Processing of nano-holes and pores on SiO$_2$ thin films by MeV heavy ions

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Abstract

Scanned beams of 0.1 MeV/u ^{197}Au ions were employed for the bombardment of silicon oxide films thermally grown on silicon (1 0 0) substrates. Subsequently the films were etched in aqueous HF solution (1% and 4%) for various times and at different temperatures. Scanning force microscopy and transmission electron microscopy images of etched films reveal conical holes with diameters from 20 to 350 nm, depending on the HF concentration and etching time. For a fixed etching temperature, hole size increased roughly linearly with etching time, and for a fixed etchant concentration, it varied exponentially with etching temperature. These porous surfaces were tested for trapping of nano-particles, as templates for deposition of porous films, and for localized etching of the Si substrate.
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1. Introduction

The damaged region around a single fast-ion trajectory in an insulating target – the latent track – exhibits a different etching rate than pristine target material. Therefore, these regions can be developed into features of desired dimensions when the bombarded surface is exposed to an appropriate etching agent [1]. Track development by etching may be used to tailor structures on surfaces or in the bulk, to modify materials properties, or simply to make tracks observable by, e.g. optical microscopy [1,2]. The processing of membranes and other microstructures represents the main road followed in technological application of ion tracks, which found a broad range of applications, such as synthesis of materials with submicron dimensions [3], molecular switches [4] or field emitters for displays [5]. Successful track etching often requires that the energy density resulting from the ion energy deposition via ion–electron collisions is large enough, whereby the latent tracks formed become approximately regions of continuous damage. Because of that, etched tracks are usually produced with heavy

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particles from high-energy accelerators in order to obtain latent tracks extending several micrometers in depth. With intermediate energy beams of heavy ions (below 1 MeV/u), a high density of excitations in a localized cylindrical track is still achievable at small depths. Here we report on the use of a 3 MV tandem accelerator to produce nanometer-scale holes on *thin* films of silicon oxide and on Si wafers. Porous layers of SiO_2, a thermally stable and chemically resistant material, may find unique applications in environments where plastic membranes are not applicable.

2. Experimental

Silicon oxide *films* of different thickness (from 50 to 500 nm) were thermally grown onto silicon (1 0 0) wafer surfaces. A standard RCA cleaning was performed before oxide growth. Different Si batches were exposed for different times to either a dry oxygen atmosphere at 1100 °C or a wet atmosphere at 1000 °C. Targets were bombarded in vacuum ($\sim 3 \times 10^{-6}$ Torr) at normal incidence by 20 MeV $^{197}Au^{7+}$ ions from the Porto Alegre 3 MV tandem accelerator. The ion fluence was around 10^8–10^9 cm^{-2} and was obtained in approximately 1 s of irradiation in a scanned beam. Subsequently, the films were etched in aqueous HF solution for various times t_e (from 1 to 20 min) at room temperature. The concentration c of the etchant was 1% or 4% by volume. Samples were also etched at different temperatures (7–55 °C) at $c = 4\%$ and $t_e = 5$ min in a water bath. After etching, the samples were immediately washed in deionised water and dried under dry nitrogen. The surfaces were imaged by scanning force microscopy (SFM, NanoScope IIIa, Digital Instruments) in the TappingMode^{TM} under ambient conditions. Subsequent to SFM analysis, selected samples etched in HF were placed in a solution of sodium hydroxide (NaOH, 0.8 M, 80 °C) for various times (3–12 min). After this step, the remaining oxide layer was removed by an additional exposure to a HF solution. The TEM observations were performed at 200 kV in cross-section specimens prepared by ion milling.

3. Results and discussion

Unetched tracks of 20 MeV Au ions on SiO_2 films display no visible craters in SFM images. Etching of the bombarded films produced conical holes (Fig. 1) with a diameter, ϕ, at the surface that increases roughly linearly with the etching time. Mean values of ϕ for different batches of oxides etched at room temperature (which could differ by ±5 °C among the different procedures) are shown in Fig. 2(a). For a fixed concentration and etching time, the diameter of the holes increases roughly exponentially with the temperature of the etching solution (Fig. 2(b)), but differences of only a few degrees about room temperature do not change the size of the etched tracks significantly. A reasonable dispersion in the hole size was observed, sometimes even with apparently similar oxide growth and etching conditions. This can be partially attributed to differences in etching rate for oxides prepared by wet or dry oxidation. Wet SiO_2 layers are somewhat more loosely structured
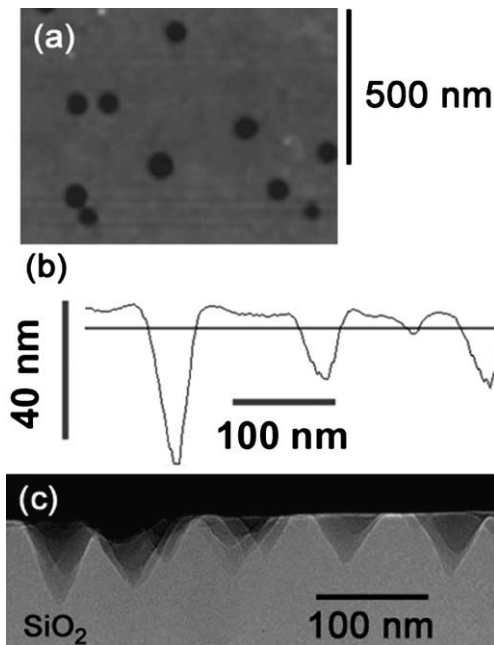

Fig. 1. (a) SFM image of a bombarded SiO_2 film etched in 1% HF for 10 min, showing circular holes. (b) Profiles of holes as seen by SFM and (c) by cross-section TEM (bright field kinematical conditions, under focus, negative image).
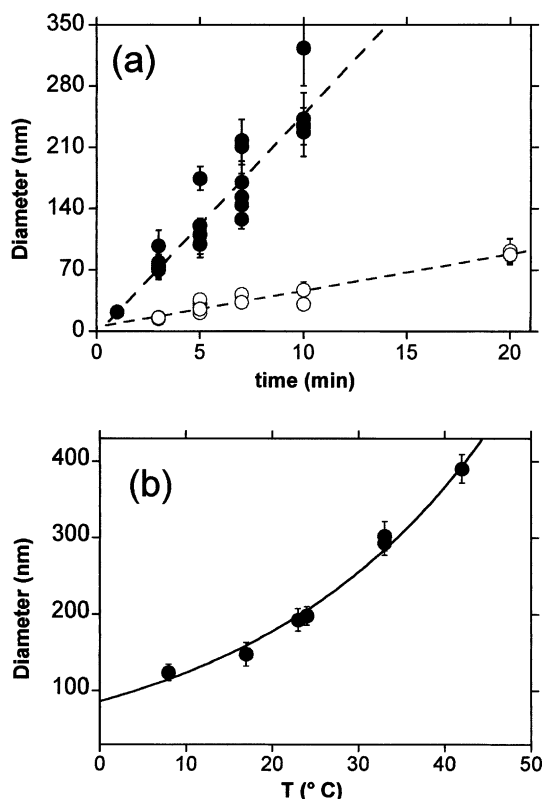
Fig. 2. Etched track diameter on silicon oxide versus (a) etching time for a 1% (open circles) and 4% (black circles) HF solution at room temperature and (b) versus etching temperature for a 4% HF solution and 5 min etching time.

and thus have a slightly higher etching rate for HF solutions than SiO_2 grown in dry ambient [6]. Furthermore, the etching rate is sensitive to the presence of contaminants, whose contents are difficult to control during the different steps of cleaning and oxidation of the films. The above results stress the importance of a strict control of the various steps of oxide layer production in order to obtain reproducible dimensions of the nano-holes on etched films.

Fig. 1(b) and (c) provides a comparison between the dimensions of etched tracks extracted from SFM images and from cross-section TEM. For a sample etched for 10 min in 1% HF, the diameters of the holes at the surface measured by TEM and SFM were almost identical, around 50 nm. The average depth of the holes measured from SFM

and TEM images were also similar (33 ± 6 nm and 39 ± 12 nm, respectively). However, holes with maximum depth around 75 nm were seen in TEM images, but never seen on the SFM images, probably because of the obtrusion of the tip at the narrower parts of the cones. The average half-cone angle of the etched tracks obtained from TEM images for that sample was $31 \pm 6°$, consistent with values found for fused silica glass [1]. From the values of the depth, z, and the half-cone angle, β of the holes, the track and bulk etch rates (v_t and v_b) can be determined using the expressions: $z = (v_t - v_b)t_e$ and $\sin \beta = v_b/v_t$ [2]. For a 1% HF solution at room temperature, $v_t \approx 2v_b$ and $v_t = 0.13$ nn/s.

Sufficient etching eventually produces an open track through the oxide layer down to the Si interface, and a porous SiO_2 film is formed. Under this condition, localized etching of the Si wafer with NaOH is feasible. NaOH attacks the porous oxide layer very little: no significant differences in the hole diameter and the film thickness were observed after NaOH etching. Upon residual oxide removal, squared openings on the Si surface were seen at the sites of the etched tracks (Fig. 3(a)). The quadratic shape of the holes on the Si surface is due to the anisotropic etching of Si crystals [7]. The considerably lower etching rates along $\langle 1\,1\,1 \rangle$ directions determine the pyramidal shape of the holes, producing a quadratic base with sides along $\langle 0\,1\,1 \rangle$ directions.

Fig. 3 illustrates two simple applications of the nano-holes: trapping of nano-particles and growth of porous metal films. Silver particles were deposited on the etched SiO_2 films and the excess of silver was wiped off with soft cotton. Only particles trapped at the holes remained on the surface (Fig. 3(b)). Fig. 3(c) shows a SFM image of a 500 nm thick Au layer sputtered onto a SiO_2 surface with pores 120–150 nm in diameter. At least up to this thickness, the pores in the Au film have holes with dimensions similar to the ones in the oxide layer. After annealing at 400 °C for half an hour the gold layer appears continuous, covering most of the holes. Upon removal of the Au film (also with soft cotton), holes were once again seen on the bare SiO_2 surface, indicating that the Au did not fill in the holes during annealing. This was confirmed by
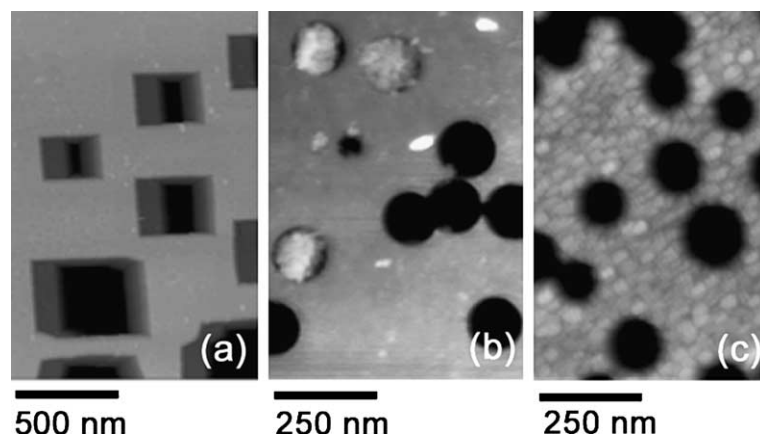
Fig. 3. (a) Pyramidal holes etched on the Si substrate by NaOH etching (0.8 M, 6 min, $T = 80$ °C) through the oxide pores. (b) Trapping of Ag particles on the pores of a SiO_2 film. (c) Porous Au layer, 500 nm thick, grown on the top of a porous SiO_2 template layer. The hole size distribution of the oxide layer remains in the Au film. All images were acquired by SFM in the Tapping mode.

TEM observations in cross-section, which detected no Au inside the SiO_2 holes.

Because of the high thermal stability of SiO_2, such perforated surfaces may in principle be used as molds for high temperature synthesis of nanoparticles or other nano-objects. Pore stability was experimentally verified by heating a sample in vacuum to a temperature of 800 °C for 1 h, without any noticeable change in hole size. These porous surfaces should of course be stable even to much higher temperatures, because of the high glass transition temperature of SiO_2.

4. Conclusions

Nanometer-scale holes and pores in SiO_2 thin films thermally grown on Si(1 0 0) surfaces were obtained by MeV heavy ions from a relatively low energy accelerator followed by a suitable chemical etching. The holes on the surface had diameters from 20 to 350 nm, depending on the etching conditions. For sufficiently thin oxide films, the etched samples produced a surface with localized hydrophilic/hydrophobic properties in a random distribution. Here we showed the usefulness of the porous SiO_2 layer for localized etching of the un-

derlying Si substrate, for trapping of nano-particles, and for the growth of porous metal layers. Such porous films can in principle be used for the growth and processing of different nano-objects even at high temperatures.

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