Semiconductor Science and Technology

Fabrication of silicon field emission points for vacuum microelectronics by wet chemical etching

Semicond. Sci. Technol. **6** (1991) 223–225. Printed in the UK

Fabrication of silicon field emission points for vacuum microelectronics by wet chemical etching

Johann T Trujillo and Charles E Hunt

Department of Electrical Engineering and Computer Science, University of California, Davis, CA 95616, USA

Received 9 July 1990, accepted for publication 9 November 1990

Abstract. The fabrication of sharp silicon tips for field emission cathodes has been investigated using anisotropic and isotropic wet chemical etching techniques. Formulations of potassium hydroxide, water and alcohol are used as the anisotropic etchants. The effects of isopropyl, secondary butyl and tertiary butyl alcohols on tip formation are examined. An isotropic etchant using a mixture of hydrofluoric, nitric and acetic acids is also used to form similar cathode structures for comparison. The silicon needles formed are intended for use in vacuum microelectronic devices.

1. Introduction

Field emission of electrons from a solid cathode can be enhanced beyond the simple levels predicted by Fowler–Nordheim theory if the cathode is a 'point source' in the vicinity of an 'infinite' plane anode. One way to approximate such a system is to make the cathode pointed and as sharp as possible, and place it in proximity to a conductive, flat-surfaced anode. Such a cathode structure is the basis of recent research in fabrication of radiation-hard, thermally insensitive, high-speed vacuum microelectronic devices [1]. To this end, we are attempting to fabricate the sharpest tips possible in silicon.

2. Experimental details

Tips were formed using a mask consisting of 10 μm squares of silicon nitride on 20 μm centres made to pattern (100) silicon wafer surfaces. Points were etched via two methods: (1) an anisotropic etchant of 4 parts potassium hydroxide and water (10 M), and 1 part alcohol [2, 3]; (2) an isotropic etchant consisting of 25 parts nitric acid, 10 parts acetic acid and 3 parts hydrofluoric (by volume, standard MOS-grade aqueous reagents) [4]. Isopropanol, secondary butanol and tertiary butanol were used in the KOH formulations to study the etching effects caused by the different alcohols. In both the anisotropic and the isotropic etches, constant temperature conditions were used. KOH etching was done at 55 °C and HF/nitric/acetic acid etching was done at room temperature, about 26 °C. Surfactants were tested in both etchants as well. The surfactant concentration used was 1% by volume. Etching was tested under both mixing and stagnant conditions.

3. Results

3.1. KOH/alcohol/water etchants

The anisotropic etch was studied first because of its greater controllability. Total etch times ranged from 30 to 40 minutes. The shape of the points etched was an octagonal pyramid with facets along the {331} planes and a radius of curvature at the tip of about 2000 Å as seen in figure 1. In general, it was found that the size of the points could be varied by changing the type of alcohol used. The tips etched using isopropyl alcohol, shown in figure 2, were the largest, with base widths (measured flat to flat) of between 12 μm for a stagnant solution without a surfactant, to 18 μm for tips etched under mixing conditions with no surfactant. The secondary butanol formulation produced tips that had bases between 13.8 and 9.6 μm in diameter. Figure 1 shows an example of these tips just at the point where the nitride masks are falling off. A difference of about 5 μm in the base diameter was noted between secondary butanol and isopropanol when the solutions were mixed. Figure 3 shows the smallest tips which were made. A formulation using tertiary butanol under stagnant conditions both with and without the surfactant was used. Again, the tips are shown just as the silicon nitride mask is falling off. These tips have bases ranging from 12 μm to 8.4 μm in diameter. Table 1 summarizes the results. It is believed this tip size variation is the result of the changing

0268-1242/91/030223+03 $03.50

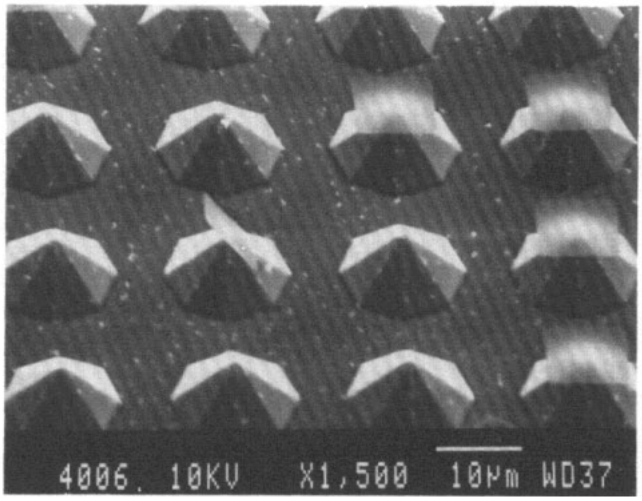

Figure 1. {331}-surfaced Si pyramid etched using 10 M KOH/secondary butanol without a surfactant. The etch was stopped just as the silicon nitride caps were falling off.

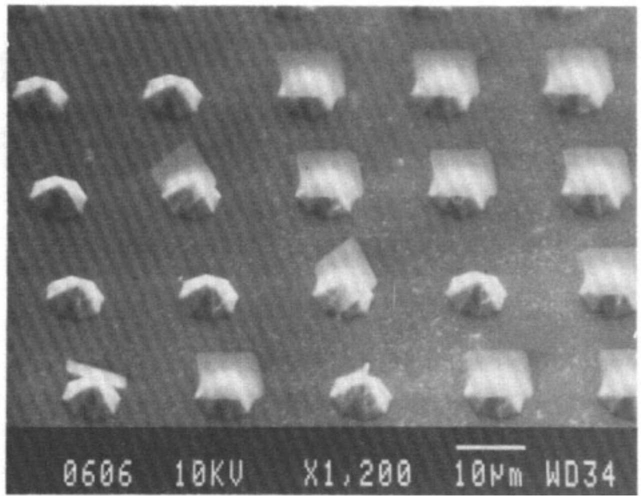

Figure 3. Field tips formed by etching with 10 M KOH/tertiary butanol.

selectivity of the etchant between the {100} plane and the {110} plane due to the effects of the alcohols in changing the surface reactivity (either in reactant adsorption or surface mobility). It is also noted that the larger tips, made using isopropyl alcohol, had a squarer base than the other tips and also had 16 planes around the surface. This results is also seen in the tips when etched at a lower KOH concentration, combined with secondary butanol. An example of such rounded bases can be seen in figure 2.

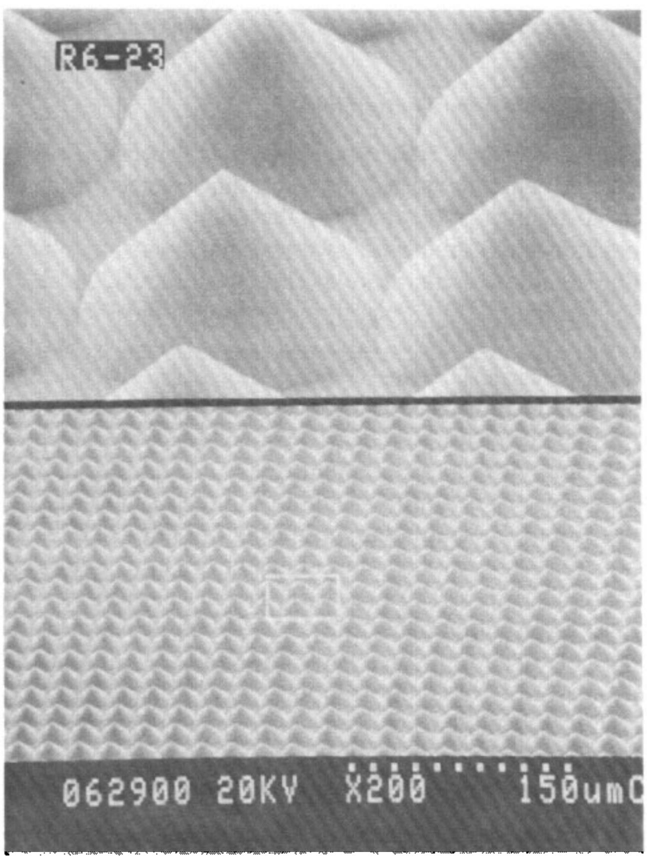

Figure 2. 16-faceted field emission tip etched in 10 M KOH/isopropanol.

3.2. HF/nitric/acetic acid etchant

The isotropic etchant also proved to form points using the same mask as the KOH etchant. In this case, however, the points had square bases and could be etched to needle-like tips having a radius of curvature of about 600 Å as seen in figure 4. Since these tips are sharper than those etched by the KOH/alcohol solution, they are inherently more promising for obtaining field emission. Since the etch rate for this formulation is about 1.43 $\mu m\ min^{-1}$ at 26 °C, the etch is hard to control, causing a non-uniform etch over the wafer surface. Surfactants slow this etch rate down to about 1.2 $\mu m\ min^{-1}$. Slight agitation (enough to keep bubbles from forming on the surface) gives a more uniform etch. Surfactants combined with agitation produce a tip uniformity similar to that of the KOH etch with some loss of tip sharpness (e.g. a radius of curvature averaging 1000 Å).

Tip sharpening experiments have been performed on the various tips discussed here [5]. This sharpening is

Table 1. KOH/alcohol/water etchant results (10 M KOH, alcohol to saturation, 55 °C). IPA = isopropyl alcohol, SBA = secondary butyl alcohol, TBA = tertiary butyl alcohol, N = no, S = surfactant, M = mixing.

Alcohol	Conditions	Base width (μm)	Height (μm)	Uniformity
IPA	NS-NM	12.0	8.5	good
	NS-M	18.0	12.7	good
	S-NM	—	—	—
	S-M	16.1	11.4	good
SBA	NS-NM	13.8	9.8	good
	NS-M	12.0	8.5	fair
	S-NM	9.6	6.8	fair
	S-M	11.4	8.1	rough
TBA	NS-NM	8.4	6.0	good
	NS-M	—	—	—
	S-NM	8.4	6.0	no good
	S-M	12.0	8.5	rough

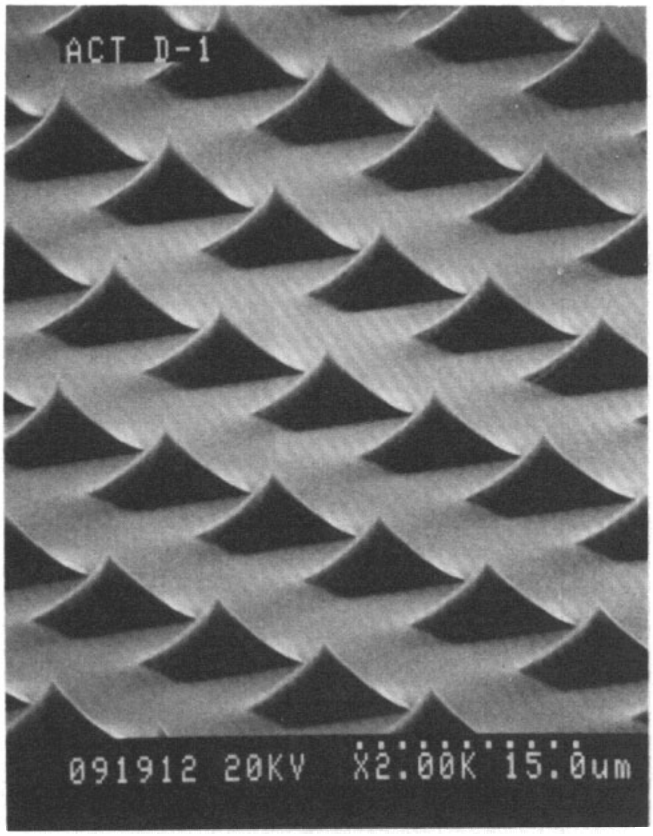

Figure 4. Field tip obtained using the same masking as in figures 1–3, with an isotropic HF/nitric/acetic acid etchant.

done by a low-temperature, dry oxidation of the tips and has resulted in points having a radius of curvature of < 50 Å. We believe these to be the sharpest silicon tips ever synthesized.

Field emission has been measured from each of the types of tips shown here. The results of electrical measurements will be reported later.

4. Summary

Silicon tips suitable for use as field emission cold cathodes have been etched by a variety of wet etchants, both anisotropic and isotropic. The sharpest tips, as etched, are obtained using the isotropic HF/nitric/acetic acid isotropic etchant. A greater degree of reproducibility and control over the etch process is obtained using anisotropic 10 M KOH solution with a saturated secondary butanol concentration and without any surfactant in stagnant conditions. The less sharp anisotropic process may be fully acceptable for forming field emission structures if subsequent tip sharpening steps by oxidation are employed.

Acknowledgments

The authors wish to acknowledge the help and collaboration of Dino R Ciarlo, William J Orvis, Wing Hui and Ed Hee at the Lawrence Livermore National Laboratory. This work was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under Contract No W-7405-ENG-48.

References

[1] Greene R, Gray H and Campisi G 1985 *Digest of Technical Papers 1985* (IEEE IEDM) p 172
[2] Bassous E 1978 *IEEE Trans. Electron. Devices* **25** 1178
[3] Bean K E 1978 *IEEE Trans. Electron. Devices* **25** 1185
[4] Thomas R N, Wickstrom R A, Schroder D K and Nathanson H C 1974 *Solid State Electron.* **17** 155
[5] Marcus R B, Ravi T S, Gmitter T, Chin K, Liu D, Orvis W J, Ciarlo D R, Hunt C E and Trujillo J 1990 *Appl. Phys. Lett.* **56** 236