NANOPORES

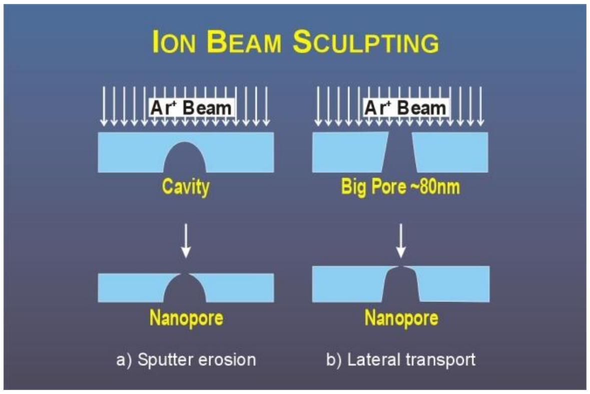
Denis Tita, March 9, 2009

Introduction

A nanopore is a small hole of the order of one nanometer in internal diameter. The idea of nanopore fabrication is fairly new and has been in development since 1995. Since then, nanometer-scale pores have been developed and used for the detection and sensing of biological molecules such as the DNA. The most widely used pores are the α-haemolysin or the biological nanopore and the synthetic nanopores which can be fabricated in laboratories. These pores offer many potential applications in the analysis and sequencing of DNA and has become a vital part in many research domains. Synthetic nanopores with pore size smaller then the α-haemolysin pores have been fabricated by electron beam techniques: these have the advantage in that they are more robust and can be adjusted dimensionally. This report is based on the fabrication of synthetic nanopores by an ion beam sculpting process described below.

Ion Beam Sculpting

When massive ions such as the noble gas ions are fired at the surface of materials, there is a nanometer –scale rearrangement of the surface atoms. This rearrangement could either be due to an erosion process by which the beam removes atoms from the outermost layers of the material creating a nanopore or by a lateral mass transport of surface atoms by which the beam generates surface adatoms for the closure of a pore. Ion beams of varying energies can be used to sculpt or design nanopores from prefabricated focused ion beam (FIB) holes in silicon nitride films. The size of a nanopore will generally depend on the intensity of the focused ion beam as well as the temperature conditions of the sample. Heavy ion beams are generally known to reduce the size of a pore since they induce a lateral mass transport thus leading to the creation of adsorbed species (adatoms) that can diffuse rapidly causing a prefabricated nanopore to shrink. On the other hand a low energy Argon ion beam will lead to sputtering erosion at the edges of a pore which increases the size of a nanopore. This implies that a Nanopore can be sculpted in two ways from a cavity in a silicon nitride film under conditions when sputtering erosion dominates or by filing in a larger pore under conditions when the lateral mass process dominates.



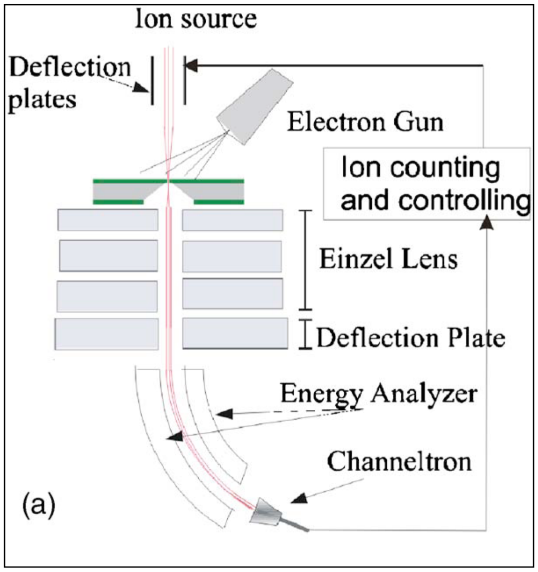
(a)The figure on the left depicts the sculpting of a nanopore from a cavity or from a through hole created by RIE or FIB in a 500 nm silicon nitride membrane.

(b) Sputtering erosion or lateral transport processes dominate, depending on the selected conditions used in the ion beam sculpting apparatus.

Low energy beam noble gas ions such as helium, argon, neon and Krypton have been widely used for the modification of surface structures on different materials at the nanoscale. The figure above presents a method by which ion beam sculpting for the noble gas Argon was achieved, by using ion beams to drastically increase, reduce or even close the prefabricated FIB holes. This process can be generalized to a variety of low energy noble gas ions such as Helium, Neon, Krypton and Xenon.

The Nanopore Fabrication Process

The sample used in the fabrication process is composed of an FIB hole on a silicon nitride membrane created by making use of a Focused ion beam and their sizes determined by Transmission Electron Microscopy (TEM). The larger FIB holes are then ion sculpted to create 1-10nm pore by low energy ion beam sculpting.



The figure on the left represents the basic schematic for the fabrication of a nanopore. The detection of ions transmitted through the sample membrane provides the physical signal necessary for the feedback loop to control the incident ion beam.

The apparatus counts the ion transmission rate through the hole in the silicon-nitride membrane with a Channeltron single ion detector during the sculpting process. The transmission rate is a direct measure of the size of the pore as function of time. The apparatus also uses the count signal to deflect the incident ion beam off the sample when the nanopore reaches the desired diameter. It is housed in a high vacuum chamber $10^{-9} - 10^{-10} mbar$ and also regulates the sample temperature, ion- beam flux and the on/off switching of the ion beam flux. The Channeltron single ion beam detector provides information on the size of the hole at any given time by counting the number of ions that passes through the hole per unit time. The size of the pore can be increased or decreased by the apparatus through temperature regulation of the sample, ion beam flux F in ions $nm^{-2}\, s^{-1}$ and the time interval that the ion beam can be switched on and off.

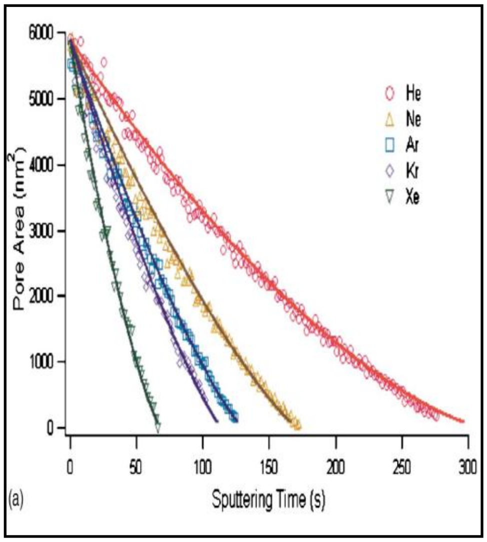


Fig 2a

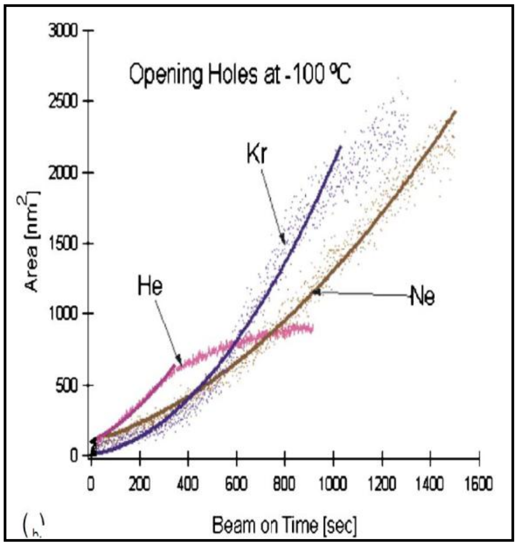
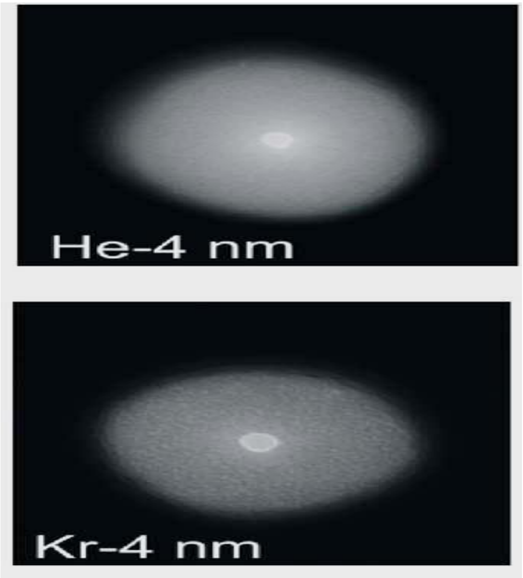


Fig 2b

Figure 2a shows a graph of Pore area (Y-axis) Vs sputtering time (x-axis) at a room temperature of 28 degrees in which ion beams of xenon; krypton, argon, neon and helium at 3Kev were used to irradiate FIB samples in a silicon nitride membrane. It is observed that the curves fall off much faster for the heavier ions than for the lighter ones. The curves for the much heavier xenon ion falls off for a sputtering time of about 56 seconds while the curve for the helium ion beam falls off at a much longer sputtering time of about 300 seconds. What is to be derived from this curve is that the heavier ions close the pore more quickly than the lighter ones since pore diameter is directly proportional to pore area. Temperature has a direct dependence on ion beam sculpting as can be seen in Fig2b. The sizes of a pore can be increased by lowering the temperatures since at low enough temperatures, surface diffusion is quenched out and the ion beam plays a dominant role in scraping away the edge of the pore leading to its opening. Keeping all parameters the same as those in figure 2(a) and cooling the samples from 28 degrees to -100 degrees causes nearly closed nanopores to open up. Figure 2(b) shows such openings for Helium, Neon and Krypton at $F{\sim}0.5\ ions/nm^2 s$. Figure (2b) further suggest that at low enough temperatures, sputter erosion responsible for pore opening, becomes the dominant factor whereas the lateral mass transport effect responsible for the closing of nanopores in ion beam sculpting becomes negligible.



The figure on the left shows a TEM image of nanopores made by Helium ions (top) and Krypton ions (bottom). Nanopore membranes made by lighter ions such as Helium and neon have less contrast and show fine grained microstructure whereas those made of heavier ions such as Argon and Krypton have heavier contrast and show coarser grain microstructure

Surface Adatom Diffusion

There are two basic theoretical models responsible for the closing of a nanopore. The first is the viscous flow model in which an impinging ion breaks bond in the silicon nitride membrane and allows for the free flow of material. Material flow lowers the energy of the ion and the hole is closed. The second theory that accounts for pore closing is the surface adatom diffusion model. This model is based on the assumption that impinging ions generate surface adatoms which move about the surface of the membrane by diffusion. The closing of a pore actually occurs when these adatoms diffuse into a pore and bind on its edge.

The concentration of surface adatoms C(r t) is governed by the two dimensional diffusion equations

$$\frac{\partial}{\partial t} C(\vec{r}, t) = FY_a - \frac{C}{T_{trap}} + D\nabla^2 C - FC\sigma$$

The first term on the right side of the equation governs adatom creation. This term depends on the flux of the ion beam F and the adatom yield Y_a which is the average number of atoms generated per incident ion. The second term describes atoms binding to the surface defects of the membrane where T_{trap} is the lifetime of the adatom. The third right hand term describes the two dimensional diffusion of adatoms about the surface of the membrane, where D is the diffusion coefficient. The last term $FC\sigma$ represents the probability of adatom ejection from the surface. Where σ represent the cross sectional area of the adatom. This implies if an adatom is hit by an incoming ion, then the adatom is ejected from the surface. We can thus conclude from the above equation that the first term is the adatom creation by ion impingement term, the second term represents the annihilation at defects, the fourth term (diffusion) is responsible for filing in the nanopore and last term is the annihilation by ion impingement term.

Applications of Nanopores

- Investigations on micro-fabricated devices for biomedical applications such as biosensors have swiftly advanced in the last few years.
  Other important applications such as the use of the PCR include
- DNA cloning for sequencing
- DNA-based phylogeny or functional analysis of genes
- The diagnosis of hereditary diseases
- The identification of genetic fingerprints (used in forensic sciences and paternity testing); and the detection and diagnosis of infectious diseases.
- In 1993 Mullis was awarded the Nobel Prize in Chemistry for his work on PCR

References

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