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Oxidation sharpening of silicon tips in the atmospheric environment

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Sharp tips are essential for high-resolution atomic force microscopy (AFM) imaging and high-performance electron emitters in vacuum microelectronic devices. Thermal oxidation at high temperature followed by oxide removal is widely used in the nanofabrication of sharp silicon AFM/emitter tips. This method relies on the fact that oxide grows slower on areas with a smaller radius of curvature. Thermal oxidation is commonly carried out in a dedicated oxidation furnace that is costly, and the tips or wafer of tips must be cleaned thoroughly using Radio Corporation of America (RCA) cleaning. Here, the authors report that oxidation sharpening can also be attained using a very low-cost generic box furnace in the atmospheric environment that does not require the tips to go through an RCA cleaning process. As is apparent, such cleaning is not convenient for millimeter-scale AFM probes. The minimum tip apex radius of 2.5 nm was obtained by oxidation at 950 °C in the atmospheric environment. The obvious application of this approach is the regeneration of sharp tips out of worn out and thus blunt AFM probes at very low cost. *Published by the AVS.* https://doi.org/10.1116/1.4998561

I. INTRODUCTION

Sharp tip structures have applications in atomic force microscopy (AFM), electron emitter displays, nanoelectromechanical systems (NEMSs), and biomedical devices that use microneedle arrays.[1–4] A number of techniques have been reported to fabricate sharp tips. For example, neon ion sputtering was used to sharpen a tungsten tip under high vacuum.[5] Sharp tips can also be obtained by dry plasma etching that gives a reentrant undercut profile although it is challenging to fabricate sub-10 nm tips reproducibly because of the very narrow process window. Thermal oxidation sharpening of silicon tips is probably the most widely employed tip sharpening method, and it is at present routinely used for commercial AFM tip fabrication.[6–8] This method has a self-limiting characteristic when it is performed below ∼950 °C, i.e., when the remaining silicon becomes very thin with the radius of curvature of just a few nanometers, oxidation will be practically stopped with rates <0.2 nm/h, rather than continuing to rapidly erode the thin silicon wire in the center till its disappearance.[9] As a result, longer oxidation will not turn the already sharpened silicon tip into a blunt one, and thus, this method has a relatively broad process window and high yield as needed for commercial applications.

It is based on the phenomena that the oxidation rate is slower on curved (concave or convex) surfaces where stress is high. Therefore, for a cone or pyramid structure like the AFM tip, silicon near the tip apex that has the highest radius of curvature will be oxidized (eroded) less than the silicon farther away from the apex, and hence after removing the oxide by hydrofluoric acid (HF), the remaining silicon cone will become sharper. Although the tip with apex <1 nm has been demonstrated using this method, the conventional thermal oxidation process is lengthy and costly when using a dedicated oxidation furnace. Moreover, oxidation sharpening of AFM probes using a dedicated tube furnace is applicable only for a full wafer of

tips because it needs a thorough Radio Corporation of America (RCA) cleaning process prior to oxidation, yet it is not convenient to carry out this cleaning process for already detached millimeter-scale individual AFM probes.

In this study, we will show that oxidation sharpening of silicon AFM tips can also be conducted using a very low cost box furnace in an atmospheric environment, rather than using pure oxygen or water that is commonly generated by the reaction of H_2 and O_2. Moreover, the process does not involve pumping, purging, and venting the furnace, and it does not require the tips to go through an RCA cleaning process before the oxidation. We obtained very sharp AFM tips with a radius of curvature of approximately 2.5 nm at the apex of the tip.

II. EXPERIMENT

We studied the oxidation sharpening process for three types of samples: (1) cone (spherical or truncated) structures with various diameters at the top fabricated by standard electron beam lithography followed by Cr liftoff and silicon inductively coupled plasma (ICP)-RIE, (2) random pyramid structures fabricated by unmasked potassium hydroxide (KOH) wet etching of a silicon wafer, and (3) commercial AFM probes.

To etch the cone structure, we employed ICP-RIE (Oxford Instrument ICP 380) using the nonswitching pseudo-Bosch recipe, which can give a broadly tunable sidewall taper angle by varying the SF_6/C_4F_8 gas flow ratio or even a negatively tapered profile (i.e., an inverse cone structure) by optimizing the etching parameters.[10,11] We utilized the following etching parameters to obtain a positively tapered etching profile to fabricate our cone structures: C_4F_8 56 sccm, SF_6 4 sccm, RF power 20 W, ICP power 1200 W, 10 mTorr, 15 °C, and 25 min with an etching rate of 80 nm/min.

The second type of structure is a pyramid structure with a random size at a random location, prepared by maskless anisotropic wet etching of silicon using KOH. To fabricate such a structure, a piece of silicon wafer was dipped into HF (1:50 diluted) for 30 s in order to remove the native oxide, and then,

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it was etched in 20% KOH at 50 °C for 10 min. The wafer was not cleaned by solvent before dipping into HF intentionally to introduce some random factor into the process.

Thermal oxidation was carried out using a low cost generic box furnace with a maximum temperature of 1200 °C and a chamber size of 10 cm.[3] Oxidation was carried out in the ambient air environment. The oxidation temperature and time were varied. The schematic oxidation sharpening process is shown in Fig. 1(a); the photo of the furnace used to grow oxide is shown in Fig. 1(b). After cooling down to room temperature, the oxide was etched away by HF (1:10 diluted with water) for 20 min.

III. RESULTS AND DISCUSSION

Figure 2 shows the oxide film thickness grown at different temperatures and time durations using a generic box furnace in the atmospheric environment. For comparison, the oxide film thickness grown using pure oxygen gas (dry oxidation) as predicted by the Deal-Grove (DG) model is also included in the figure.[12] As seen, the oxidation rate in the atmospheric environment is two to three times that of dry oxidation for 900 and 950 °C growth and is close to twice for 1000 °C growth. In all cases, the oxidation rate is far slower than the wet oxidation rate using water (not shown, e.g., 900 °C for 2 h will grow 250 nm wet oxide).

To see the composition of the grown oxide film, we carried out energy-dispersive x-ray spectroscopy (EDX)
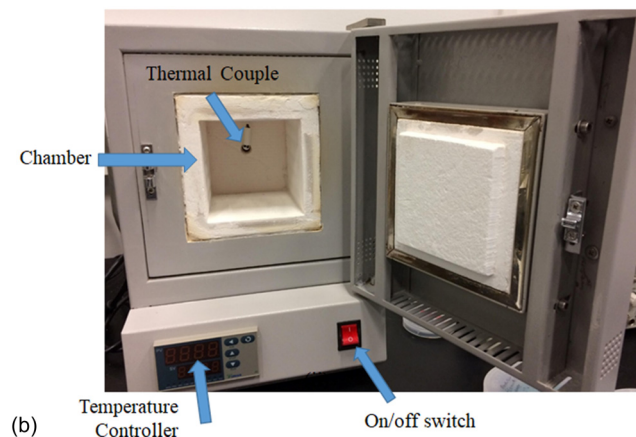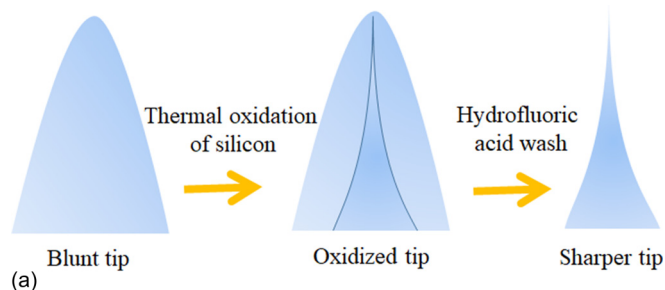

(a)

(b)

FIG. 1. (Color online) Schematic drawing of (a) oxidation sharpening process; (b) photo of the furnace used to grow oxide. The chamber size is $10 \times 10 \times 12$ cm, and it is heated by resistive heating to a maximum temperature of 1200 °C. The heating up rate can be accurately controlled within a range of 0–15 °C/min, but there is no active control of the cooling down rate.
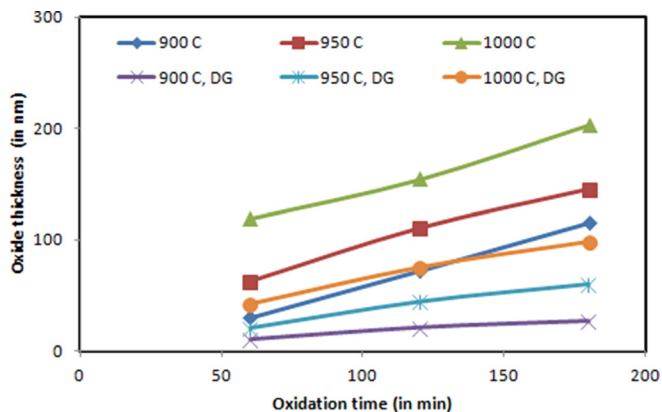
FIG. 2. (Color online) Oxide film thickness grown using a generic box furnace in the atmospheric environment. For comparison, the film thickness predicted by the DG model for dry oxidation using pure oxygen gas is also included in the graph.

measurements. As shown in Fig. 3, only Si and O were found in the film, and N was not found in the spectrum even though air contains 78% nitrogen. We also tested the etching rate of our oxide in HF and found that our oxide film has an etching rate very close (<10% difference) to that of oxide grown using a dedicated oxidation furnace. Since silicon nitride is etched far slower than oxide in HF, our film should have negligible nitride in it, which is in agreement with the EDX study.

For thermal oxidation, two process parameters are important in order to obtain a well sharpened tip: temperature and oxide thickness. As aforementioned, the sharpening is caused by the stress dependent growth rate. When silicon is oxidized, its volume is expanded, leading to high compressive stress. However, when the oxidation temperature is high, the stress can get partially released by the viscous flow of the oxide. Therefore, oxidation sharpening is typically carried out at 950 °C or lower when the oxide film has very high viscosity, and there is virtually no sharpening effect at a high temperature of 1200 °C.[13] Regarding the oxide film thickness, best sharpening is obtained on an oxide film under ~80 nm. Silicon oxidation occurs at the SiO_2/Si interface, and O_2 (or H_2O for wet oxidation) must diffuse through the already grown oxide film to react with the silicon at the interface. The oxidation rate can be limited either by the chemical reaction rate when the film is thin (roughly <80 nm) or by the gas molecule diffusion rate when the oxide film is thicker; oxidation sharpening is most effective when the growth is limited by the chemical reaction rate that depends on the stress (although the diffusion rate also depends on stress).[14,15] Consequently, the oxide film should be below ~80 nm for best sharpening. If the initial diameter or half-cone angle at the tip apex is too large, multiple cycles of oxidation/oxide removal should be performed, rather than growing one very thick oxide and then removing it.

Figure 4(a) shows the SEM image of the cone array structure etched by the nonswitching pseudo-Bosch process, with a cone height of 1.87 μm, a diameter at top of 75 nm, and a sidewall taper angle of approximately 11.9°. After thermal oxidation in the atmospheric environment at 1000 °C for 2 h, the cone diameter at the top was increased to 95 nm [Fig.
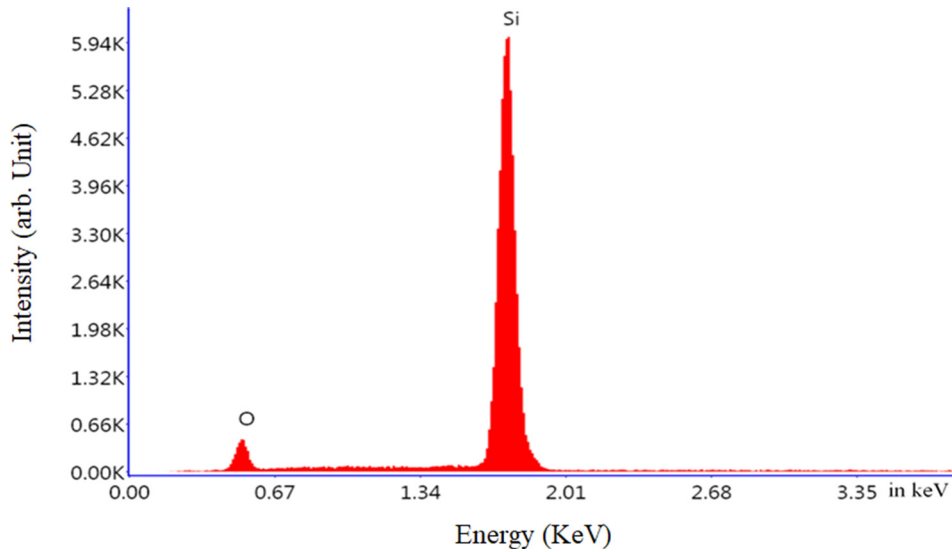
FIG. 3. (Color online) EDX spectrum of 100 nm thermal SiO_2 grown on the Si wafer, showing Si K (wt. % 90.87) and O K (wt. % 9.13) peaks. The peak for Si is far higher than that of oxygen because of the contribution from the bulk silicon substrate.

4(b)] due to the 2.2× volume expansion when silicon is fully oxidized [Fig. 4(b)]. After removal of the grown oxide by using diluted HF, the resulted sharp cone array is shown in Fig. 4(c) with the cone diameter at the apex reduced to only 14 nm, which is less than the typical commercial AFM tip specification of 20 nm (10 nm radius of curvature). As such, our low cost oxidation sharpening process can meet the standard of the commercial AFM tip manufacturing.

When the diameter at the top of the truncated cone is too large, the structure will not get sharpened. Instead, as compared in Fig. 5(a) with Figs. 5(b) and 5(c) after two oxidation

sharpening cycles at 1000 °C for 2 h, the edge of the top surface became sharpened because here the edge rather than the top has the smaller radius of curvature. Figure 5(d) shows a pyramid formed on a silicon wafer using maskless wet etching using KOH. Although the pyramid is already very sharp with a small radius of curvature at the apex, it has a very large cone angle of approximately 89.2°, and thus, multiple oxidation sharpening cycles were needed in order to generate a pointed structure with a much smaller half-cone angle at the apex [Fig. 5(e)]. In addition, as expected, the surface was found to become smoother after the oxidation sharpening cycles.
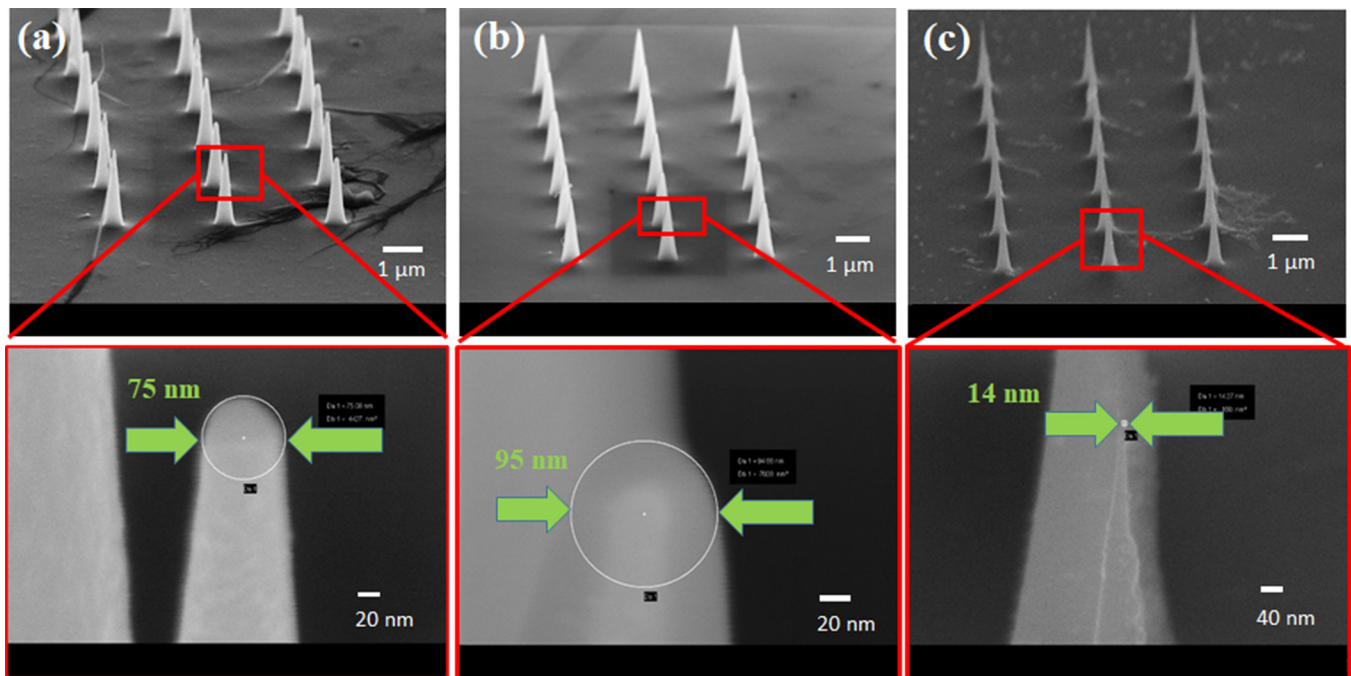

FIG. 4. (Color online) SEM images of cone structures fabricated on the Si wafer. (a) Before oxidation in the atmospheric environment; (b) right after oxidation; (c) after HF etching of oxide. The apex diameters are 75, 95, and 14 nm, respectively.
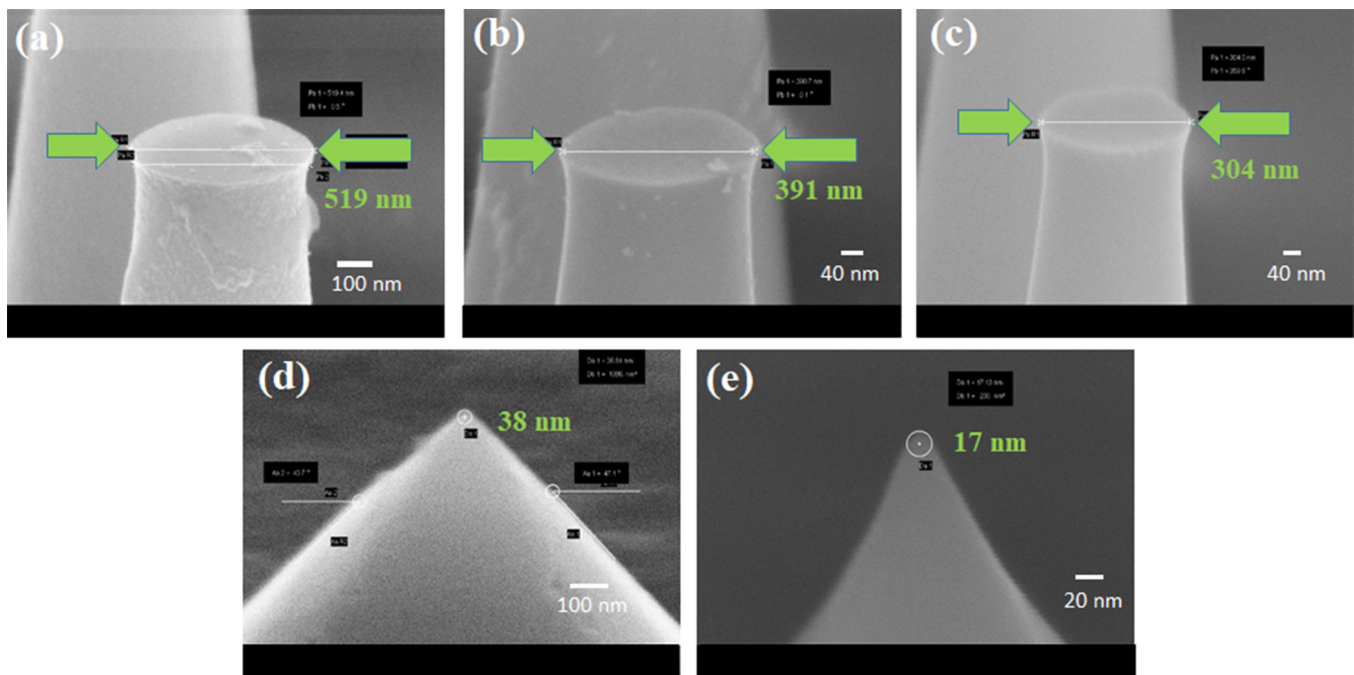
FIG. 5. (Color online) (a)–(c) SEM images of truncated cone structures fabricated on Si. (a) Before oxidation; (b) after first oxidation and HF etching of oxide; (c) after second oxidation and HF etching; [(d) and (e)] SEM images of random pyramid structures fabricated on Si using maskless KOH etching. (d) Before first oxidation; (e) after third oxidation and HF etching of oxide, showing a pointed apex.

Finally, we sharpened a commercial AFM probe by oxidation at 950 °C for 2 h. A helium ion microscope (HIM) was utilized to image the tips for its higher resolution than SEM. Since SEM in our laboratory cannot provide a clear high resolution (higher than 3 nm) image, we used HIM to demonstrate the high resolution image (here, 2.5 nm) of the tip apex. As shown in Fig. 6, this tip has an initial diameter at the tip apex of 32 nm, and it was decreased to 5 nm diameter after just one oxidation sharpening cycle, thus demonstrating the effectiveness of our low cost tip sharpening process. This process may be applied to recycling the worn out and thus blunt tips for reuse.

IV. SUMMARY AND CONCLUSIONS

We showed that oxidation sharpening of silicon AFM tips can also be realized using a low cost generic box
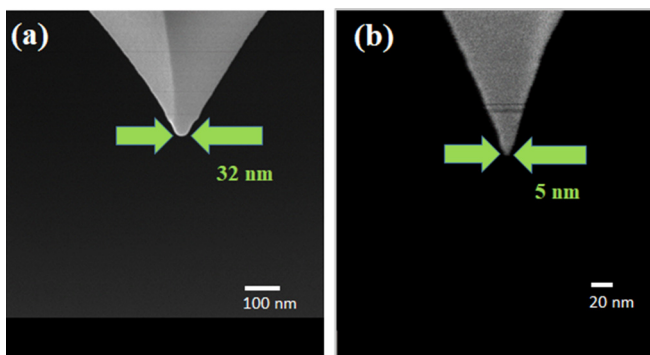

FIG. 6. (Color online) HIM images of a commercial AFM probe. (a) Before oxidation; (b) after oxidation and HF etching of oxide, with the diameter at the tip apex reduced to 5 nm.

furnace in the atmospheric environment. The minimum tip apex radius of 2.5 nm was obtained by oxidation at 950 °C in the atmospheric environment. The oxide growth rate in the atmospheric environment was found to be between that of dry and wet oxidation using a dedicated furnace. The EDX measurement did not show any detectable nitrogen in the film. One obvious application of our method is the regeneration of sharp tips out of worn out AFM probes at very low cost.

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