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Effects of electrons on the shape of nanopores prepared by focused electron beam induced etching

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Abstract

The fabrication of nanometric pores with controlled size is important for applications such as single molecule detection. We have recently suggested the use of focused electron beam induced etching (FEBIE) for the preparation of such nanopores in silicon nitride membranes. The use of a scanning probe microscope as the electron beam source makes this technique comparably accessible, opening the way to widespread fabrication of nanopores. Since the shape of the nanopores is critically important for their performance, in this work we focus on its analysis and study the dependence of the nanopore shape on the electron beam acceleration voltage. We show that the nanopore adopts a funnel-like shape, with a central pore penetrating the entire membrane, surrounded by an extended shallow-etched region at the top of the membrane. While the internal nanopore size was found to depend on the electron acceleration voltage, the nanopore edges extended beyond the primary electron beam spot size due to long-range effects, such as radiolysis and diffusion. Moreover, the size of the peripheral-etched region was found to be less dependent on the acceleration voltage. We also found that chemical etching is the rate-limiting step of the process and is only slightly dependent on the acceleration voltage. Furthermore, due to the chemical etch process the chemical composition of the nanopore rims was found to maintain the bulk membrane composition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanopore based biosensors can be used to monitor changes in ionic current that occur upon translocation of a single analyte molecule through the nanopore by electrophoresis [1, 2]. Interest in this detection scheme has grown in recent years [3–8] given recent developments in advanced fabrication methodologies which allow for the controlled fabrication of pores assuming nanometric dimensions in solid membranes. Such nanopores offer several advantages compared to natural protein channels, including engineering flexibility, improved

durability, and lab-on-a-chip integration potential [2, 9, 10]. Different methodologies for the fabrication of nanopores have been recently summarized in several comprehensive reviews [8, 9, 11]. Generally, the most common approaches for nanopore fabrication include direct drilling or shrinking larger pores by high energy focused electron or ion beams [12–15]. These techniques provide improved lateral resolution and generally shorter fabrication times than achieved with indirect, multi-step chemical or reactive ion etching based nanopore formation techniques [11]. In particular, the use of the highly energetic focused electron beam of a transmission

electron microscope (TEM) for nanopore drilling has become widespread in recent years [13, 16]. This is in large part due to the finding that the electron beam can be used for post-treatment tuning of the pore size [13, 16, 17].

We have recently demonstrated that a focused electron beam induced etching (FEBIE) process, in which a low energy electron beam is used to locally enhance chemical etching by a gaseous etchant [18], provides an alternative approach for the formation of nanopores in silicon nitride [19]. In this process, the low energy electron beam of a scanning electron microscope (SEM) changes the chemical content of the surface by the reduction of silicon nitride and the release of nitrogen that accompanies this event. Spontaneous etching of the silicon in situ by XeF₂ occurs in a reaction that yields volatile SiF₄ and Xe₂ species. The use of SEM as an electron source, instead of TEM or focused ion beam (FIB) instruments, makes this method more accessible. We have found that nanopore size can be controlled by modulating the duration of exposure to the focused electron beam and is also affected by the gas pressure that controls the chemical reaction and volatile gas diffusion rates. Nanopores as small as 20 nm in diameter were fabricated, making this technique compatible with protein biosensing [20-24]. Other studies have shown that the ability of an electron beam to ionize precursor gas molecules, making them highly reactive in the vicinity of the electron beam, can also be utilized for the formation of nanopores, allowing for the use of inert gases such as H₂ and N₂ [25], or water vapor [26] instead of XeF₂ as a gas precursor.

For biosensing applications, quantitative information on the three-dimensional shape of the nanopores is crucial since it can affect the magnitude and duration of the sensing signal. This shape was found to depend on the preparation methodology and specific fabrication conditions. While nanopores prepared by direct ion drilling adopt a conical shape [27], the formation of hourglass-shaped nanopores was found for nanopores prepared by direct focused electron beam drilling [17, 28, 29]. Since the shape of nanopores prepared by the FEBIE process has not been revealed yet, we present here a detailed characterization of thus prepared nanopores. Assessing the morphology of nanopores using TEM and atomic force microscope (AFM) imaging, combined with thickness maps obtained by electron energy loss spectroscopy (EELS), demonstrated the formation of a funnel-like entity due to shallow etching of the peripheral region at the top of the membrane. Such morphological characterization techniques were used to monitor changes in the dimensions of the central nanopore and the shallow-etched peripheral region as a function of the duration and acceleration of the electron beam used for their fabrication.

2. Experimental details

2.1. Nanopore fabrication

Nanopores were fabricated as previously reported [18]. Briefly, 20 nm thick silicon nitride membranes (Protochips, Raleigh, NC, USA) were plasma-cleaned (in Ar) and loaded into a high-resolution electron beam lithography system with FEBIE



Figure 1. Schematic illustration of the FEBIE set-up and process. (A) The FEBIE fabrication set-up. (B) The cyclic process involved in the formation of a nanopore in a silicon nitride membrane: (I) an electron beam reduces the silicon nitride surface into elementary silicon and volatile N_2 ; (II) XeF₂ etches Si, yielding volatile species; (III) the process proceeds until the formation of a nanopore. The drawing is not to scale.

capacity (E-Line, Raith, Dortmund, Germany). The samples were exposed to electron beam pulses aimed at a fixed position on the surface and simultaneously exposed to XeF₂ gas (figure 1). Electron acceleration voltages of 2, 10 and 20 kV, with currents of 0.18, 0.29 and 0.44 nA, respectively, were used. The time of exposure to the electron beam was varied from 4 to 24 s by controlling the number of 1 ms electron beam pulses separated by switch-off times of 0.01 or 1 ms. Continuously flowing gas was introduced through a nozzle positioned 9.5 mm above the surface. The nozzle was kept at a temperature of 75 °C in all experiments to allow fast transport of the gas to the reaction area. The temperature in the gas reservoir was used to control the gas pressure in the chamber at 11.4×10^{-6} mbar (unless otherwise stated). To minimize contamination effects, especially due to deposition of carbonaceous material, the initial chamber pressure was maintained at 6.5×10^{-7} mbar. A matrix of nanopores was prepared in each membrane by varying the exposure time and acceleration voltage of the electron beam. The reproducibility of the process was tested using both repeated conditions on the same membrane and on different membranes.

2.2. Nanopore characterization

Nanopores were imaged by TEM (FEI Tecnai 12 G2, 120 kV) operated with a tungsten filament at an acceleration voltage of 120 kV. High-resolution images and EELS maps were obtained using a monochromated and Cs aberration-corrected (Cs \approx (-10) - (2) μ m) field emission gun S/TEM (Titan 80-300 S/TEM, FEI), equipped with an energy filter (Tridiem 866 ERS, Gatan). Nanopore size was estimated by measuring the area of the nanopore in the plan-view image, from which the diameter was calculated. Averaged results of at least two different nanopores are presented. A nanopore thickness profile was obtained by multiplying the log-ratio between the



Figure 2. Morphology of the nanopore. (A) Plan-view TEM micrographs and (B) AFM topography images of two-line matrices of nanopores. (C) Line scans along the dotted line in (B). Nanopores were fabricated at 20 kV with total exposure times of between 4 and 18 s, as indicated, and with a XeF₂ pressure of 9×10^{-6} mbar. The TEM images were acquired using the minimal electron dose that allows for high-resolution imaging, thereby minimizing beam damage and maintaining nanopore shape.

total EELS energy and the zero-loss peak (plasmons) and the plasmon mean free path, which we have previously estimated to be 155 nm for the same type of membrane [29, 30]. This value yielded a total membrane thickness of 19 nm, a value in good agreement with the manufacturer's stated value. The EELS signal of the Si L-edge was used to monitor sample composition in the vicinity of the nanopore.

The morphology in the vicinity of the nanopores was determined by AFM (Solver P47-PRO M, NT-MDT, Ru) in semi-contact mode using a cantilever with a force constant of 1.74 N m^{-1} (NSG 03, NT-MDT, Ru).

3. Nanopore size and shape

The formation of nanopores by the FEBIE process involves electron beam induced reduction of silicon nitride into silicon followed by spontaneous chemical etching of the silicon by XeF₂, leaving only volatile reaction species (figure 1). Figure 2(A) presents TEM images of two sets of nanopores fabricated at 20 kV with a total exposure time of 4–18 s. The formation of nanopores was observed after 6 s, with increasing diameter appearing as the total exposure time increased, in agreement with our previous studies [18]. The nanopores appeared to assimilate a jagged shape and the membrane around them obtained a granular texture. Treating the samples with plasma after the formation of the nanopores did not affect this rough morphology, eliminating the possibility that this morphology originates from the deposition of carbonaceous material. Hence uneven etching has probably produced this texture; probably arising from inhomogeneity of the membrane. Indeed, in some of the cases, incomplete etching was observed; in such cases an ultrathin layer was covering part of the pore area.

The evolution of the etching process was further monitored by AFM (figure 2(B)). An increase in the depth of etching was observed at the beginning of the etching process, as indicated in the AFM image of the two sets of nanopores and the corresponding line scans along the marked lines (figure 2(C)). After 6 s, the depth of the cavity became constant, indicating no further depth etching, in agreement with the TEM data. It should be noted that the size of the tip prevents its penetration all the way through the nanopore, and hence the observed thicknesses are smaller than that of the membrane [31].

In addition to increases in the size and depth of the nanopore, a shallow-etched peripheral region was observed around each nanopore (figures 2(B) and (C)). This is in contrast to the formation of volcano-shaped nanopores in the ion sculpturing process due to field-assisted material migration from the bulk membrane [32], or deposition of electron beam induced carbonaceous material [26, 33]. This shallow-etched peripheral region, also demonstrated in our previous work [18], was shown to increase with electron exposure time, as discussed below.

A representative plan-view TEM image shows a nanopore with a diameter of 91 nm (figure 3(A)). A dark circular area in the EELS map indicates the formation of a nanopore (figure 3(B)). We note that despite the formation of a pore penetrating the entire membrane, plasmon delocalization [34] and detector background noise [35] resulted in an EELS signal within the nanopore vacuum region. As such, determining the nanopore diameter from the EELS maps was found to be less accurate. Since for a single-material sample the low-loss EELS signal is proportional to the thickness of the sample, the darkening of the contrast from the edges of the image toward the nanopore indicates a gradual thinning of the membrane in the vicinity of the nanopore, in agreement with the AFM results. A cross-section of the membrane along a line that crosses the nanopore was obtained by examining the logratio EELS intensities [30] (figure 3(C)), providing quantitative information on the thickness of the membrane. Comparing the EELS data with the TEM image reveals that the deep slope observed in the EELS map at the central nanopore is due to noise and suggests that the nanopore itself assumes a cylindrical shape. Indeed, the formation of cylindrically shaped nanopores was suggested to be energetically favored for nanopores with a diameter that is at least twice the membrane thickness [36], as is the case for the nanopore presented here.

As indicated above, the nanopore seems to be surrounded by an extended area in which the membrane is thinned. For the specific fabrication conditions employed, the etching depth was found to reach a value of 3 nm at the central nanopore rims. An AFM topographic image and the corresponding line scan along the nanopore clearly show three regions around the nanopore (figures 3(D) and (E)). At distal locations, the membrane is unaffected by the etching process. The roughness



Figure 3. Nanopore shape. (A) Plan-view TEM imaging of a nanopore. (B) EELS thickness map of the nanopore in (A). (C) Cross-section of the membrane as calculated from the EELS signal along the dotted line in (B). Dashed lines indicate the nanopore diameter extracted from the plan-view TEM in (A). The inset shows a schematic 3D representation of the nanopore. (D) 3D topographic AFM image. The three main regions are marked. (E) A line scan along the dashed blue line in (D). The nanopore was fabricated using a 20 kV electron beam with a total exposure time of 18 s and a XeF₂ pressure of 9×10^{-6} mbar.

of the membrane at this area was found to be about 0.35 nm, in agreement with the data supplied by the manufacturer. A second shallow, peripheral thinning region was observed around the central nanopore, with a diameter of \sim 430 nm and a depth of ~ 2 nm. Finally, there is the nanopore. The value of the shallow-etched region obtained by AFM appears to be about 70% of the value obtained upon EELS analysis. These observations suggest that membrane thinning mostly occurs at the top part of the membrane, which is exposed to the etchant molecules. Indeed, nanopore broadening at the bottom of the membrane, a phenomenon which is attributed to the knock-on mechanism employed for nanopore preparation by electron beam induced drilling, is less likely to have occurred here due to the low electron acceleration voltage [37]. These observations suggest that the nanopore adopts a funnel-like shape (figure 3(C), inset), where the funnel 'cap' presents a diameter which is much larger than its 'stalk'; nevertheless the cap is comparably shallow (i.e. 20% of membrane thickness for the representative example presented). This unique shape provides a comparably large volume of narrow channel that may result in an improved resolution for biosensing detection due to a larger effective sensing volume.

The generation of the peripheral-etched region is already observed in the initial stages of the process, before the formation of the nanopore. For example, a peripheral-etched region 200 nm in diameter and about 3 nm deep is observed

in the AFM image after 6 s, while a TEM image of the same area clearly indicates that a nanopore has not yet formed (figure 4(A)). This shows that the peripheral etching occurs by a different process than does nanopore formation, namely one that extends laterally on the top surface of the membrane but with a slow etching rate [37]. Another interesting observation was that the shallow-etched peripheral region was spherical in shape, regardless of the nanopore shape (figure 4(B)). In several cases, elliptical-shaped nanopores were formed, probably due to misalignment of the electron beam or a small tilting of the membrane. An example of such a nanopore is shown in the inset of figure 4(B), where the minor diameter of the nanopore was found to be 35% of its major diameter. The AFM scan, however, indicates the formation of a circular peripheral-etched region with diameter variations of less than 5%. This observation points to the isotropic nature of these processes. Similar observations were made by Randolph et al who etched a square in a silicon oxide sample by a raster scan of the electron beam [38], and by Spinney et al who fabricated nanopores relying on a process similar to ours [26]. In both cases the formation of a round peripheral region around the main etching area was observed.

The progression of the nanopore and peripheral shallow etching was followed by extracting EELS thickness maps of nanopores fabricated with 20 kV electron acceleration voltage as function of exposure time (figure 5(A)). As suggested



Figure 4. Morphology of nanopores prepared under different conditions. (A) AFM topographic image of a nanopore at the early stage of the process (fabrication conditions: 2 kV, 6 s). (B) AFM topographic image of an elliptical nanopore (fabrication conditions: 10 kV, 14 s and 11.4×10^{-6} mbar). A circular peripheral-etched region is observed around both nanopores. The corresponding TEM images are presented in the insets. The dashed lines are added to help the reader gauge the diameters of the peripheral-etched region. The dotted white ellipse in (B) represents the nanopore.

above, the formation of a shallow-etched peripheral region was observed from the initial steps of the etching process, before a nanopore penetrating the entire membrane was formed. Etching progressed vertically in the central region and laterally in the peripheral region, both for times shorter than 6 s. After 6 s, once a hole was formed, the diameters of the nanopore and the shallow-etched region further increased at a slower rate, as can be observed in the time trace of both diameters (figure 5(B)). Such nanopore expansion kinetics were previously observed for nanopores drilled by a high-energy focused electron beam in Si_3N_4 [17] and Al_2O_3 [39], and, as we have previously reported, for FEBIE nanopore formation [18]. Initial expansion rates of 6 and 17.5 nm s⁻¹ were observed for the central and peripheral regions, respectively, for times shorter than 10 s. For times longer than 10 s, the etching rate was reduced to 1 and 4 nm s^{-1} , respectively. Vertical etching, however, seemed to occur much more slowly at the periphery. While after 8 s a hole was formed in the central region, peripheral etching was only 3 nm thick, indicating an etching process at the latter position that is \sim 7 times slower than at the former. It is thus clear that two different etching mechanisms occur spontaneously, with one being more localized and faster and the other being less localized and slower. As suggested above, the main mechanism of local etching is likely to involve the reduction of silicon nitride and spontaneous fast etching of the resulting silicon by XeF₂. A slow delocalized etching process could occur due to the activation of XeF₂ molecules by electrons in the gas phase [25, 26, 40]. These reactive species, which can etch silicon nitride at a faster rate than can non-activated XeF₂ but at a slower rate than achieved in etching of elemental silicon, may diffuse within the gas phase over larger distances, thus resulting in extended long-range etching of the silicon nitride.

The diameter of the hole ($\sim 100 \text{ nm}$ after 22 s) is larger than the diameter of the electron beam striking the material, which was calculated to be 4 nm by Monte Carlo simulation, taking into account elastic scattering [41, 42]. This suggests that an area with excess silicon is formed around the electron beam probably as a result of reduction of silicon nitride by secondary electrons or field-assisted silicon migration [32, 43]. These changes in the stoichiometry of the silicon nitride induce remote etching. Once a hole is formed, the electrons pass through it without interacting with the material. At this point, reduction of silicon nitride by the electron beam ceases and the process proceeds only by etching of the Si that was reduced at earlier stages of the process and by the slow etching of silicon nitride by XeF₂ and its activated species. This results in a much slower overall rate of etching. The fact that the peripheral etching expansion rate also diminishes once a hole has been formed indicates that this process is also affected by interaction of electrons with the material.

4. Lateral extent of electron effects

The electron interaction volume is known to decrease with increased acceleration voltage [44]. This offers an ability to control the nanopore size, which is of critical importance. In order to understand how the acceleration voltage affects the kinetics of the process and its extent, nanopore diameter was monitored as a function of electron exposure time for acceleration voltages of 2, 10 and 20 kV (figure 6(A)). As expected, increasing the acceleration voltage decreases the overall dimension of the resulting nanopores (figures 6(A)) and (B)). Both the minimal diameter of the nanopores, averaged from different nanopores at the threshold time $(n \ge 3)$, and the maximal diameter, calculated as the average diameter of the last three nanopores formed during the slow expansion period, decreased with increasing acceleration voltage (figure 6(B)). Similar behavior was observed by Spinney et al for nanopores prepared by electron-activated chemical etching [26]. In this case, the observed changes were found to correlate with the diameter of elastic interactions in the material, albeit with larger values. These observations suggest that further increasing the acceleration voltage may improve the resolution of the technique. We note that the size of the nanopores can be further tuned by the gas pressure. Indeed, in our former studies, in which a substantially lower XeF₂ gas pressure was used, nanopores with pore diameter of 20 nm were achieved with a 2 kV acceleration



Figure 5. Nanopore and peripheral region formation kinetics. (A) EELS thickness cross-sections of nanopores fabricated with total exposure times between 4 and 22 s. Cross-sections were aligned to the nanopore center and plotted in the range of ± 250 nm beyond which the membrane presented the bulk thickness value. (B) Nanopore diameters measured from plan-view TEM images (average of two different nanopores), and the diameter of the peripheral-etched region obtained from EELS thickness cross-sections (averaged from both sides of the nanopore), as function of electron beam exposure time. Lines are plotted to help the reader follow the three stages in nanopore formation, i.e. membrane thinning and fast and slow expansion. Nanopores were fabricated using an acceleration voltage of 20 kV and a XeF₂ pressure of 9×10^{-6} mbar.

voltage. The results also indicate that the reproducibility of the process is quite good with a standard deviation lower than 15% when comparing nanopores prepared under the same conditions. This value was found to be similar to the one obtained for nanopores prepared by TEM drilling [12, 39], FIB drilling [45] and ion track etching [46]. However, we note that in some cases only a limited reproducibility was obtained, especially for the shorter etching times (figure 5(B)). The large variation in the nanopore diameter in this case may be attributed to a defected membrane in which local defects resulted in significantly smaller nanopores for identical preparation conditions. This can be observed, for example, for one of the nanopores prepared with a 12 s exposure time, for which a significantly smaller nanopore was formed in one of the cases (figure 2(A)).



Figure 6. Effects of acceleration voltage on nanopore diameter. (A) Nanopore diameters measured from plan-view TEM images (average of two different nanopores) as a function of electron beam exposure time for nanopores prepared with acceleration voltages of 2, 10 and 20 kV. Lines are plotted to aid the reader. (B) Minimal (i.e. averaged results of nanopore diameters at a threshold time for at least three different pores) and maximal nanopore diameters (i.e. averaged results from the last three pores formed in the slow expansion region) as a function of acceleration voltage. The elastic interaction diameter was calculated according to [41] and was in agreement with Monte Carlo simulations of the electron trajectories [42].

The kinetics of the process involving the three steps of membrane thinning, rapid pore expansion and the subsequent slower expansion process were assessed at the three acceleration voltages tested. Analysis of several nanopores revealed that the first step lasted between 8-10 s for acceleration voltages of 2 and 10 kV, and 6-8 s for acceleration voltage of 20 s. After 10 s, the etching rate decreased regardless of the acceleration voltage applied, with the rate of expansion being the slowest at the higher acceleration voltage. These data suggest that the acceleration voltage has only a minor effect on the rates of membrane thinning in the first step of the process, and during the termination of the fast expansion process. We attribute the behavior we observed to the nature of the FEBIE process, which depends on both electron-material interactions, and the chemical etching process. The fact that the threshold time and onset of slow expansion region only slightly depend on the acceleration voltage suggests



Figure 7. Ratios of the final to initial diameters of the central nanopore and the peripheral-etched region formed at acceleration voltages of 10 and 20 kV. Nanopores were fabricated at a XeF₂ pressure of 10.5×10^{-6} mbar.

that the rate-determining process is the chemical etching process. The extent of the etched region, however, decreases with increasing acceleration voltage in a manner similar to the elastic interaction volume, a region designated by its diameter in figure 6(B). This is probably due to the fact that a larger volume around the electron beam containing excess amounts of silicon is formed with the decreased energy of the primary electron beam. This is in agreement with the model proposed by Crozier for an electron induced transformation process [25]. Interestingly, the ratio between the nanopore and elastic interaction diameters is smaller at the lower acceleration voltage. This is probably due to the larger proportion of inelastic electron interactions at the lower acceleration voltage. As suggested above, once a pore is formed, electrons pass directly through, such that any interaction with the material ceases to occur. This results in a pronounced decrease in the etching rate, regardless of acceleration voltage. In the third step of the process, the etching rate is dictated by the slow yet spontaneous chemical etching of the silicon nitride. This rate is enhanced by excited species gas diffusion and by etching of residual silicon formed during the earlier steps of the process, as discussed above. Hence, the etching rate depends on the acceleration voltage.

The size of the peripheral shallow-etched region was also found to depend on the acceleration voltage, with a maximal diameter of about 330 and 280 nm for the 10 and 20 kV acceleration voltages, respectively. However, the impact of the acceleration voltage is larger for the central nanopore dimensions than for the peripheral pore region. Hence, while the maximal nanopore diameter was ~2-fold greater for an acceleration voltage of 10 kV as compared to 20 kV, the maximal peripheral etching diameter was only 1.3-fold greater. In addition, similar to the expansion of the central nanopore, a slow increase in the diameter of the shallowetched peripheral region was observed for both acceleration voltages with increasing exposure time. This slow expansion rate was quantified as the ratio of the diameter measured at 24 s and that measured at 6 s (figure 7). The expansion ratio of the central nanopore and the peripheral region was found to be smaller at the larger acceleration voltage. Furthermore,

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Figure 8. Nanopore chemical composition. (A) Si L-edge EELS spectra at the nanopore rims (1, red), at the peripheral-etched region (2, yellow) and over the bulk membrane (3, green). Spectra were acquired in the S/TEM mode and background has been subtracted. The inset shows a TEM image of the nanopore with the corresponding position of points 1–3. The nanopore was fabricated with 20 kV acceleration voltage for 6 s and with a XeF₂ pressure of 6.7×10^{-6} mbar. (B) AFM phase image of nanopores fabricated at 20 kV, with a total exposure time of between 4 and 18 s (corresponding to the nanopores in figure 2).

at both acceleration voltages considered, the expansion ratio was found to be smaller for etching of the peripheral region than for etching at the central nanopore. In addition, the nanopore was found to occupy 17% of the peripheral-etched diameter at the 20 kV acceleration voltage level. This value increased to 27% at the 10 kV electron acceleration voltage level. These results further highlight the influence of the electron interaction volume on the nanopore formation process. Since at a lower acceleration voltage more radiolysis and diffusion processes occur, these affect both the central etching region and the shallow-etched peripheral region, resulting in a larger interaction volume. The dependence of the shallow-etched peripheral region processes makes it less sensitive to the magnitude of the acceleration voltage.

5. Chemical composition of the membrane in the pore vicinity

The chemical composition of the nanopore surroundings was examined by following the Si L-edge signal in the EELS spectra at the nanopore rims, the peripheral-etched region and the bulk membrane (figure 8(A)). The three spectra show a similar shape, with a peak at about 107 eV, which is characteristic for amorphous silicon nitride [47–49]. No significant changes in the spectra were observed, suggesting that the chemical composition of the membrane remains intact after the etching process, both at the nanopore rims and at the surrounding shallow-etched area. The lower signal intensity noted at the nanopore rim is due to its emergence from a thinner membrane. We note that the small shift in the energy

of the peak is within the resolution of the measurement, which was ~ 0.6 eV. Similar results were obtained for nanopores fabricated using other acceleration voltages and process time conditions (data not shown). These results are further supported, especially for the low-etched peripheral region, by phase contrast AFM images (figure 8(B)). The phase in the vicinity of the nanopore does not show pronounced differences from the phase at membrane areas that were not affected by the electron beam, suggesting a similar chemical composition. These results indicate an efficient removal of elemental silicon formed by the electron beam during the FEBIE process. The FEBIE process thus allows the formation of a nanopore bordered by rims presenting the same chemical composition as the bulk membrane. This is in contrast to direct nanopore drilling using a high acceleration voltage electron beam, where pronounced reduction of the material is observed in the vicinity of the nanopore [49]. The existence of stable silicon nitride surfaces provides a platform for chemical functionalization by, for example, simple silinization processes that can be used to further control the properties of the nanopores [50].

6. Conclusions

We have studied the three-dimensional shape of nanopores fabricated by a FEBIE process. The nanopores were found to adopt a funnel-like shape, with a central cylindrical nanopore penetrating the entire membrane and an extended shallowetched region at the top of the membrane. The comparably high aspect ratio of the central nanopore cylinder may provide increased sensitivity in biosensing experiments. The central nanopore is formed upon reduction of the silicon nitride membrane by the electron beam, as well as long-range radiolysis and diffusion processes that result in nanopore dimensions that exceed the size of the electron beam. The rate of the etching process is, however, dominated by spontaneous etching of silicon, an event that is somewhat accelerated by electron beam effects. As a result, increasing the applied acceleration voltage results in a smaller pore diameter and a smaller peripheral-etched region, with only minor changes in the rate of the process. Moreover, the effective etching of silicon-rich areas leaves the chemical composition of the nanopore rims and peripheral region similar to the composition of the bulk of the membrane.

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