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by Joshua B. Ratchford, Nelson Y. Mark, Madhu Roy, William L. Benard, and Cynthia A. Lundgren

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14. ABSTRACT

We report a method to fabricate silicon nanopillars with high-aspect ratios. Electron-beam lithography and a negative resist were used to pattern nanometer scale etch masks onto silicon wafers. Inductively coupled plasma-reactive ion etching (ICP-RIE) with mixtures of Cl_2 and HBr was used to etch nanostructures into the wafers. Silicon nanopillars with tip diameters of 80 nm and aspect ratios of 10 were readily obtained.

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1. Introduction

Several researchers have shown substantial improvements in the cycle lifetime of silicon (Si) anodes in lithium (Li)-ion batteries by nanostructuring Si (*1–3*). These reports suggested that damage to the Si was reduced because the ratio of surface area-to-volume of these nanostructures was larger than that of bulk Si. Specific explanations as to why nanostructures substantially improved the cycle lifetime of Si anodes in Li-ion batteries are lacking.

The objective of this work was to develop a method for fabricating nanostructures with user-defined profiles and separations. We report a method to form Si nanostructures that takes advantage of techniques used to fabricate electronic elements in semiconductor processing. Si nanopillars with tip diameters of 80 nm and aspect ratios of 10 were readily obtained. This method will enable basic research on the mechanical properties of Si nanostructures in Li-ion batteries.

2. Experimental

2.1 Nanopattern Fabrication

Nanopillars were fabricated as follows: a Si wafer with 100 nm of thermal oxide was pretreated with 10 ml of liquid hexamethyldisilazane (HMDS) for 40 s. The HMDS was removed by rotating the wafer at 500 rpm for 5 s. 3 ml of a negative electron-beam resist (NEB31A) were then added to the surface. The wafer was then rotated at 4000 rpm for 55 s, and then heated to 115 °C for 2 min on a hotplate. The resulting thickness of the resist layer was 300±30 nm, as measured by spectroscopic reflectometry and confirmed by profilometry.

Electron-beam lithography (Vistec EBPG5000+HR) was used to expose circular etch masks into the layer of resist. The diameter of each mask was 80 nm. The centers of the masks were separated by 230 nm. A 100 kV acceleration voltage, 600 pA beam current, and 80 μCcm^{-2} dose were used. Each cell contained $1x10^4$ masks. The writing time of each cell was less than 1 min. A post-exposure bake at 95 °C on a hotplate for 4 min was used. The resist was developed in Shipley Microposit MF-321 for approximately 10 s.

2.2 Inductively Coupled Reactive Ion Etching (ICP-RIE)

An ICP-RIE system (Unaxis, VLR 700) was used to remove the unpatterned thermal oxide. Plasma made with 1 mTorr CHF_3 and 4 mTorr CF_4, and a coil power of 500 W, and a bias power of 50 W were used. ICP-RIE with various mixtures of Cl_2 and HBr were used to etch nanostructures into the patterned wafers. The total pressure of each mixture was 5 mTorr. The flow rate of the mixture through the chamber was 40 sccm. The coil power used to generate plasma was 300 W. The etch time was 360 s. Table 1 lists the various compositions of the mixtures and the bias powers used to etch the patterned wafers. Samples were treated with plasma made with 1 Torr O_2 and RF power 500 W for 60 s after etching.

Table 1. Composition of gas mixtures, bias powers, and aspect ratios.

Sample	**Cl_2/mTorr**	**HBr/mTorr**	**Bias Power/W**	**Aspect Ratio**
A	2.5	2.5	20	11
B	2.5	2.5	90	10
C	0.4	4.6	40	10

The profiles of the resulting nanostructures were observed by scanning electron microscopy (SEM). Images were captured 45° from plan view, with samples rotated ~15° around their vertical axis. Aspect ratios, *A*, were calculated from the SEM images using equation 1:

$$A \cong \frac{\sqrt{2} \times S}{T}, \quad (1)$$

where *S* is the stem length and *T* is the tip width. Examples of these values are marked in figure 1a. Profilometry was used to confirm the etch rates that were observed by SEM.

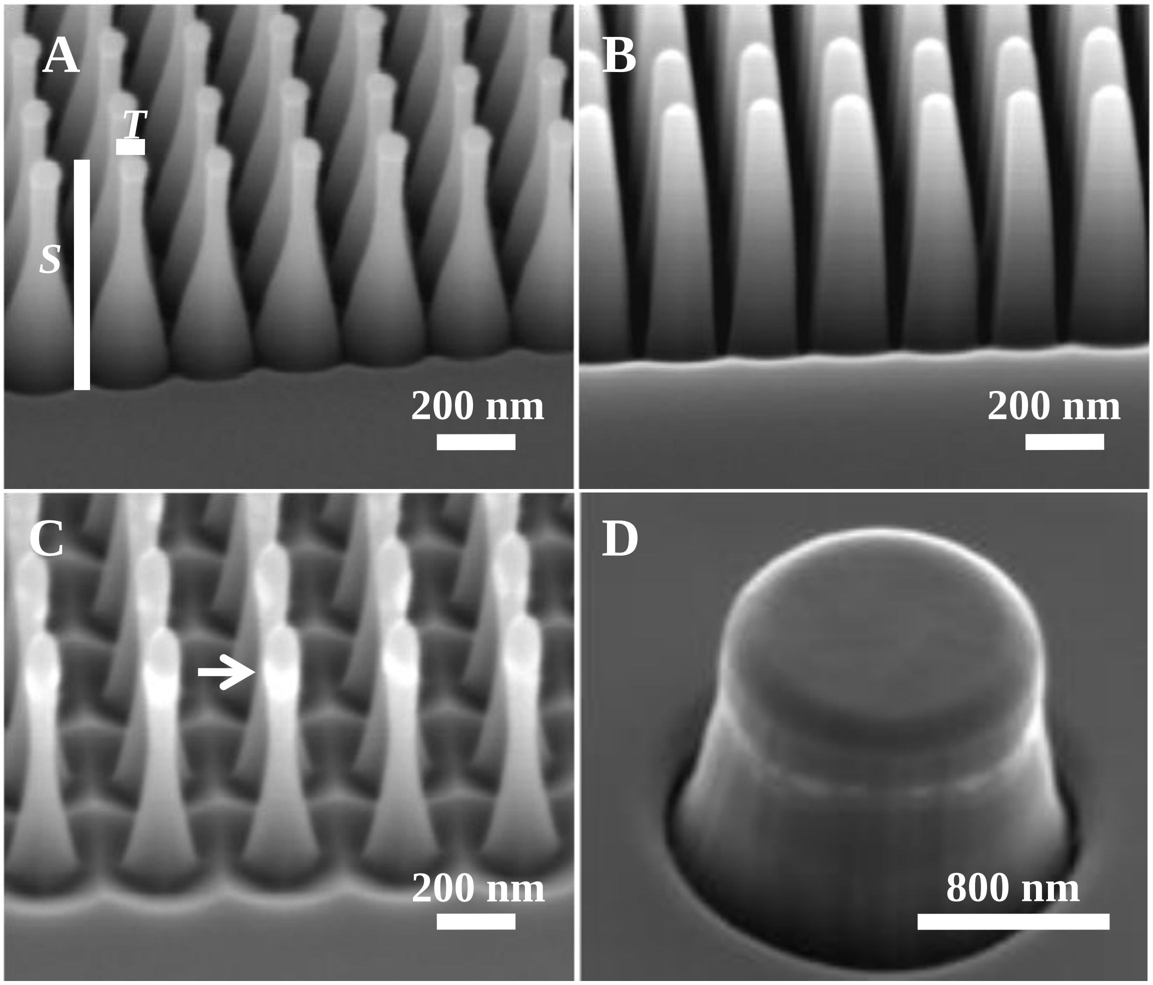

Figure 1. Panel of SEM images taken from Si nanostructures. The conditions used to prepare samples A–C are shown in table 1.

3. Results and Discussion

Low-magnification, plan-view SEM images of cells after etching showed that all patterns were transferred into the Si surface with excellent fidelity; no stitching errors or aberrations of the original image were observed. Figure 1 shows high-magnification SEM images of nanopillars formed from the circular etch masks using the corresponding conditions listed in table 1.

As the values in table 1 show, nanopillars with aspect ratios of 10 were readily fabricated. The etch rate of Si using these conditions was 160±20 nm/min. We presume that the particles, like that marked with the white arrow in figure 1c, are residues from the etch process.

Figure 1d shows a representative image of a nanopillar formed from a 1300 nm diameter etch mask. Because the anisotropy of etched nanostructures decreases as the diameter of the etch mask increases (*4–6*), this structure was used for comparison with those made from the 80 nm diameter etch masks. Indeed, SEM images of nanopillars formed from the 1300 nm etch masks showed that their anisotropy was not markedly affected by any of the conditions used. However, as figure 1 shows, the anisotropy and profile of nanopillars made from 80 nm diameter etch masks were strongly dependent on the conditions of the plasma.

Further inspection of figure 1 reveals the effects that the bias power and the composition of the gas mixture had on the profile of the nanopillars. For example, comparison of figure 1a to 1b clearly shows that significantly increasing the bias power from 20 to 90 W enhanced the anisotropy of the nanopillars—presumably because the larger power increased the bombardment energy and amount of reactive ions that form volatile Si chlorides and Si bromides on the unpatterned surface (*5*). However, figure 1b also shows that increasing the bias power caused substantially more microtrenching (*7*).

Other reports (*4, 6, 8*) have shown that perfectly anisotropic structures can be made in neat HBr plasmas. We were unable to reproduce these process conditions in our instrument with neat HBr. However, anisotropy was improved by decreasing the partial pressure of Cl_2. For example, figure 1c shows nanopillars that are more anisotropic than those of figure 1a. Further inspection of figure 1c also shows that microtrenching of this sample was reduced as compared to the microtrenching of the sample in figure 1b. This result is attributed to the significantly reduced bias power used.

4. Conclusion

A method to fabricate Si nanopillars with aspect ratios greater than 10 was developed. The anisotropy of these Si nanopillars was affected by the partial pressures of Cl_2 and HBr used during ICP-RIE. The amount of microtrenching around the nanopillars was controlled by the bias power used.

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