Fabrication of submicron apertures in thin membranes of silicon nitride

A. Amar, R. L. Lozes,[a] Y. Sasaki, J. C. Davis, and R. E. Packard

Physics Department, University of California, Berkeley, California 94720

A technique for manufacturing submicron apertures used for investigating hydrodynamic quantum phenomena in the superfluids ^{4}He and ^{3}He is described. The apertures are fabricated in ~ 100 nm thick suspended membranes of silicon nitride by using e-beam lithography and reactive ion etching.

I. INTRODUCTION

We have fabricated single apertures (holes and slots) of width 200–500 nm in ~ 100 nm thick membranes. These structures are employed in the study of quantum phenomena in the flow of superfluids ^{4}He (below 2.2 K) and ^{3}He (below 2.5 mK). Apertures of these dimensions behave as phase-slip nucleation centers[1] for both ^{4}He and ^{3}He, and as Josephson junctions[2] for the superflow of ^{3}He. Previously, submicron holes and slots for superfluid studies have been made using ion-beam milling on thin metal foils.[3,4] Other techniques for fabrication of submicron structures in various substrates have been reported in the literature.[5]

We choose low-stress silicon nitride as the material in which to fabricate the apertures because of its (1) smoothness and flatness, (2) mechanical strength to survive ordinary handling and differential pressures of up to 1 atm, (3) ability to withstand thermal shock and repeated cycling to liquid helium temperatures, and (4) ease of fabrication.

Fabrication starts with the deposition of thin films of nitride on silicon and then etching away the silicon to leave suspended membranes. The holes and slots are formed by e-beam lithography on PMMA[6] and transferred into the underlying nitride membrane by reactive ion etching.

In Sec. II, we describe the process steps to produce the silicon nitride membranes. Section III concerns the e-beam lithography, followed in Sec. IV by the techniques of aperture etching and determination of the aperture's dimensions.

II. FABRICATION OF SUSPENDED THIN MEMBRANES

Deposition of low tensile stress nitride films on silicon wafers[7] and techniques of anisotropic etching of the silicon to form suspended membranes[8,9] have been previously reported in the literature. Here we describe the salient features of our recipe.

First, a film of silicon nitride is grown on both sides of a 100 mm diam p-type $\langle 100 \rangle$ oriented silicon wafer [Fig. 1(b)] using low-pressure chemical vapor deposition (LPCVD). The wafers are device-grade, with resistivity 15–30 Ω cm, nominally 500 μm thick and polished on one side (the front side). The deposition is carried out at 850 °C in a quartz furnace[10] by the reaction of dichlorosi-

lane (DCS) and ammonia (NH$_3$). The flow rates used are 80 sccm (STP cm^3/min) (DCS) and 20 sccm (NH$_3$), and the furnace pressure during the deposition is 270 mTorr. The deposition proceeds at about 4.5 nm/min, and we grow films of thickness 60–200 nm by varying the deposition time.

The films thus produced are amorphous, silicon-rich, nonstoichiometric (Si$_{3+x}$N$_4$) and possess at room temperature a residual tensile stress[11] of $\sim 2 \times 10^8$ N/m^2, which is about ten times lower than that in stoichiometric LPCVD nitride. Generally speaking, for a fixed value of deposition temperature, increasing the DCS:NH$_3$ ratio reduces the film tension, and it is possible to cross over into a regime of compressive residual strain for sufficiently high ratios.[7,12] The latter situation is undesirable for our purposes, since the suspended membranes come out wrinkled rather than flat. In our experience, increasing either the ratio DCS:NH$_3$ or the deposition pressure or temperature makes the films less and less tensile. A 4:1 ratio of DCS:NH$_3$ at 850 °C produces nitride that is low-stress tensile, whereas a 6:1 ratio at the same temperature results in compressively strained films. Allowing the deposition pressure to go up to 330 mTorr (but maintaining the temperature at 850 °C and DCS:NH$_3$ at 4:1) produces compressive films. However, since it is difficult to replicate the deposition conditions from one furnace to another, the numbers given above should serve merely as a guide to arrive at the optimal recipe for a given furnace.

The thickness (60–200 nm) of the nitride film is such that it can be conveniently determined by measuring the reflectivity or interference patterns for several wavelengths in the optical range.[13] We find that on any given wafer, the film is quite uniform, being thicker at the periphery than at the center by less than 4%.

After the film deposition, square openings through the nitride are patterned on the (unpolished) back side of the wafer by standard photolithographic techniques and SF$_6$/He plasma etching[6] [Fig. 1(c)]. These windows are aligned with the orientation of wafer flats in order to ensure smooth etching in EPW (see below).

After the removal of photoresist, the wafer is dipped in 10:1 diluted aqueous HF for 5 s (to remove any oxide), then rinsed in water and spun dry, then immediately lowered into an etchant[9] consisting of 1000 ml ethylenediamine (E), 160 g of (pyro)catechol (P), 132 ml of water (W), and 6.0 g of pyrazine. EPW is an anisotropic etchant of silicon which etches the {100} planes much faster than

[a]Presently at Etec Systems, Inc., Hayward, CA 94545.

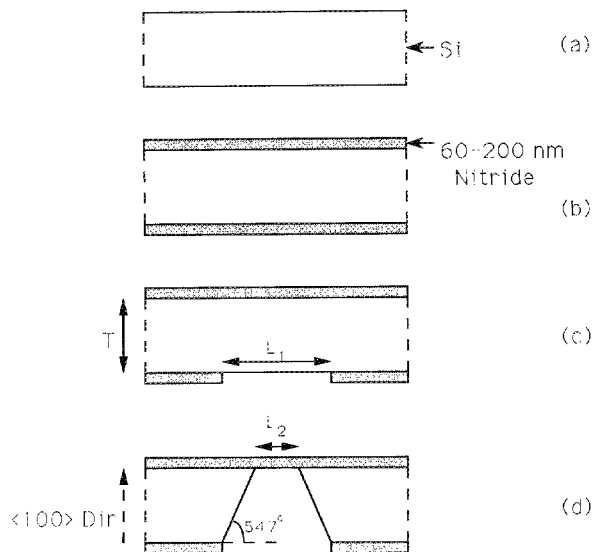FIG. 1. Process steps for the fabrication of thin, suspended windows of silicon nitride.

FIG. 2. (a) Layout of the pattern on the back side of wafer. The two alignment windows are marked "w." (b) Enlarged view of one of the 16 dice.

the {111} planes, and is easily masked by silicon nitride (and also by SiO_2). Thus, the etch stops at the nitride film on the front side after going through the entire thickness of the wafer [Fig. 1(d)]. At 110 °C, in a freshly prepared EPW solution, the silicon etching rate is 40 μm/h in the $\langle 100 \rangle$ direction. We etch for 13–14 h to ensure that the etch goes through the wafer thickness completely.

During the etch, some thinning of the nitride occurs as well. From measurements of the film thickness before and after the etch we deduce a nitride etching rate of ~ 3 nm/h. After removal from the etchant, the wafer is allowed to cool to room temperature, and then rinsed several times in water. This is followed by cleaning in piranha (5:1 H_2SO_4:H_2O_2) and subsequent spin drying after more rinsing in water. At this point the wafer is ready for the next processing step.

Since ethylenediamine is a carcinogen, the etching must be carried out in an appropriate fume hood, and the beaker containing the EPW covered with a lid to prevent the escape of vapors. An alternative to EPW is to do the anisotropic etch in a 33% (by weight) KOH solution. The latter, however, is quite toxic, and once again proper care must be taken in handling it.

From the geometry of the etched pit [Fig. 1(d)], it follows that the size (linear) L_2 of the suspended membrane is related to the size L_1 of the opening on the back side by

$$L_2 = L_1 - 2^{1/2} \ T,$$

T being the wafer thickness. Thus, for a 500 μm thick wafer, starting with a 730 μm square opening, one ends up with $\sim 25 \times 25$ μm membranes.

On each wafer, the membranes are patterned on a 1 cm grid in a 4×4 or 6×6 array, so that there are either 16 or 36 chips per wafer. (Patterning a larger array greatly increases the chances of wafer breakage in the processing steps that follow the anisotropic etch.) To facilitate the
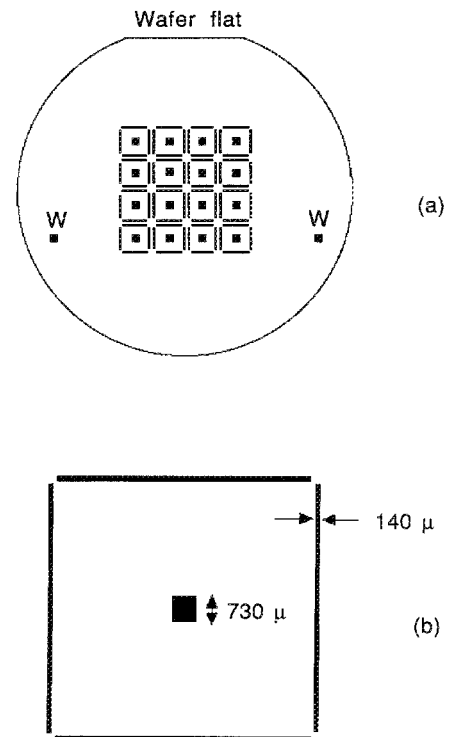
eventual dicing of the wafer into individual chips, we also etch ~ 100 μm deep v-shaped grooves along the chip boundaries on the back side [see Figs. 2(a) and 2(b)] in the same EPW etch. In addition, we etch two extra membranes of size 25 μm to help align patterns to the front side of the wafer in a subsequent photolithographic step following the anisotropic etch.

The suspended membranes produced by the method described in this section are quite flat and mechanically strong. The etched wafer with the membranes routinely survives all of the remaining processing steps as long as it is not dropped or impacted. As for the membranes themselves, they can easily support a differential pressure of 1 atm, and withstand repeated thermal cycling between room temperature and 4 K. Inspection under the scanning electron microscope (SEM) as well as vacuum leak checks using a helium leak detector show that the membranes are pinhole-free.

III. E-BEAM EXPOSURE TO DEFINE THE HOLES AND SLOTS

Before the wafer is ready for e-beam patterning, it is put through one more stage of photolithography. With the centers of the two alignment windows used as reference coordinates, we expose and plasma etch sets of crossed index marks 4 μm wide and ~ 1 μm deep at specific locations (away from the membranes) on the wafer front, to be used later by the e-beam machine for determining the location of the membranes on the wafer. Simultaneously we re-
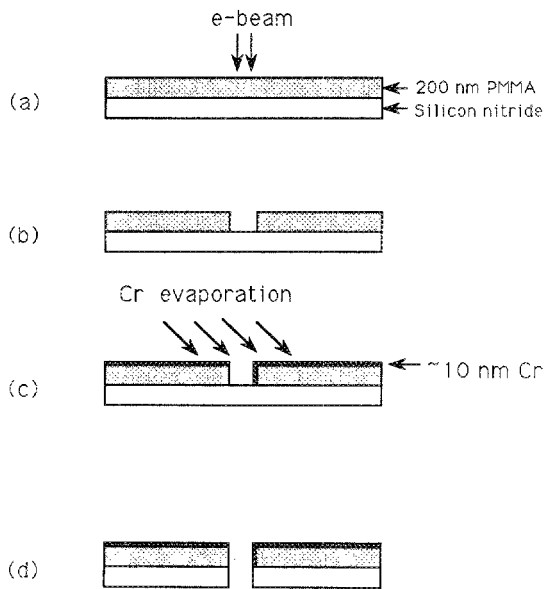
e-beam

FIG. 3. Process steps for producing apertures in the nitride: (a) e-beam exposure of the resist PMMA; (b) After development of the resist; (c) Evaporation of Cr at a shallow angle; (d) After RIE in SF$_6$/He.

move, by plasma etching, the nitride from a 3 mm annulus on the wafer front around its circumference, exposing bare silicon in order to provide electrical contact to the wafer during the e-beam exposure.

The wafer is once again cleaned in acetone, followed by a piranha clean. Then a 200 nm thick layer of 2.5%, 456 K mol wt PMMA is spun on, using a special chuck that holds the wafer without pulling vacuum under it. This is to ensure that the suspended nitride membranes do not sag, otherwise, the coated PMMA layer would not be uniform. The wafer is then baked in air at 180 °C for 60 min.

The e-beam exposure is carried out on a commercially available e-beam machine designed for wafer lithography.[14] The machine reads the index marks on the front side to set the wafer coordinates, and then exposes a single dot or slot in the center of PMMA on top of each membrane [Fig. 3(a)]. The features end up within 2 μm from the exact center of any membrane.

The e-beam column is set up to write features of sizes 0.20–0.45 μm. After doing a series of test exposures at different beam currents and voltages, we found an exposure of 200 μC/cm^2 at a beam voltage of 20 keV to be optimal for the PMMA on our nitride membranes. At this exposure, PMMA still behaves as a positive resist, i.e., the exposed regions dissolve during the development [Fig. 3(b)].

The development of PMMA is carried out at 22 °C in 1:1 methylisobutylketone: isopropyl alcohol (IPA) for about 60 s. On one of the membranes, a set of parallel bands, each of width 2 μm is exposed by the e-beam to facilitate end point monitoring during the development. Pure IPA is used as a stop after development. At this stage the wafer can be broken into individual chips before further processing. Cracking along any of the etched grooves is cleanly accomplished by pressing down from the back

side, while the wafer front rests atop a thin tungsten rod that is aligned with the groove.

IV. TRANSFER OF THE EXPOSED PATTERN INTO THE NITRIDE

After the e-beam exposure and development of PMMA, the holes and slots in the PMMA are transferred into the silicon nitride substrate using reactive ion etching (RIE) in a plasma of SF$_6$ and He. It is advisable to first bake out solvents from the PMMA at about 100 °C for 10–20 min in order to harden the resist against etching in the RIE.

A major problem is that the PMMA is etched at about the same rate as the submicron features in nitride; the situation becomes worse as the etch power is increased. Thus, we find it necessary to etch at very low powers (~ 10 W), but even then, almost all the PMMA is gone by the time the nitride etching is completed. Another problem encountered sometimes is the formation of PMMA residues during the RIE which are extremely resistant to removal by solvents or by oxygen plasma ashing.

To circumvent these problems, we deposit ~ 10 nm of Cr on top of the PMMA to protect it during the plasma etch. The Cr is deposited under vacuum in a standard evaporator; the evaporation must be done at a shallow angle to the membrane so as not to fill up the bottom of the pit in the PMMA [Fig. 3(c)].

By choosing the evaporation angle suitably, we can cover part of the exposed membrane with Cr, thus, making it possible to produce holes and slots that are narrower than the original features in the resist. With the layer of Cr to protect the PMMA, the RIE can be carried out at a power of 50 W. Afterwards, the Cr is lifted-off by dissolving the PMMA in boiling acetone. To ensure complete removal of the resist, a piranha treatment can be given after the acetone.

Imaging of the holes and slots on a SEM is not trivial. Because of the thinness of the membranes, the yield of secondary electrons (signal of interest) is very low. Tilting the sample (typically 20°) improves the image contrast by producing more secondary electrons. Also, since the membranes are quite smooth and featureless, we define (during the e-beam writing) 5 μm wide index marks in the silicon near the location of the suspended membrane, and find it efficient to first focus on these index marks before scanning the membrane for the etched hole or slot. Figure 4 shows typical SEM images of the apertures.

In addition to SEM imaging, we employ a simple scheme based on gas effusion to determine the hole size. At a temperature T, the number of molecules per second of a gas of molecular weight, M passing through a hole of cross-sectional area A is given in the ballistic regime (mean-free-path much longer than the hole dimensions) by

$$dN/dt = (nA/4)(8RT/\pi M)^{1/2},$$

where n is the number density of molecules on one side of the hole (the other side being under vacuum), and R is the gas constant. By using helium gas at room temperature and
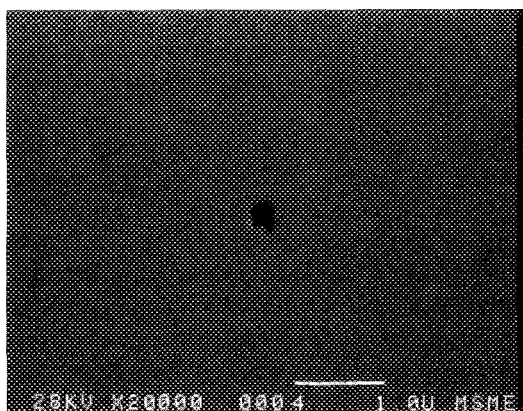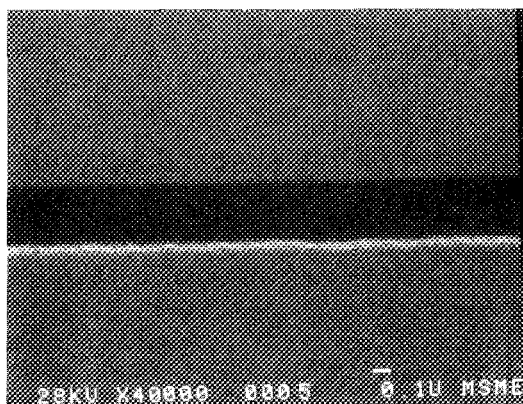
FIG. 4. SEM pictures of etched holes/slots in the nitride films.

a calibrated leak detector to measure dN/dt, we obtain cross-sectional areas that agree with those from the SEM to within 10%.

ACKNOWLEDGMENTS

[1]O. Avenel and E. Varoquaux, Phys. Rev. Lett. 55, 2704 (1985); A. Amar, Y. Sasaki, R. L. Lozes, J. C. Davis, and R. E. Packard, ibid. 68, 2624 (1992).
[2]O. Avenel and E. Varoquaux, Phys. Rev. Lett. 60, 416 (1988); J. R. Hook, Jpn. J. Appl. Phys. 26-3, 159 (1987); J. Kurkijarvi, Phys. Rev. B 38, 11184 (1988).
[3]B. P. Beecken and W. Zimmermann, Jr., J. Vac. Sci. Technol. A 3, 1839 (1985).
[4]P. Sudraud, P. Ballongue, E. Varoquaux, and O. Avenel, J. Appl. Phys. 62, 2163 (1987).
[5]See for instance, A. Murray, M. Isaacson, I. Adesida, and B. Whitehead, J. Vac. Sci. Technol. B 1, 1091 (1983); K. S. Ralls, R. A. Buhrman, and R. C. Tiberio, Appl. Phys. Lett. 55, 2459 (1989).
[6]See any standard text on microelectronic IC fabrication, e.g., Integrated Circuit Fabrication Technology, 2nd ed., edited by D. J. Elliott (McGraw–Hill, New York, 1989).
[7]M. Sekimoto, H. Yoshihara, and T. Ohkubo, J. Vac. Sci. Technol. 21, 1017 (1982).
[8]R. M. Finne and D. K. Klein, J. Electrochem. Soc. 114, 965 (1967).
[9]A. Reisman et al., J. Electrochem. Soc. 126, 1406 (1979).
[10]The furnace used was a LPCVD tube originally manufactured by Tylan Corp., which has gone out of business. The furnace is now serviced by TYSTAR, Torrance, CA 90501.
[11]Determined by measuring wafer curvature on a Flatgage Sonic Probe before and after film deposition. Before the postdeposition measurement, the film must be removed from the back side.
[12]L. A. Field in EECS/ERL Research Summary (1987), U. C. Berkeley, CA 94720.
[13]The film thickness was measured on a Nanospec/AFT system (Nanometrics Inc., Sunnyvale, CA 94086).
[14]AEBLE 150 TM, Etec Systems, Inc., Hayward, CA 94545.