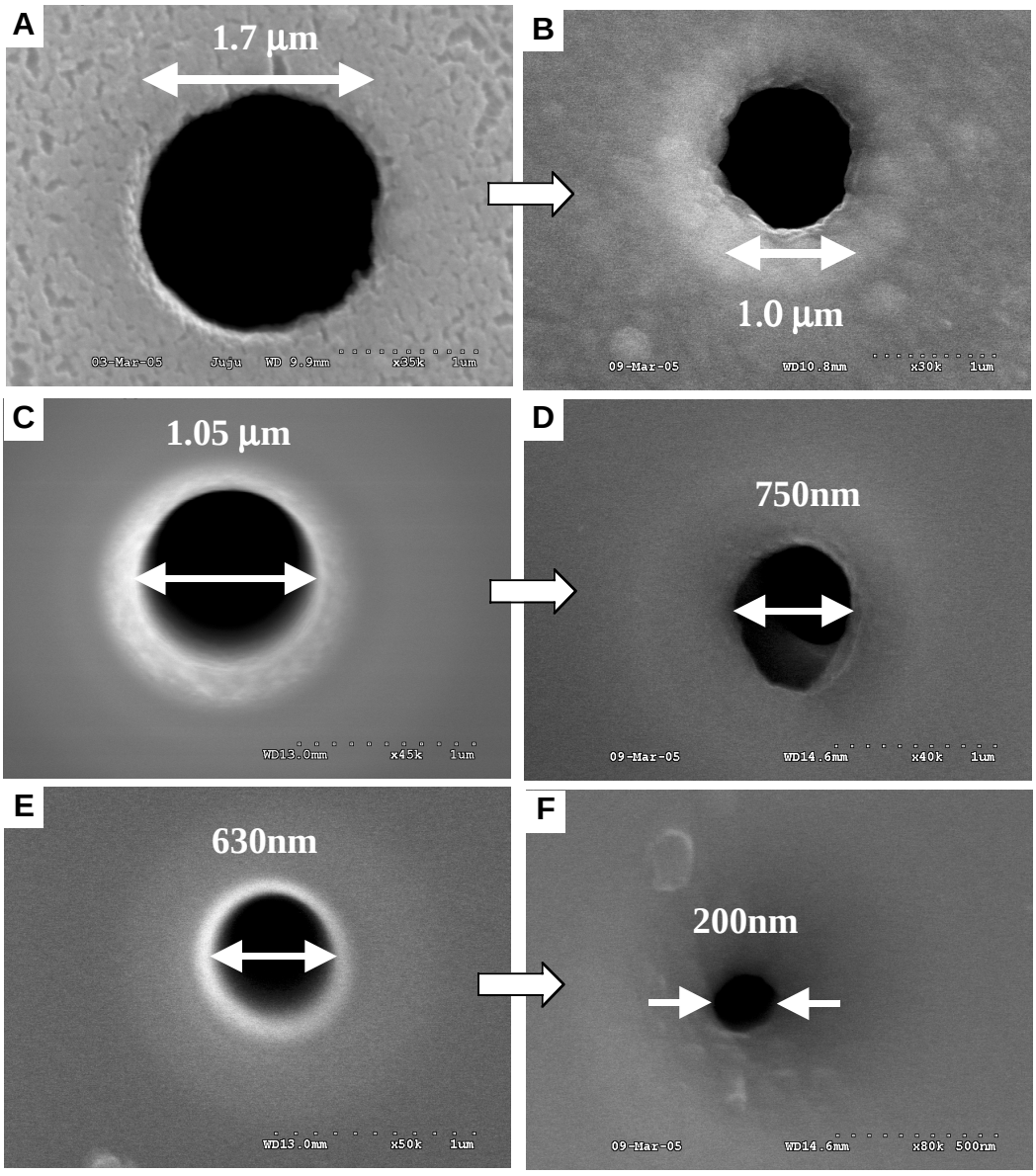


Figure 2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1.7 µm
03-Mar-05 Juju WD 9.9mm x35k 1um
B
1.0 µm
09-Mar-05 WD10.8mm x30k 1um
C
1.05 µm
WD13.0mm x45k 1um
D
750nm
09-Mar-05 WD14.6mm x40k 1um
E
630nm
WD13.0mm x50k 1um
F
200nm
09-Mar-05 WD14.6mm x80k 500nm

Figure 3

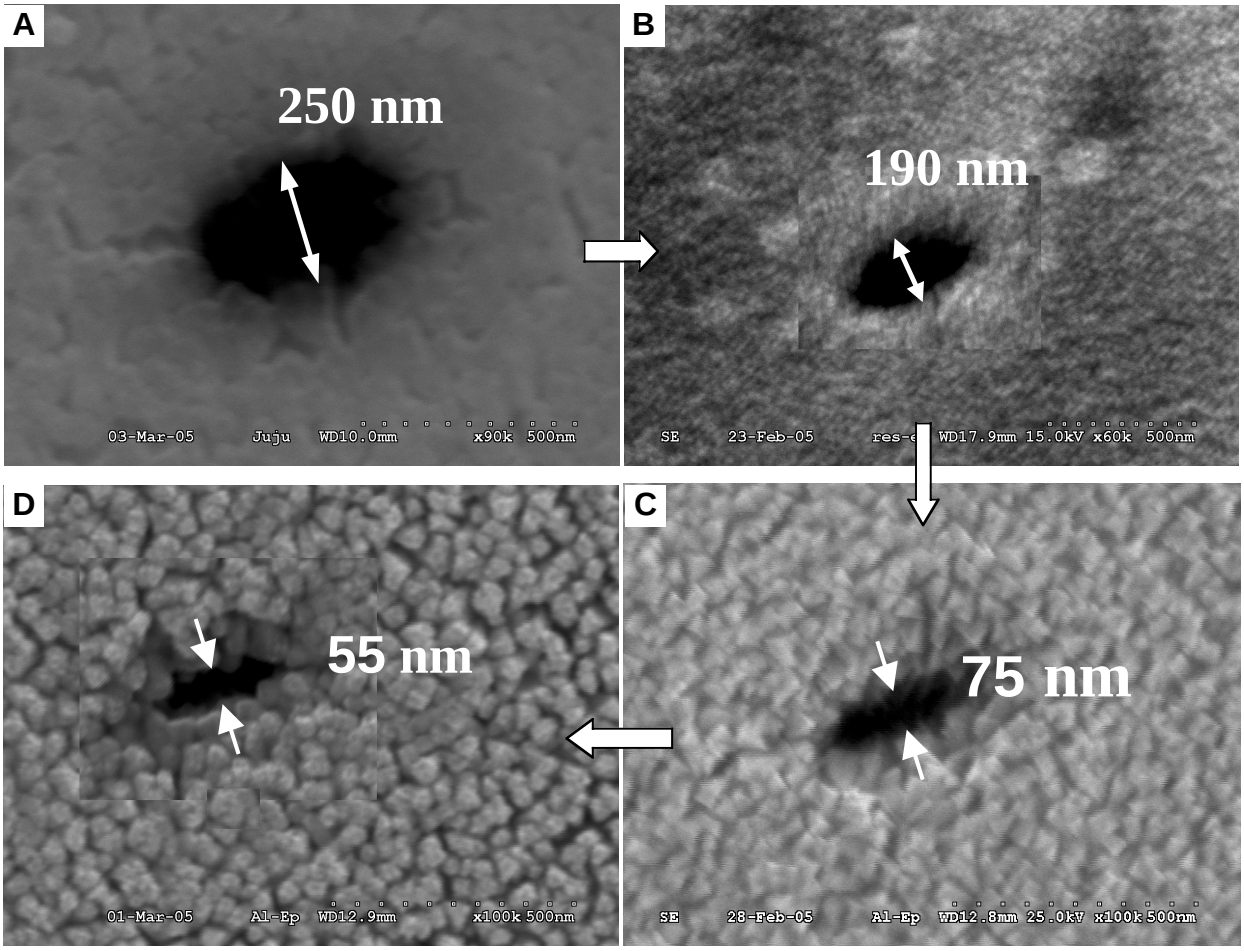
A
250 nm
03-Mar-05 Juju WD10.0mm x90k 500nm
B
190 nm
SE 23-Feb-05 WD17.9mm 15.0kV x60k 500nm
C
75 nm
SE 28-Feb-05 Al-Ep WD12.8mm 25.0kV x100k 500nm
D
55 nm
01-Mar-05 Al-Ep WD12.9mm x100k 500nm

Figure 4