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Fabrication of symmetric sub-5 nm nanopores using focused ion and electron beams

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Abstract
Nanopores fabricated in solid-state membranes have previously been used for the rapid electrical detection and characterization of single biopolymer molecules. Various methods for producing solid-state nanopores have been reported, but fabricating nanopores of desired sizes controllably is still challenging. Here we report a fabrication technique which uses a focused ion beam (FIB) system to engineer nanopores precisely. This technique provides visual feedback over the formation process. The present method can produce highly symmetrical nanopores with diameters smaller than ∼5 nm and can be used to create an array of multiple nanopores simultaneously. In addition, nanopores produced using the focused ion beam sculpting technique can be tailored down to less than 1 nm in diameter using high-energy electron radiation.

A nanopore is a nanometre-sized hole that can be synthesized biologically (e.g. alpha-hemolysin channels formed on a lipid bilayer) or that can be fabricated on a solid-state membrane using various techniques. In a pioneering experiment by Kasianowicz *et al* [1], it was demonstrated that a nanopore can be used to detect and characterize single DNA molecules passed through it by the force of an external electric field. Since then, both biological and solid-state nanopores have been used successfully as single-molecule detectors to characterize nanoscale molecules [2, 3]. An interesting early theoretical analysis of the molecule translocation process was given by De Gennes [4]. Recent experiments also showed that solid-state nanopores could have certain advantages over biological ones, including flexibility in the choice of diameters and improved mechanical and chemical stability [1–12]. A nanopore is most effective as a single-molecule detector when the diameter of the pore is close to the diameter of the molecule being detected (typically 2–10 nm).

Fabricating a solid-state nanopore with such a small diameter is difficult. For instance, it is almost impossible to etch a pore below 30 nm in diameter consistently (or reproducibly) in terms of size and shape using commercial focused ion beam (FIB) systems. It is possible to etch nanopores using a high-energy focused electron beam, but the low etch rate places limits on the thickness of the membrane in such an approach [8]. By applying an *unfocused* ion beam [3, 9–11] or a high-energy electron beam [12], it was possible to reduce the diameter of solid-state nanopores from ∼50–100 nm down to 10 nm or less. In addition, ion-beam-assisted thin-film deposition [13] as well as electrochemical etching [14–16] have also been used to fabricate solid-state nanopores. Although each of the listed techniques has its own advantages and limitations, it is still very desirable to develop new methods for fabricating nanopores of diameters less than ∼10 nm. To manufacture nanopores in a relatively simple and efficient manner, we devised a nanofabrication technique that used only two commercial instruments: an FIB system and a transmission electron microscope (TEM). Physically, our method is similar to the one developed in the Golovchenko group at Harvard [3, 9–11], which was termed an 'ion beam sculpting' technique. We follow this terminology here. The difference is that, in our case, the ion beam sculpting is performed by scanning the focused ion beam of our commercial FIB system rather than in a custom-built ion exposure system. Since the machine is equipped with a scanning electron microscope (SEM), it is possible to image the pore between the ion beam scans and thus control the 'sculpting' process. In addition, an array of multiple pores can be tuned simultaneously using our

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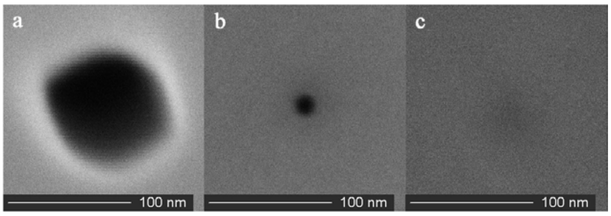

Figure 1. SEM images of a nanopore (a) before and (b) and (c) after the focused ion beam 'sculpting' process. (a) An irregularly shaped pore with an initial pore size of 106 × 88 nm is etched using the focused ion beam for 0.2 s. (b) A symmetrically shaped pore of diameter ∼15 nm is achieved as a result of 'sculpting', i.e. ion imaging (ion beam scanning) of the pore and the surrounding area. Apparently, such ion scans 'melt' the SiN and allow the pore to symmetrize and shrink in diameter, possibly due to the surface tension. (c) Continuing the process of imaging closes the pore completely.

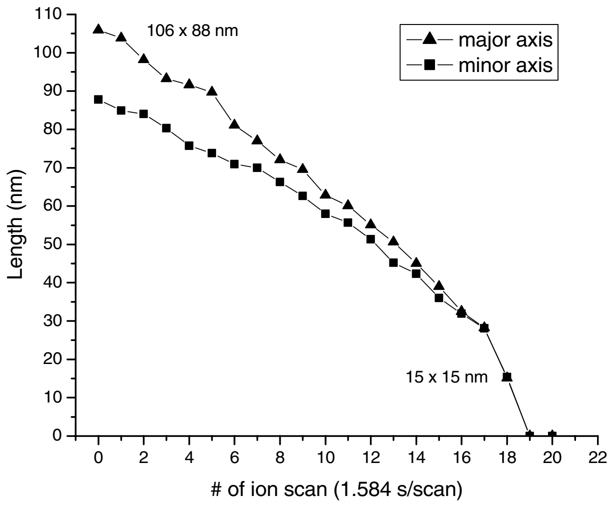

Figure 2. Observed pore size versus the number of times the focused ion beam scanned the surface. Each scan continued for about 1.6 s. The graph shows how the initial nanopore of size 106 nm × 88 nm gradually shrank to a ∼15 nm diameter pore after the 18th ion scan. The process continued and the nanopore closed after 20 scans. Triangle and block points represent, respectively, the major and the minor axes of the initially asymmetric pore. The graph illustrates that asymmetry disappears (below ∼30 nm) in the process of ion beam sculpting, and the final nanopore had a circular shape. The curve also shows that shrinking accelerates as the pore becomes smaller. This happens because the surface tension becomes larger with decreasing diameter.

technique. Nanopores produced using our sculpting method are also highly symmetrical in shape.

For all experiments, we used a FEI Strata 235 Dual Beam FIB system. The instrument consists of an ion beam column for sample modification and an electron beam column (SEM) for imaging. The starting samples in our study were low-stress silicon nitride (SiN) membranes supported by a silicon (Si) frame (Structure Probe Inc.). The thickness of the silicon nitride is 100 nm and the supporting silicon frame has dimensions suitable for a standard TEM holder. The membranes were coated with 1–2 nm of gold–palladium (AuPd) to help imaging and to prevent the charging effect during exposure to ion or electron radiation. The vacuum chamber was plasma cleaned, and the experiments were conducted under a vacuum chamber pressure lower than 4×10^{-6} mbar. Initial 'large' nanopores were etched through the membrane using a 30 keV Ga^+ focused beam with a beam current of 30 pA. These initial diameters of pores are in the range 50–100 nm. Such dimensions could be achieved reproducibly. Our smallest diameter achieved with direct etching with the ion beam focused on a spot was ∼30 nm in a 30 nm thick membrane.

Figure 1(a) shows an asymmetric, irregularly shaped pore of size 106 nm × 88 nm etched by focusing the ion beam on a spot for 0.2 s. After the hole was formed, we applied ion scans on the pore and its surrounding area. One ion scan lasted ∼1.6 s, with an ion beam current of 30 pA. The beam scanned an area of 1–2 μm^2 surrounding the pore. We found that such FIB scans reduced the size of the pore. Figure 2 shows the gradual shrinking of the pore size and the change of pore geometry in a regular fashion, during the sequence of ion scans. These changes were investigated using low-energy electron beam imaging, which does not change the pore in any visible way. After 18 ion scans, the initial pore of size 106 nm × 88 nm was transformed into a highly symmetrical nanopore of diameter 15 nm. The complete ion exposure time was approximately 1 min. We continued the sculpting process until the pore closed, as shown in figures 1(c) and 2. By varying the initial pore sizes and the timeframe of the ion sculpting process, we fabricated symmetrically shaped nanopores of different diameters down to a sub-10 nm range, as shown in figure 3. For these pores, we did not image with the electron beam after each ion scan. Instead, we blanked the ion beam for 1–2 s between scans, to allow the SiN to relax after each scan. The smallest diameter was ∼4 nm, as shown in figure 3(e).

If a diameter smaller than 5 nm is desired, it is convenient to apply another technique, namely to use 200 kV electron radiation in order to reduce the pore size gradually and controllably. A similar approach, in which a nanopore in a silicon dioxide (SiO_2) membrane was reduced from 20 to 2 nm, has previously been reported by Dekker's group [12].

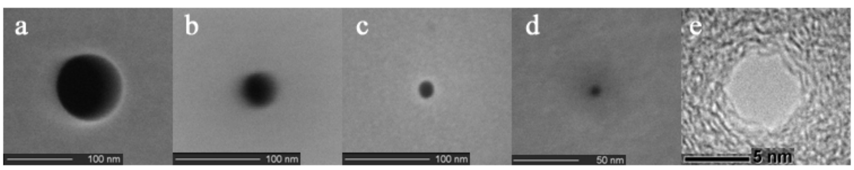

Figure 3. Examples of five different nanopores (i.e. different samples) fabricated using the ion beam sculpting technique. Each hole was first etched through the SiN membrane by the direct application of a focused ion beam. Then the diameter of each example pore was further reduced by scanning the beam during the ion imaging process. From left to right: nanopores of diameters (a) 100 nm, (b) 40 nm, (c) 20 nm, (d) 10 nm, and (e) 5 nm. The last image (e) was obtained using a transmission electron microscope (TEM).

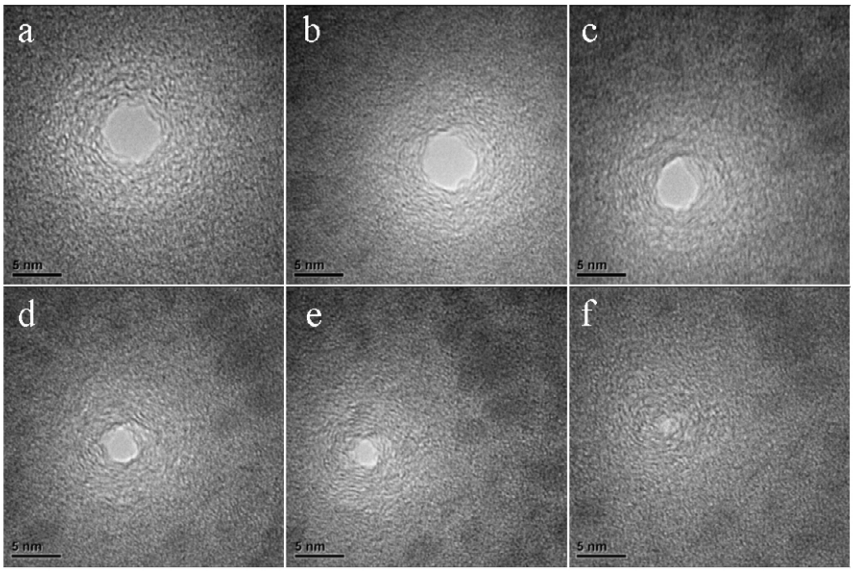

Figure 4. (a) Reduction of the nanopore diameter under the influence of high-energy electron radiation. Pictures (a)–(f) represent images taken every 15 min under continuous exposure to a 200 kV electron beam on TEM. The pore gradually shrank from ~5 nm to less than 1 nm. The closing time was longer than one hour, which was slow enough to stop the process at any desired pore diameter. We speculate that the shrinking occurs because the high-energy electronic bombardment makes atoms of the SiN more mobile, thus allowing them to diffuse rather fast. The hole might shrink due to surface tension forces.

To achieve a gradual reduction in pore diameter, we exposed a 5 nm pore (figure 3(e)) fabricated using our FIB sculpting method to an electron beam of energy 200 kV in a transmission electron microscope (JEOL 2010 Lab6). In agreement with Storm *et al* [12], we found that there was a visible reduction of the pore diameter when the electron beam was focused on the pore and its surrounding area. As shown in figure 4, the pore of an initial size of 5 nm gradually shrank to less than 1 nm in diameter. A possible interpretation for this size reduction is that the electron radiation makes the mobility and diffusivity of Si and N atoms quite high, thus inducing a mass flow directed to the reduction of the surface tension energy [12]. Such effective 'melting' of SiN is responsible for the reduction of the pore size in the case of both ion- and electron-beam radiation.

To study the change of the pore geometry further during our FIB scanning, we applied the same technique to other nanoscale structures. By varying the expose time of the ion beam, we fabricated a sample containing three 'bowl'-shaped etch pits and an asymmetric pore of approximately 100 nm × 50 nm (figure 5(a)). The structures are marked i, ii, iii, and iv, respectively, and the membrane used was 100 nm thick SiN. The sample was subsequently scanned with a focused ion beam, i.e. the sculpting process was performed. After applying 11 ion scans of 10 pA beam current and a scanning time of 3 s per scan, it was observed that not only did the pore reduce in size but also the etch pits became less pronounced, as shown in figure 5(b). Contrary to intuitive thinking that the bottom of the etch pit should open up under exposure to the ion beam, our images indicated that the width of the etch pits decreased as the surface of the membrane was etched during the sculpting process. A possible explanation for this phenomenon could be that the surface atoms became temporarily mobile under the exposure of an ion beam and were drawn towards and filled the etch pits due to surface tension. A similar explanation was suggested by Golovchenko and co-workers [10, 11]. Similar experimental and theoretical results regarding the diffusive mechanism of the surface atoms caused by ion bombardment have also been reported previously by other groups [17–19].

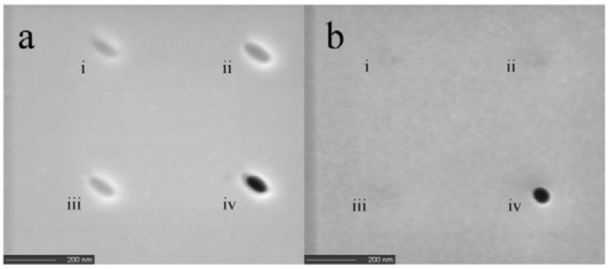

Figure 5. (a) Patterns i–iv were produced using FIB by focusing the ion beam at a spot and using etching times of 0.16, 0.22, 0.19, and 0.25 s, respectively. The beam current was 10 pA. The SiN membrane thickness was 100 nm. (b) The sample after two ion scans of ~6 s each. The etched pits of i–iii became less pronounced, while hole iv experienced a significant reduction in size and became more circular.

One advantage of our method is that it allows multiple nanopores to be processed at the same time. As shown in figure 6, an array of 16 nanopores was initially milled under the FIB for a total of 3.2 s, and each pore had a size of approximately 100 nm. Subsequently all 16 pores underwent the ion scanning (sculpting) process. After a number of scans, all pores shrank to symmetrically shaped nanopores of diameter 20 nm. This demonstrated the capability of the FIB sculpting technique to adjust the size and the shape of multiple nanopores simultaneously. Features of this size are very difficult to obtain using other lithography techniques

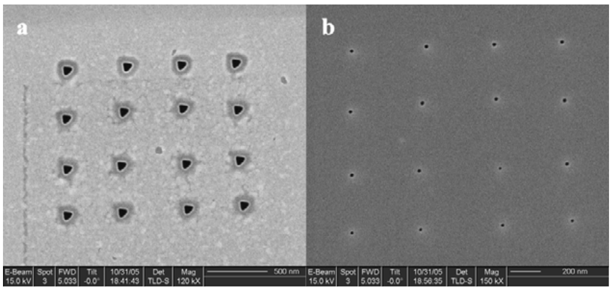

Figure 6. Multiple nanopores have been reduced in size and made more symmetrical using the FIB sculpting process. (a) An array of 16 asymmetric pores of sizes ∼100 nm was initially drilled under FIB, with a drilling time of 0.2 s for each pore. (b) All nine pores were tuned simultaneously to symmetrically shaped nanopores of diameter ∼20 nm.

such as electron lithography and scanning probe lithography. More importantly, such an array of nanopores can be used as templates for several other applications, such as photonics and the synthesis of nanostructures [20, 21].

In summary, we have described a method of using a standard focused ion beam system for the fabrication of symmetric nanopores with dimensions below 5 nm. Initial pores of various sizes and irregular shape can be drilled using the FIB and subsequently tuned to symmetrically shaped nanopores simply by scanning the surface of the membrane with the ion beam. The beam provides some mobility to the material of the membrane around the pore and allows the pore to shrink in diameter due to surface tension. This sculpting process also allows an array or a pattern consisting of multiple nanopores to be fine-tuned at the same time. A high-energy electron beam was applied to tune the size of the pore to even smaller dimensions. The smallest diameter achieved was ∼1 nm.

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