Title

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Simple method for formation of nanometer scale holes in membranes

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When nanometer scale holes (diameters of 50 to a few hundred nm) are imaged in a scanning electron microscope (SEM) at pressures in the 10^{-5} to 10^{-6} torr range, hydrocarbon deposits built up and result in the closing of holes within minutes of imaging. Additionally, electron beam deposition of material from a gas source allows the closing of holes with films of platinum or TEOS oxide. In an instrument equipped both with a focused ion beam (FIB), and an SEM, holes can be formed and then covered with a thin film to form nanopores with controlled openings, ranging down to only a few nanometers.

The ability to form holes in membranes with diameters of only a few nanometers (1 to 10 nm) is of interest in many fields of nanometer scale science including single molecule studies, ion proximity lithography, and single atom doping [1-5]. Electron beam lithography followed by dry etching has been used to form holes with diameters in the range of tens of nanometers, but resist resolution and etching of high aspect ratio holes in membranes make formation of holes with diameters below 5 nm very challenging [6]. Direct hole drilling can be achieved with focused ion beams, but available beam diameters are about 10 nm, limiting achievable hole sizes. Holes can also be drilled directly with electron beams, and hole diameters as small as 1 to 2 nm have been reported in 100 nm thick sheets of Al_2O_3 [7]. Formation of synthetic nanometer

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scale holes with diameters below 10 nm has further been reported by several groups who used swift heavy ion track etching [3], or ion beam sculpting with keV argon ions [1, 8]. In this letter, we describe a simple method for nano-hole formation based on monitored closing of 100 nm scale holes by electron beam deposition of thin films. For our experiments at the National Center for Electron Microscopy at LBNL we used an FEI dual beam FIB, a system combining a focused ion beam with an SEM column.

Samples in our study were membranes of low stress silicon nitride with a thickness of 200 nm on silicon frames. Membranes were coated with 5 nm of a gold palladium alloy to prevent charging during exposure to charged particle beams. A 30 keV Ga^+ beam with an intensity of 1 pA in spot with a diameter of 10 nm was used to drill holes into the membranes. Initial hole diameters ranged from about 50 to 200 nm. The base pressure in the FIB vacuum chamber was 3×10^{-6} torr. For hole closing with hydro-carbon films (also known as contamination resist [9]), an electron beam (5 keV, 1 nA, nominal spot size 2 nm) was rastered over the area with the initial hole pattern at a magnification of 150,000 to 350,000 at a rate of 5 scans per second. After an exposure interval of 30 s to one minute, the sample area was imaged with a slower, higher contrast scan, and the process was repeated. In Figure 1, we show a sequence of images of three holes taken immediately following FIB drilling (a) and after several minutes of electron beam exposure (b and c). Under these conditions, the rate of hole closing was linear with a slope of 0.3 nm/s (Figure 2). The chemical composition of the deposited material can be elucidated through a comparision of SEM and ransmission electron microscope images of closed holes. In Figure 3, we show a pattern of closed holes in SEM (a) and TEM (b) images. In SEM, contrast was obtained by detection of backscattered electrons, the yield of which is proportional to the square of the atomic number of imaged materials ($\sim Z^2$) In SEM images, the Au/Pd islands appear bright, while the silicon nitride substrate and the material that covers the holes appear dark. In TEM, contrast is based on absorption and scattering of electrons by atoms in the films, and contrast is reversed compared to SEM with backscattered electrons. The high Z Au/Pd film appears dark, while the silicon nitride is lighter and the material that closed the holes is very light. TEM contrast is a convolution of film composition and film thickness. Comparison of SEM and TEM images makes the conclusion plausible that the holes close due to built-up of a low Z hydrocarbon layer during electron beam exposure. The possibility of formation of a film from the Au/Pd layer can be excluded. TEM images also confirm that the holes have not been closed completely. Rather the original hole diameter was reduced to about 5 nm, well below the resolution of direct FIB drilling.

Holes can also be closed by electron beam deposition of selected materials, like TEOS oxide and many metals. Here, the to be deposited material is introduced into the vacuum chamber through a gas needle that exposes an area of interest to the selected compound. We have tested this for platinum deposition. The platinum containing gas was admitted into the chamber for pulses of few seconds during which the electron beam rastered over the region of interest. As expected, the holes closed during deposition of the platinum film. In the examples shown in Figure 4, the diameters of two holes were reduced from 175 nm to 30 nm by electron beam deposition of platinum. The hole diameters were reduced at an average rate of 10 nm/s, over thirty times faster then for deposition of hydro-carbon films. The hole closing rate was found to slow down to a rate of 6 nm/s after 10 s, an effect that is currently under closer investigation. Reduction of hole diameters from 225 nm to 40 nm by thin film deposition with magnetron sputtering was reported by Ruchhoeft et al. [4]. In these studies, apertures closed at a rate of 0.64 nm per nm of deposited Au. The advantage of the local electron beam deposition described here is that hole evolution is monitored directly, so that the formation of very small holes becomes possible. Control of gas flux and local pressure are important for the reproducible formation of holes with desired sizes, and with minimal contamination of the area exposed to the seed gas. Hole closing rates, and film thicknesses for a given hole size for hydrocarbon or metal deposition depend on many parameters, such as electron beam current, scan rate, residual vacuum composition, and systematic studies of hole closing by electron beam deposition are underway. *In situ* electron beam or ion beam deposition of metal nanowires enables integration of nano-holes with electrodes for switching and monitoring of selected holes.

The results shown here demonstrate a simple method for the formation of nanometer scale holes by electron beam deposition of thin films. Holes, formed by FIB drilling or other methods, can be closed while their structure is being monitored. Electron beam deposition of thin films allows the formation of holes in a wide variety of materials (contamination resist, metals and TEOS oxide). Hole evolution can be monitored *in situ* down to the resolution limits of the available SEM (typically 2 to 5 nm). Hole diameters of about 2 nm are important for single molecule studies, potential applications in DNA sequencing [1-3], and ultrahigh resolution single atom doping [5]. Scaling of hole closing rates under controlled conditions allows formation of holes with diameters at and even below the SEM resolution limit. The presented simple method represent a hybrid of top down and bottom up techniques and enables structure formation beyond primary beam size limits though a primitive form of self organization during thin film deposition.

Acknowledgments

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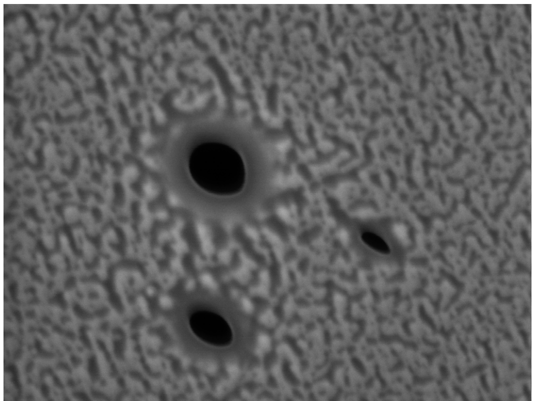
Figure captions:

Figure 1: SEM images of three FIB drilled holes in a 200 nm thick silicon nitride membrane. The original holes (top) close after minutes of exposure to the 5 keV electron beam (middle, bottom). The surface structure surrounding the holes is from the thin Au/Pd film.

Figure 2: Hole diameters as a function of time of electron beam exposure. The line is a linear fit to one data set and shows a closing rate of 0.3 nm/s.

Figure 3: SEM (left) and TEM (right) images of holes after closing by electron beam exposure. Contrast in the SEM is from backscattered electrons, which yields Z contrast. The high Z Au/Pd film appears bright, while the silicon nitride and the hole closing film appear darker. In TEM, contrast is reversed, and the hole closing film appears bright, indicating hole closing with low Z hydro-carbons.

Figure 4: Two FIB drilled holes (top) are closed by platinum deposition from an organometallic vapor during electron beam exposure (middle, bottom).



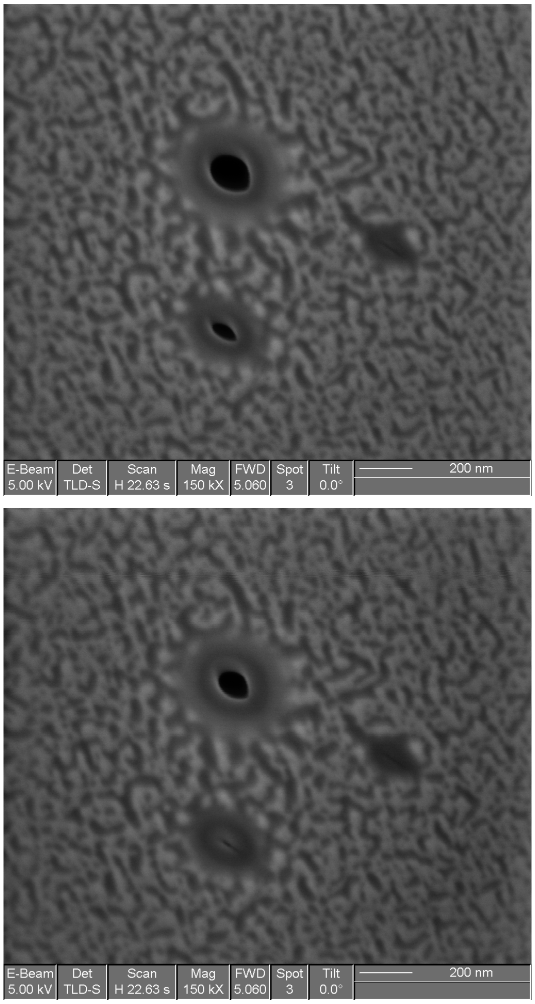

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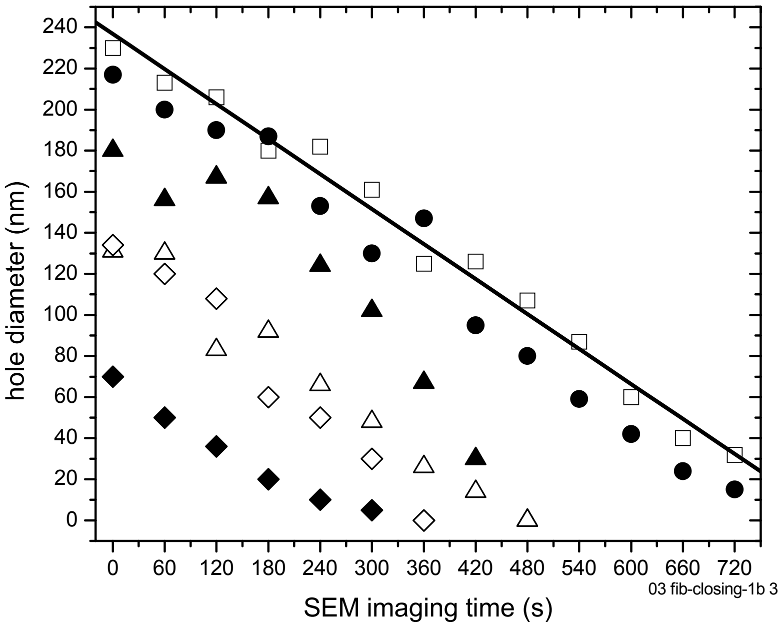
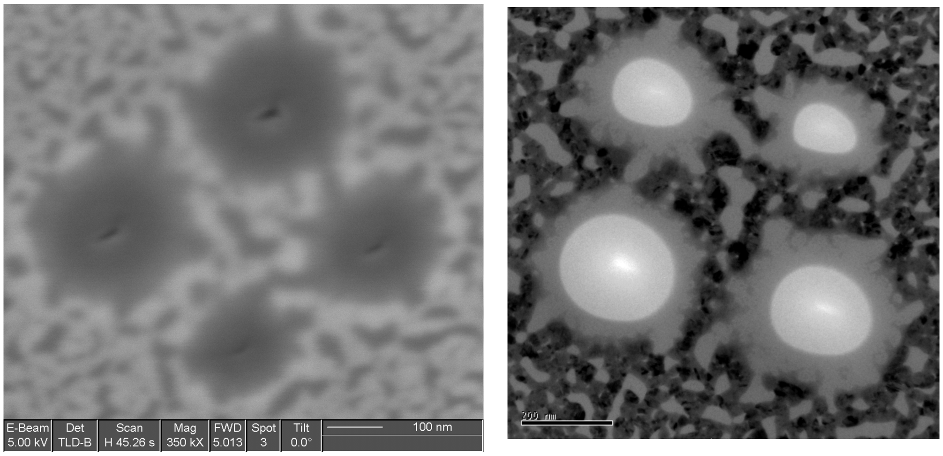
Figure 1



240
220
200
180
160
140
120
100
80
60
40
20
0
hole diameter (nm)
0
60
120
180
240
300
360
420
480
540
600
660
720
SEM imaging time (s)
03 fib-closing-1b 3

Figure 2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100 nm
200 nm

Figure 3

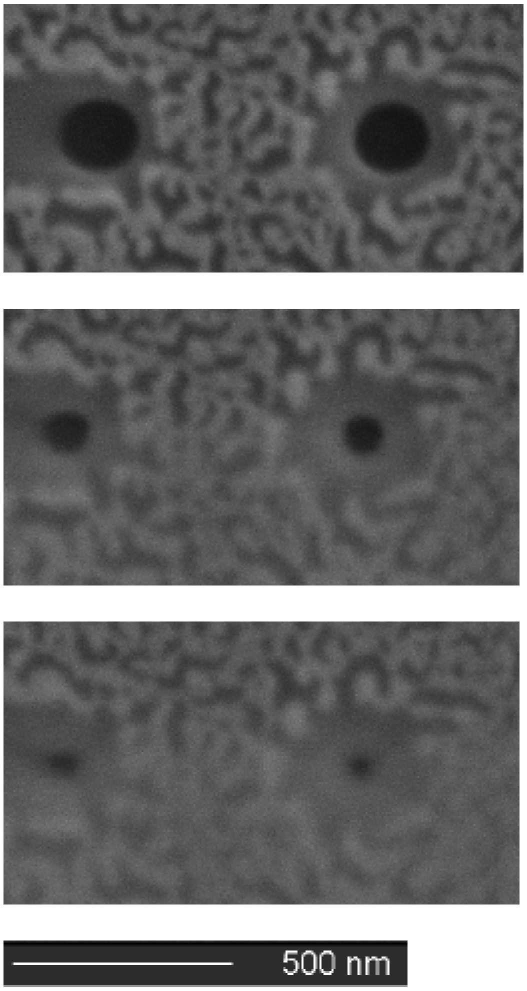

Fig. 4