Processing of nano-holes and pores on SiO₂ thin films by MeV heavy ions

C. Milanez Silva a, P. Varisco a, A. Moehlecke a, P.P. Fichtner b, R.M. Papaléo a,*, J. Eriksson c

a Faculty of Physics, Catholic University of Rio Grande do Sul, Av Ipiranga 6681, CP 1429, 90619-900 Porto Alegre – RS, Brazil
b Dept. of Metallurgy, Federal University of Rio Grande do Sul, C.P. 15051, 91501-970 Porto Alegre – RS, Brazil
c Department of Chemistry, Swedish University of Agricultural Sciences, Box 7015, 75007 Uppsala, Sweden

Abstract

Scanned beams of 0.1 MeV/u 197Au ions were employed for the bombardment of silicon oxide films thermally grown on silicon (100) 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.

© 2003 Elsevier Science B.V. All rights reserved.

PACS: 61.82.Ms; 61.46.+w; 81.07.-b

Keywords: Ion tracks; Nano-pores; Silicon dioxide

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 ions.
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 SiO2, 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 (100) 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 (~3 x 10⁻⁶ Torr) at normal incidence by 20 MeV 197Au⁷⁺ ions from the Porto Alegre 3 MV tandem accelerator. The ion fluence was around 10⁸–10⁹ 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 tₑ (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 tₑ = 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™ 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 SiO₂ 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 SiO₂ layers are somewhat more loosely structured

![Fig. 1. (a) SFM image of a bombarded SiO₂ 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).](image)
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 obstruction 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 ± 6°, consistent with values found for fused silica glass [1]. From the values of the depth, $z$, and the half-cone angle, $\beta$ 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 $v_t = 0.13$ nm/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 $\langle 111 \rangle$ directions determine the pyramidal shape of the holes, producing a quadratic base with sides along $\langle 011 \rangle$ 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. 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.
TEM observations in cross-section, which detected no Au inside the SiO\textsubscript{2} holes.

Because of the high thermal stability of SiO\textsubscript{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\textsubscript{2}.

4. Conclusions

Nanometer-scale holes and pores in SiO\textsubscript{2} thin films thermally grown on Si(100) 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\textsubscript{2} layer for localized etching of the underlying 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.

Acknowledgements

This work has been partially supported by FAPERGS, CNPq, and FINEP (Brazil).

References