Formation of a few nanometer wide holes in membranes with a dual beam focused ion beam system

T. Schenkel,[a] V. Radmilovic, E. A. Stach, S.-J. Park, and A. Persaud
E. O. Lawrence Berkeley National Laboratory, Berkeley, California 94720

(Received 1 July 2003; accepted 8 September 2003; published 5 December 2003)

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 build up and result in the closing of holes within minutes of imaging. Additionally, electron or ion beam assisted deposition of material from a gas source allows the closing of holes with films of platinum or tetraethylorthosilicate oxide. In an instrument equipped both with a focused ion beam, and a 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, well below resolution limits of primary beams.
[DOI: 10.1116/1.1622935]

I. INTRODUCTION

The ability to form holes in membranes with diameters of only a few nanometers (1 to 10 nm) is important 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-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] Anisotropic etching of hollow scanning near-field optical microscopy SiO_2 pyramids followed by thin metal film deposition has been shown to produce holes with 50 nm diameters reproducibly.[8] In this article, we describe a simple method for nanohole formation based on monitored closing of 100 nm-scale holes by electron- and ion beam deposition of thin films.

II. EXPERIMENT

For our experiments at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory we used an FEI Strata 235 Dual Beam focused ion beam (FIB), a system that combines a FIB with a scanning electron microscope (SEM) column. The samples in our study were membranes of low stress silicon nitride with a thickness of 30 to 200 nm on silicon frames. The membranes were coated with 5 nm of a gold palladium alloy to prevent charging during exposure to electron and ion beams. A 30 keV Ga^+ beam with an intensity of 1 pA in a spot with a diameter of 10 nm was used to drill holes into the membranes. Initial hole diameters ranged from about 50 to 600 nm. The base pressure in the FIB vacuum chamber was 3×10^{-6} Torr. For hole closing with hydrocarbon 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/s. After an exposure interval of 30 s to 1 min, the sample area was imaged with a slower, higher contrast scan, and the process was repeated. For deposition of Pt form an organometallic precursor gas, we used a 30 keV Ga^+ beam with a beam current of 10 pA. The ion beam impinged on the sample at normal incidence.

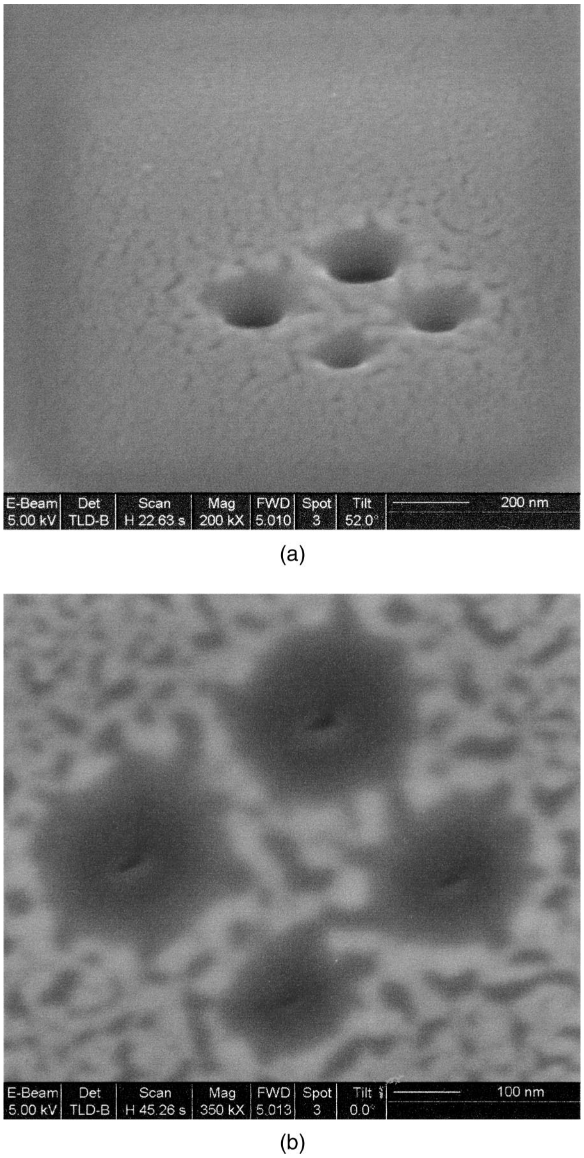
III. RESULTS AND DISCUSSION

A. Electron-beam deposition of contamination resist

In Fig. 1, we show SEM images of four holes before (top) and after (bottom) extended exposure to the imaging electron beam. Here, holes closed with a rate of 0.3 nm/s during electron-beam imaging. The chemical composition of the deposited material can be inferred from a comparison of SEM and transmission electron microscope (TEM) images of closed holes. Figure 2 shows TEM images of the holes from Fig. 1 after closing. 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 these 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 a build up of a low-Z hydrocarbon layer during electron-beam exposure. TEM images also confirm that the

---

[a] Electronic mail: t_schenkel@lbl.gov



(a)

(b)

FIG. 1. SEM images of four FIB drilled holes in a 200 nm thick silicon nitride membrane, before (a) and after (b) closing of holes during electron-beam imaging.

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.

B. Ion beam deposition of platinum

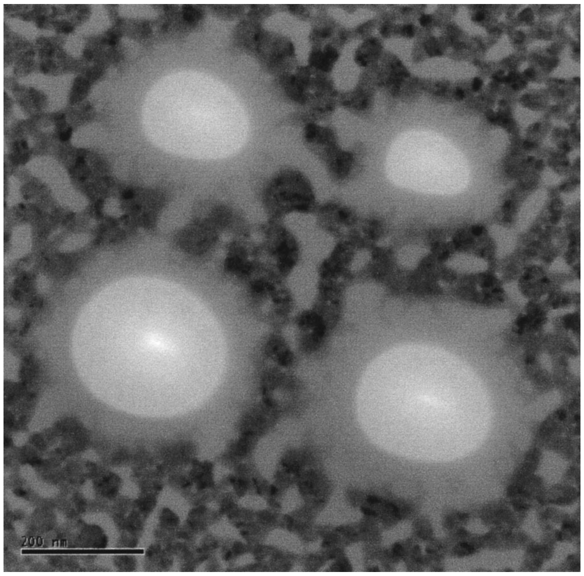
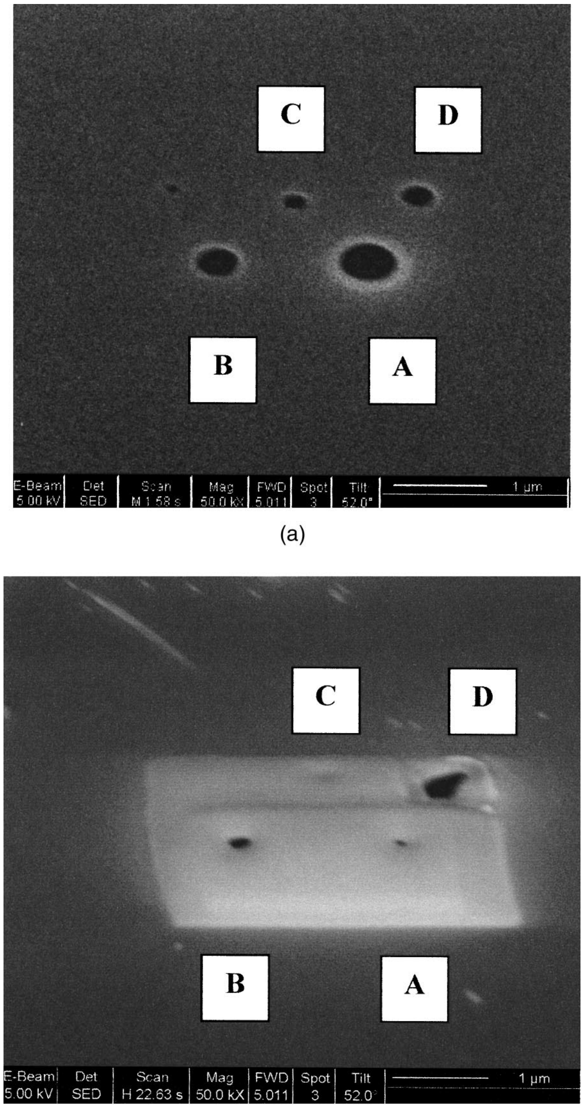


FIG. 2. TEM image of holes after electron-beam exposure.

Holes can also be closed by ion beam or electron-beam assisted deposition of selected materials, like tetraethylorthosilicate (TEOS) oxide and many metals. Here, the material to be deposited is introduced into the vacuum chamber through a gas needle that exposes an area of interest to the selected compound. The compound molecules are cracked by the ions or electrons from the probe beam and the material is deposited only in the sample area exposed to both the gas flux and the probe beam. We report here only on results from hole closing by ion beam assisted thin-film deposition of platinum. The platinum containing organometallic gas was admitted into the chamber for pulses of a few seconds during which the ion beam was rastered over the region of interest. Figure 3 shows five holes with initial diameters ranging from 100 to 600 nm before [Fig. 3(a)] and after [Fig. 3(b)] ion beam assisted Pt deposition. Holes were characterized by scanning transmission electron microscopy (STEM) following thin-film deposition. In Fig. 4, we show two line scans of Pt x rays across hole numbers A and B from Fig. 3. Pt x rays were generated with a 300 keV electron beam in STEM mode. The Pt x-ray line scans show that the hole diameters were reduced to 14 nm (B, top) and 4.3 nm (A, bottom), respectively. The STEM step size was 0.7 nm. Hole C was found to be closed in STEM images. For hole D, Pt deposition was performed with an ion beam scan area of 500 nm by 500 nm, an area less than half the ion beam scanning area for holes A and B. The balance of ion beam sputtering and thin-film deposition is crucial. For the 10 pA Ga^+ beam, and the given Pt gas influx, the area selected around hole D was small enough so that the ion beam sputtered more material away than was deposited.

Hole A was reduced from a diameter of about 600 nm down to only 4.3 nm. Ruchhoeft *et al.*[4] have found a ratio of 0.6 of hole diameter reduction to film thickness during thin-film deposition and hole closing by magnetron sputtering. We have not determined the aspect ratio of the holes described here. Assuming a similar ratio of hole diameter reduction to film thickness as reported by Ruchhoeft *et al.*,[4] we estimate that the film thickness was about 800 nm, and this indicates remarkably high aspect ratios $>50:1$. The estimated film thickness is consistent with Pt deposition rates for our process conditions with a 10 pA, 30 keV Ga^+ beam, and direct measurements of film thickness by FIB cross sectioning are underway. Information on hole wall geometries is contained in the Pt x-ray line scans. Pt x-ray intensities drop from maxima at the hole rims to zero at the bottom of holes over distances of about 14 to 24 nm for both holes. An asym-



(a)

(b)

FIG. 3. SEM image of holes before (a) and after (b) closing by ion beam assisted deposition of a Pt film.

metry in wall steepness is observed for both holes and can be attributed to a shadowing effect due to injection of the Pt-precursor gas under an angle of about 45° relative to the surface normal.

IV. CONCLUSIONS

The advantage of the local electron- and ion beam deposition techniques described here is that hole evolution is monitored directly, so that the reproducible 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- or ion beam current, scan rate, residual vacuum composition, and systematic studies of hole closing rates by electron- and ion beam deposition are in progress.

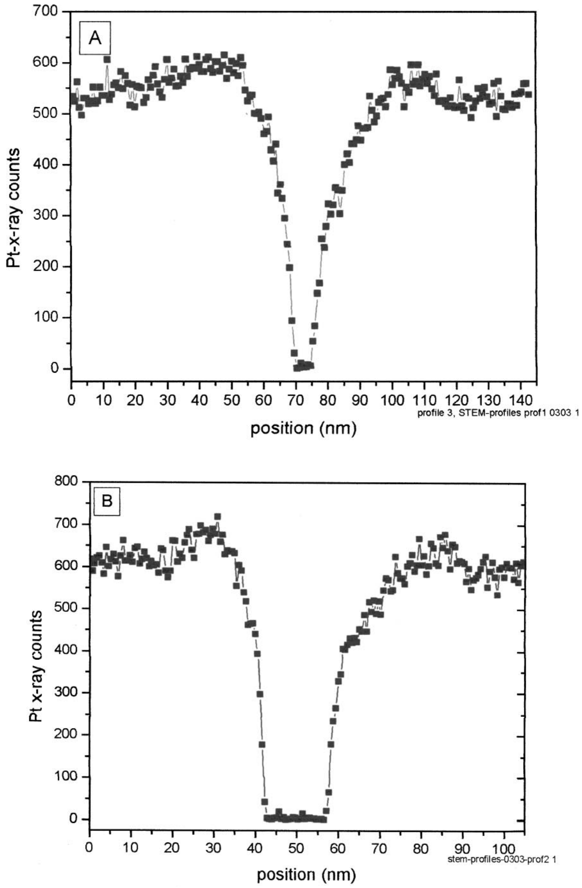


FIG. 4. STEM line scans with Pt x-ray intensities across holes A (a) and B (b) from Fig. 3.

The results shown here demonstrate a simple method for the formation of nanometer-scale holes. Holes, formed by FIB drilling or other methods, can be closed while their structure is being monitored. *In situ* electron- or ion 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 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 deoxyribonucleic acid sequencing,[1–3] and ultrahigh resolution single atom doping.[5] The presented simple method represents 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

This work was performed at the National Center for Electron Microscopy at the E. O. Lawrence Berkeley National Laboratory and was supported by the National Security Agency and Advanced Research and Development Activity under Army Research Office Contract No. MOD707501, and by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1] J. Li, D. Stein, C. McMullan, D. Branton, M. J. Azis, and J. A. Golovchenko, Nature (London) **412**, 166 (2001); D. Stein, J. Li, and J. A. Golovchenko, Phys. Rev. Lett. **89**, 276106 (2002).
[2] A. Meller, L. Nivon, and D. Branton, Phys. Rev. Lett. **86**, 3435 (2001).
[3] Z. Siwy and A. Fuliski, Phys. Rev. Lett. **89**, 198103 (2002).
[4] P. Ruchhoeft, J. C. Wolfe, J. L. Torres, and R. Bass, J. Vac. Sci. Technol. B **20**, 2705 (2002).
[5] T. Schenkel, A. Persaud, S. J. Park, J. Meijer, J. R. Kingsley, J. W. McDonald, J. P. Holder, J. Bokor, and D. H. Schneider, J. Vac. Sci. Technol. B **20**, 2819 (2002).
[6] A. N. Broers, A. C. F. Hoole, and J. M. Ryan, Microelectron. Eng. **32**, 131 (1996).
[7] M. E. Mochel, J. A. Eades, M. Metzger, J. I. Meyer, and J. M. Mochel, Appl. Phys. Lett. **44**, 502 (1984).
[8] A. Volland, G. Georgiev, O. Rudow, M. Müller-Wiegand, and E. Oesterschulze, J. Electrochem. Soc. **148**, G587 (2001).
[9] W. W. Molzen, A. N. Broers, J. J. Cuomo, J. M. E. Harper, and R. B. Laibowitz, J. Vac. Sci. Technol. **16**, 269 (1979).