Formation of silicon tips with <1 nm radius

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Electron emitters in vacuum microelectronic devices need sharp tips in order to permit electron emission at moderate voltages. A method has been found for preparing uniform silicon tips with a radius of curvature less than 1 nm. These tips are formed by oxidation of 5-μm-high silicon cones through exploitation of a known oxidation inhibition of silicon at regions of high curvature.

A growing interest in vacuum microelectronics has stimulated the development of cold cathode field emitter tips as electron sources on silicon substrates.[1–3] In order to obtain Fowler–Nordheim emission at moderate voltages, the tips need to be sharp; it would also be useful if the tips were made of materials compatible with Si processing. A number of studies have been made with conical emitters formed from bulk silicon by isotropic or anisotropic etching under a nitride mask.[3,4–12] Typical tip radii are 20–40 nm, and there is some evidence that the actual emission site is considerably smaller, near atomic dimensions, possibly at sites of work function lowering.[10,11,13] Instabilities during emission[13] and successful emission from only 1–3% of cones in an array[9] are both thought to be due in part to uncontrollable variations in tip morphology.

We studied a method for producing atomically sharp Si tips by exploiting an anomaly of silicon oxidation which occurs at regions of high curvature.[14] This anomaly is due to the stress configuration created at the Si-oxide interface on a nonplanar surface due to the increase in molar volume when Si is oxidized. This stress is intrinsic to the oxidation process and builds up in the growing oxide only for temperatures less than 1050–1100 °C; above this temperature range the decreased viscosity of the oxide permits oxide flow which relieves the stress. The stress configuration at a Si step reduces the oxidation rate locally, probably through an increase in the energy barrier for the reaction.[19] Local thinning has been experimentally verified at steps and edges for dry (O_2) and wet (H_2O) oxidations in the temperature range 900–1050 °C,[14–18] and thinning has also been modeled for wet oxidation at steps.[19] While the same ideas have also been applied to the fabrication of Si emitter tips,[8,20] until the present study no investigation has yet been made of the effect of conical Si tip curvature on oxidation kinetics.

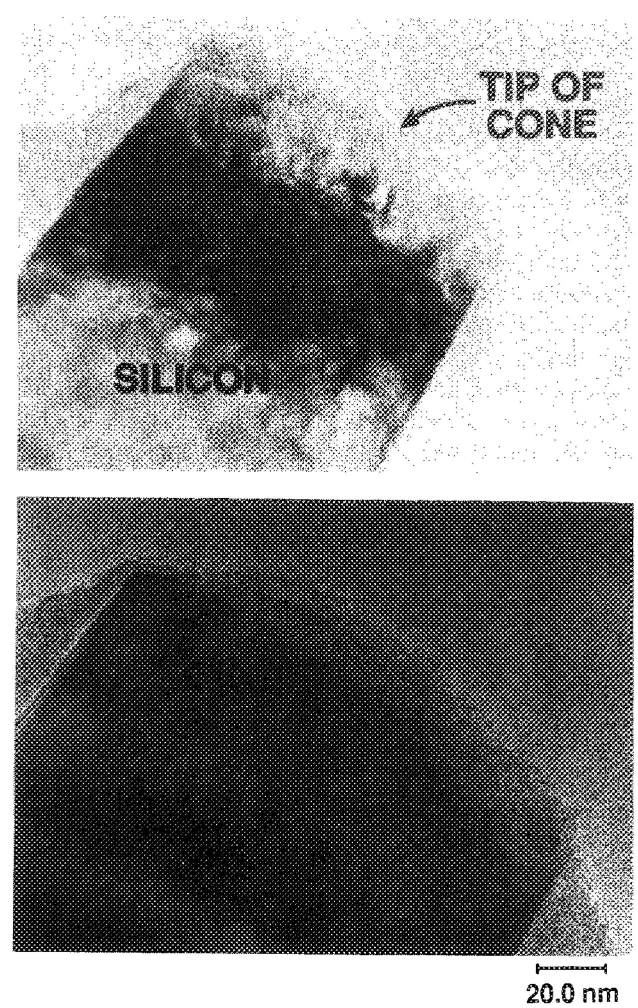

FIG. 1. Silicon conical tips before dry oxidation. The tips are slightly rounded and range in width from 25 to 150 nm.

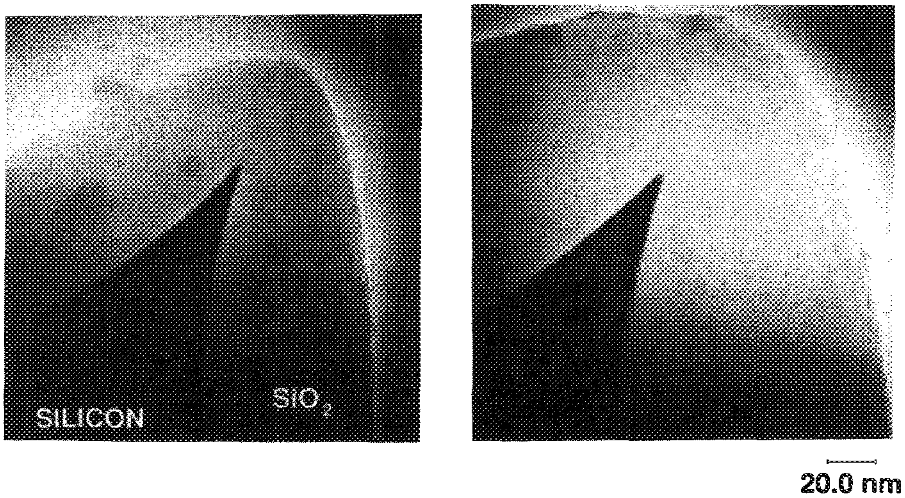

FIG. 2. Silicon tips after dry oxidation for times sufficient to grow 60 nm (left) and 120 nm (right) SiO_2 on flat surfaces.

The present study examines this process in some detail. Silicon cones were produced on {100} surfaces by defining $10\times 10\ \mu m$ square pads of Si_3N_4 on 20 μm centers, etching the Si in an isotropic etch of 25 parts nitric acid, 10 parts hydrofluoric acid, and 3 parts acetic acid for 6.5 min, followed by oxidation in wet O_2 for 15 min at 900 °C. This treatment is sufficient to just remove the nitride "hats," leaving cones with slightly rounded (convex) tips of diameter 25–150 nm. These statistics were obtained by viewing about 100 adjacent tips by transmission electron microscopy (TEM). The variation in tip diameter is random, and possibly reflects a memory of the random excursions of the edge of the resist used to define the nitride etch mask. TEM studies were performed at 400 keV with a JEOL 4000FM. TEM photos of typical cone tips before oxidation sharpening are shown in Fig. 1.

Dry oxidation at 950 °C for 2 and 5.5 h (times sufficient to grow 60 and 120 nm on planar Si surfaces, respectively) produced the results shown in Fig. 2. The interfaces between the oxide and Si are clearly seen. In addition to the single tips shown, multiple tips (2–3 per cone) are also found; they are about 1–2 nm apart and their origins are not yet understood.

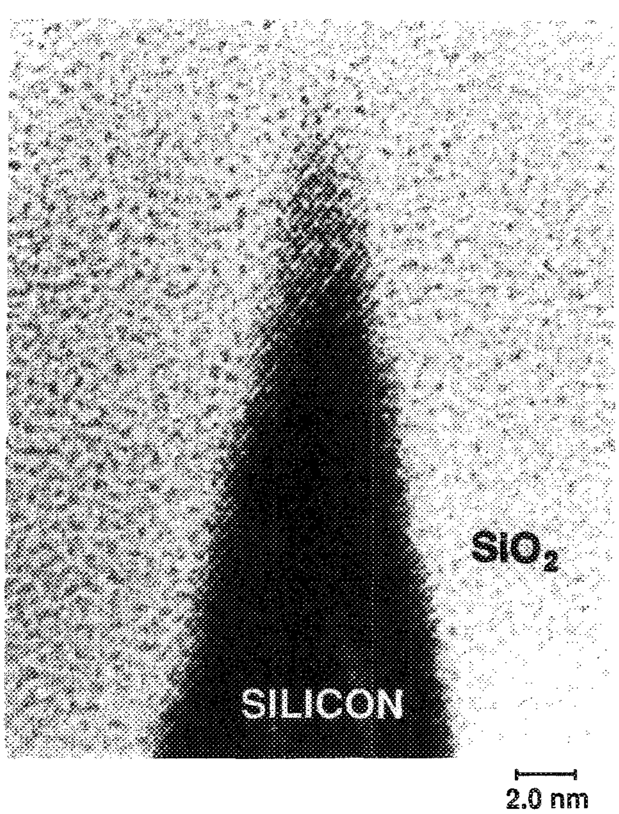

FIG. 3. High-magnification TEM image of the tip shown at the left in Fig. 2, showing lattice fringes correspond to the Si {111} planes with a spacing of 3.13 Å. Tip curvature is less than 1 nm.

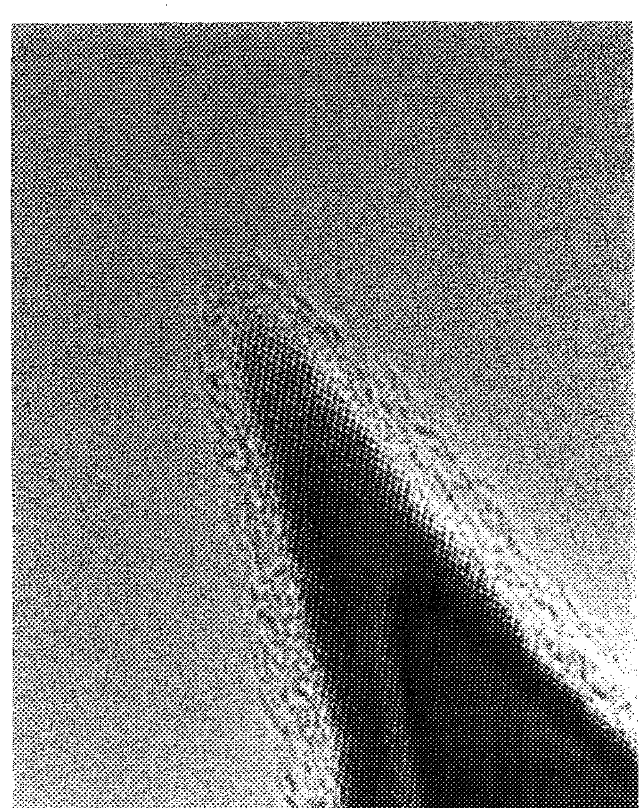

FIG. 4. High-magnification TEM image of another tip after removal of thermal oxide.

A higher magnification of the tip shown at the left of Fig. 2 appears in Fig. 3. Fringes of the Si {111} planes with a spacing 3.13 Å are seen at the tip, and fringe contrast disappears when the tip diameter is less than 1 nm. Fringe contrast disappears because there are too few atoms left to scatter the incident electron beam. The tip can be seen in greater detail after removing the thermal oxide and passivating with concentrated HF in Fig. 4. The 15–20 Å amorphous material coating the tip is mostly an artifact caused by polymerization of hydrocarbon by the electron beam. This TEM image is typical, and tip radii are clearly less than 1 nm.

Oxidation is inhibited at the cone tip. Curvature in this region is more complex than for the case of a step edge for two reasons: (i) curvature at the tip end approximates a part of a spherical surface while curvature at a step approximates a part of a cylindrical surface, and (ii) curvature just "below" the tip end approximates a total cylindrical surface. The effect of spherical and cylindrical geometry on oxidation kinetics, exclusive of stress, has been modeled,[21] but no model has yet been presented to describe the effect of intrinsic oxidation stress at these geometrical regions on changing tip morphology during oxidation.

Except for the occurrence of multiple tips, the variation of Si tip morphology after the growth of 60 and 120 nm thermal oxide is too small to measure. About 50 oxidized tips were examined by TEM, and all were found to have the same shapes regardless of oxidation time and regardless of known variations in initial morphology; only the region closer to the base of the cones showed a different shape for the two oxidations. Evidently, a final "end point" configuration is asymptotically approached during oxidation at an ever decreasing rate due to increasing oxidation inhibition with increasing curvature. These effects create a remarkable uniformity of tip morphology with atomic level sharpness which is important for application of these structures as field-emitting electron beam sources. Electrical measurements of these atomically sharp field emitters are under way.

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