

Scanning tunneling microscopy investigations of the Si(111) topography produced by etching in 40% NH₄F: Observation of an optimum etch duration

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The time evolution of the topography of an oxidized Si(111) surface immersed in an aqueous 40% NH₄F etching solution is investigated *ex situ* by STM. The topography of a rough oxide layer of thickness ≈ 24 Å becomes smoother as this layer is thinned. An exposure of 75 s completely removes the surface oxide and a minimum obtainable roughness of ≈ 1.4 Å rms is observed ≈ 15 s, hence. With continued etching, two processes—etching of the silicon surface and gas evolution—operate in conjunction to produce pillars of silicon at locations on the Si(111) surface which are shielded from etching by adsorbed gas bubbles. Gas evolution and roughening are suppressed by the addition of the reductant NaCNBH₃ (0.50%) to the etching solution.

Investigations of the chemical mechanism of etching of the Si(111) surface in aqueous hydrogen fluoride (HF) solutions have assumed heightened importance with the discovery by Chabal and co-workers that a defect-free monohydride termination of the Si(111) surface is produced by etching in aqueous 40% NH₄F solutions.¹⁻⁴ Here, the topography of the Si(111) surface produced by etching in aqueous 40% NH₄F for various durations is probed by *ex situ* STM imaging in air. *In situ* investigations of an etching silicon surface are preferable and are technically feasible in principle. However we have found that an accurate time evolution of the topography is not obtained by *in situ* STM experiments due to the nucleation of gas bubbles—generated by the etching reactions—in the tip-sample gap which block etching of the Si(111) surface. Previously, *ex situ*^{5,6} and *in situ*⁷ investigations of etched silicon surfaces have elucidated aspects of the chemical mechanisms of oxidation and etching. The present study is motivated by the purely practical need for Si(111) surfaces of near-atomic smoothness for experiments to be conducted in an air ambient.

Si(111) samples of two different types were employed in the investigations described here, *p*-type (B-doped) and *n*-type (As-doped, $\rho > 1000$ Ω cm), however the conclusions we report are generally applicable to a variety of other silicon samples we have investigated. As received Si(111) wafers were first cleaned in concentrated H₂SO₄ (Fisher, ACS), rinsed with Nanopure water ($\rho > 18$ MΩ cm), ultrasonically agitated in chloroform (Fisher, HPLC grade) and etched in aqueous 2% HF until a hydrophobic surface was just obtained. Following this chemical cleaning sequence, an 800 Å (by ellipsometry) thermal oxide was grown: Wafers were baked at 1050 °C in dry O₂ at atmospheric pressure for 2 h followed by annealing in pure N₂ at 900 °C for 2 h. This thermal oxide was then stripped in 2% HF, the wafer was rinsed with water and methanol (Fisher, HPLC grade), and the surface was ther-

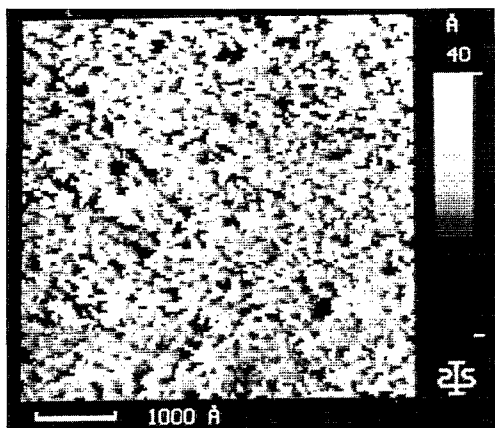
mally reoxidized exactly as before. Following this second thermal oxidation, wafers were diced into 12×12 mm squares (suitable for insertion into the STM) prior to the final etching sequence described below.

A procedure based on that of Higashi *et al.*³ was employed for the final etching sequence (following each of these etching steps, the sample was thoroughly rinsed with water and methanol): 12×12 mm squares were etched in 7:1 aqueous NH₄F:HF (Aldrich, ACS and Fisher, Electronics Grade) until a hydrophobic surface was just obtained. A 20–25 Å thick oxide was then grown by exposing the surface to a freshly prepared solution of H₂O:HCl:H₂O₂ (Fisher, ACS), 5:1:1 at 80 °C for 10 min. The surface so obtained served as the starting point for the final etching in aqueous 40% NH₄F: exposures to this solution of from 30 s to 6.5 min were investigated. Samples removed from the aqueous 40% NH₄F were immediately rinsed with water and methanol, ohmically contacted, and mounted on an aluminum sample holder for STM imaging. The elapsed time from the initial emersion of the crystal to the acquisition of STM data was typically 30 min. For some samples as noted below, the final etching solution contained 0.50% NaCNBH₃ (Aldrich).

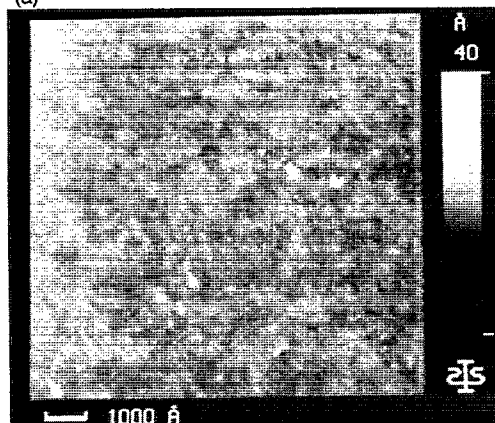
A Gaertner Scientific L117 Ellipsometer operating at a wavelength of 632.8 nm and an incident angle of 70° was employed for oxide film thickness measurements. Constant current STM imaging with a commercial instrument⁸ was accomplished in air using a tip bias of +2.0 V versus sample and tunneling currents of 0.035–0.5 nA. The STM tips employed in all experiments were mechanically cut or electrochemically etched Pt wires. Raw STM image data were processed only by the subtraction of a linear background. For each 12×12 mm segment, STM images were obtained (and roughness statistics were acquired) at twelve 1.0×1.0 μm sites for each etch duration.

The starting point for final etching step in aqueous 40% NH₄F is the oxide-covered surface obtained by treatment in hot 5:1:1, H₂O:HCl:H₂O₂. Due to the insulating nature of the ≈ 20 +Å thick oxide layer,⁹ STM images of

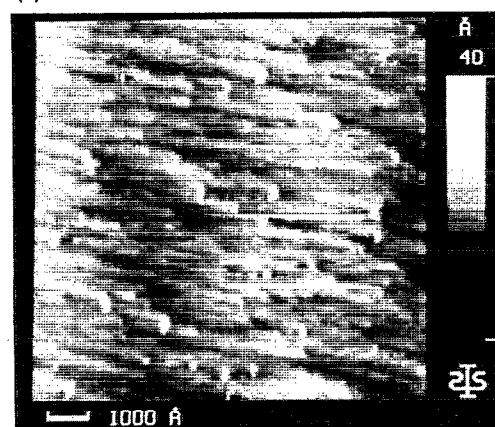
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(a)



(b)



(c)

FIG. 1. STM images in air of lightly oxidized Si(111) surfaces (*vide infra*) exposed to aqueous 40% NH_4F for various durations as follows: (A) 1.00 min; (B) 1.50 min; (C) 5.00 min.

this surface prior to exposure to the etching solution are not obtainable. The oxide must first be thinned by exposure of the crystal to 40% NH_4F for 45 s before STM imaging became possible. The surface of the crystal at this juncture is hydrophilic and STM images, like that shown in Fig. 1(A), indicate the presence of pores having a typical diameter of 100–300 Å.

With an additional 30 s exposure to the etching solution (75 s total), the surface of the crystal is hydrophobic after rinsing with water indicating the complete removal of the oxide layer. Ellipsometry measurements nevertheless

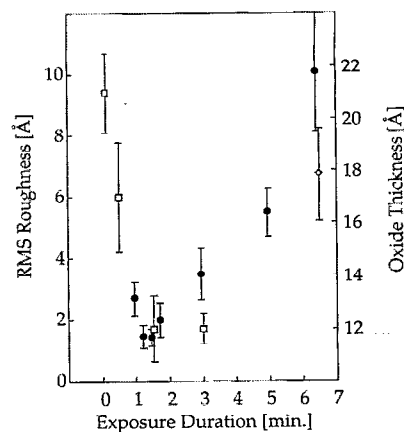


FIG. 2. Oxide film thickness (from ellipsometry) and rms roughness (from STM images) of oxidized silicon surfaces exposed to aqueous 40% NH_4F as a function of the etch duration. Filled circles: rms roughness vs etch duration. Error bars indicate $\pm 1\sigma$ as indicated. For the 6.50 min etch duration, the open diamond indicates the roughness obtained for etching in aqueous 0.50% NaBH_3CN , 40% NH_4F . Open squares: Oxide film thickness vs etch duration. Error bars indicate $\pm 1\sigma$ for three measurements at each of the three locations on the crystal.

register the presence of a thin (≈ 12 Å) layer of low dielectric constant ($\epsilon \approx 1.5$) on the emersed Si(111) surface. For etching durations of 90 s, further reductions of the surface roughness are not obtained and STM images of the Si(111) surface, like that shown in Fig. 1(B), reveal no discernable topography. The rms roughness of this surface is 1.4 Å rms which is the minimum obtainable.

The identity of the 12 Å thick layer detected by ellipsometry is unknown. As indicated in Fig. 2, this layer is observed even following much longer etching exposures of up to 3 min. One possibility is that a thin oxide grows on the silicon surface after etching following a brief exposure to air. Surface contamination may contribute to the apparent thickness of this layer. The extremely low roughness estimate of the Si(111) surface obtained by STM at the 90 s etch duration implies that any surface oxide which is present is distributed as a layer of uniform thickness. This conclusion follows from the fact that the STM will “interpret” the presence of a heterogeneous oxide layer (i.e., a layer of nonuniform thickness) on a topographically smooth surface as surface roughness due to the high barrier to tunneling electrons presented by the oxide.⁹

With continued exposure to aqueous 40% NH_4F for times in excess of 90 s, the Si(111) surface becomes gradually rougher. The surface emersed at 5.00 min for example, is shown in Fig. 1(C). This image, and many similar images obtained in this etch duration regime, clearly indicate that roughening of the Si(111) surface does not occur in a uniform and nonspecific fashion, but is due instead to the emergence of pillars of silicon from the Si(111) surface. In the data of Fig. 1(C), for example, these pillars appear as white disks approximately 200–300 Å in diameter and 15–20 Å in height. At yet longer exposures, some increase in the diameter of these pillars is observed (300–500 Å at 6.5 min), the number density of pillars increases, and a pronounced growth in the height of the tallest pillars

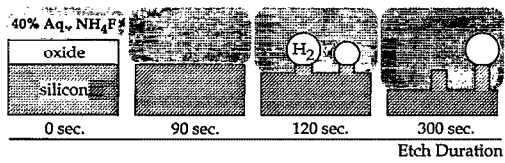


FIG. 3. Schematic diagram of proposed mechanism of roughening for Si(111) surfaces exposed to aqueous 40% NH_4F .

is observed until at 6.5 min pillars as high as 30 Å exist on the Si(111) surface. Roughening of the Si(111) surface is accompanied by gas evolution from the etching surface which becomes visible to the eye at an etching duration of ≈ 3 min. Gas bubbles are evolved from the edges of the crystal and at many points on the face of the Si(111) surface far from the edges. As shown schematically in Fig. 3, it is feasible that the etching of the silicon surface and concurrent gas evolution operate in conjunction to produce pillars of silicon at locations on the Si(111) surface which are shielded from etching by adsorbed gas bubbles, probably of hydrogen.

The mechanism indicated in Fig. 3 is supported by an experiment in which 0.5% of the strong reductant NaCNBH_3 is added to the aqueous 40% NH_4F etchant. In this solution, visual gas evolution is suppressed and a marked decrease in the number density and size of pillars was observed on the Si(111) surface emersed at 6.5 min. The roughness statistics obtained for this etch duration in the presence and absence of NaCNBH_3 are compared in Fig. 2. To first order, the intervention of NaCNBH_3 in the

etching mechanisms proposed previously by Gräf *et al.*¹⁰ and by Jacob and Chabal¹¹ [for stepped Si(111) surfaces] can be easily understood: The nucleophiles OH^- and H^- compete for surface hydride (i.e., Si-H) at steady state in the etching solution; attack by OH^- (or conceivably by H_2O) produces oxide termination and H_2 ,^{10,11} whereas attack by H^- regenerates the hydrogen termination of the surface. The rate of H_2 evolution in the presence of H^- is therefore reduced.

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