

## Etching of 10-nm Si structures using self-assembling pattern formation

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Self-formation of nanoscale etching masks has been found to occur during ECR etching when the sample is cooled to a low temperature, at which condensation of the reaction products or the etching gas starts to occur. We have also found that if nucleation sites are present on the surface, the condensation occurs preferentially on the nucleation sites and the resulting condensates act as etching masks, leading to the fabrication of Si nano-pillars. The average diameter of the pillars and its standard deviation are 11 nm and 2.5 nm, respectively. The narrow distribution of the diameter suggests that self-assembling phenomenon takes part in the formation of the etching masks.

### 1. Introduction

There has been much interest in the fabrication of Si nanostructures and many attempts have been made for this aim [1-3]. However, it is difficult for conventional lithography methods to reach the dimensions less than 10 nm, and new methods should be explored to overcome this barrier. We have found that a self-assembling phenomenon takes place on Si surfaces during electron cyclotron resonance microwave-plasma etching (ECR etching) at low temperatures, leading to the automatic formation of etching masks for nanofabrication. Here, we present formation of 10-nm patterns using this phenomenon.

### 2. Results and Discussion

Figure 1 shows scanning electron microscope (SEM) micrographs of Si surfaces after ECR etching with  $\text{SF}_6$ . The substrate temperature during the etching was (a)  $-135^\circ\text{C}$  and (b)  $-125^\circ\text{C}$ . The incident

microwave power and the rf power applied to the sample were 250 W and 5 W, respectively. The

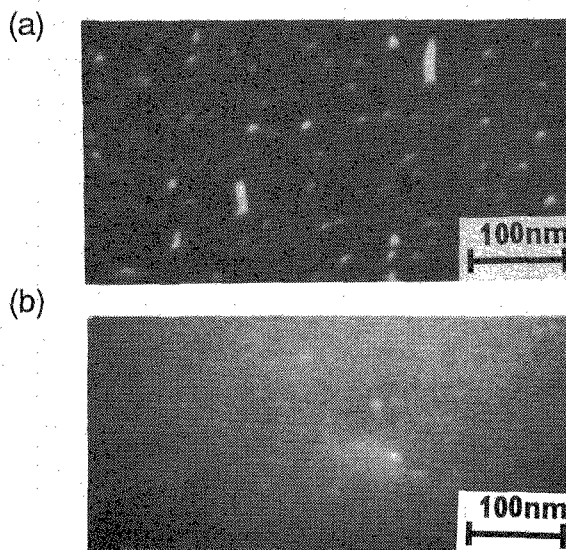


Fig.1 SEM micrographs Si surfaces after ECR etching at (a)- $135^\circ\text{C}$  and (b)- $125^\circ\text{C}$ . The tilt angle is  $40^\circ$ . Pillars of  $\sim 10$  nm diameter are formed in (a), but not in (b).

substrate was HF-cleaned before the etching. As seen in fig.1 (a), there appear narrow pillars and small dots on the Si surface after the ECR etching at  $-135^{\circ}\text{C}$  although no patterning was made beforehand. The diameter of the fabricated pillars were around 10 nm. Since no pillars were formed by the etching at  $-125^{\circ}\text{C}$ , the temperature during the ECR etching is of the key importance in this phenomenon.

Let us consider the formation mechanism of the pillars. It is known that the reaction products such as  $\text{Si}_x\text{F}_y$  or  $\text{S}_x\text{F}_y$  may condense and block the etching below  $\sim -135^{\circ}\text{C}$ . [4-6] Thus under limited condition, the condensation does not occur uniformly

but does only on specific sites which results in formation of etching masks with 10-nm dimensions.

Accordingly, if suitable nucleation sites for the condensation are introduced onto the surface, it will facilitate the pillar formation. To examine this assumption, we carried out the following procedure. First, PMMA (average molecular weight= $6 \times 10^5$  amu) with 75 nm thickness was coated on Si (100) substrates. The coated substrates were scratched with a tungsten needle and rinsed in acetone for three minutes. The tip diameter of the tungsten needle used was  $50 \mu\text{m}$ , and a weight of 50 g was applied to the needle during scratching. According to our previous study [7], some of the PMMA molecules adhere to the Si substrates by the scratching pressure and become insoluble in acetone. Then the substrates were etched by the ECR etching. The etching conditions were the same as above except for the sample temperature.

Figure 2 shows SEM micrographs of the scratched areas after ECR etching at (a)  $-140^{\circ}\text{C}$ , (b)  $-130^{\circ}\text{C}$ , and (c)  $-120^{\circ}\text{C}$ . At  $-140^{\circ}\text{C}$ , the sample was not apparently etched, and no pillars were observed in fig.2 (a). This is probably because the condensation of the etch-products covers the whole surface at this temperature. At  $-130^{\circ}\text{C}$ , pillars with  $\sim 10$  nm diameter and  $\sim 100$  nm height were observed in the scratched area while they were not observed in the unscratched area. In other words, the pillars were fabricated only on the area where nucleation sites were made. Although the sample was etched by  $\sim 100$  nm at  $-120^{\circ}\text{C}$ , no pillars were formed on the surface in fig.2 (c). This is because the condensation does not occur at  $-120^{\circ}\text{C}$ .

To summarize these results, there is a temperature region where the condensation of etch products occurs only at the nucleation sites and nucleation sites enables us to act as etching masks. In fig.1 (a), the nucleation sites may originate from contamination or defects, which were unintentionally onto the surface.

We evaluated the diameter distribution of the

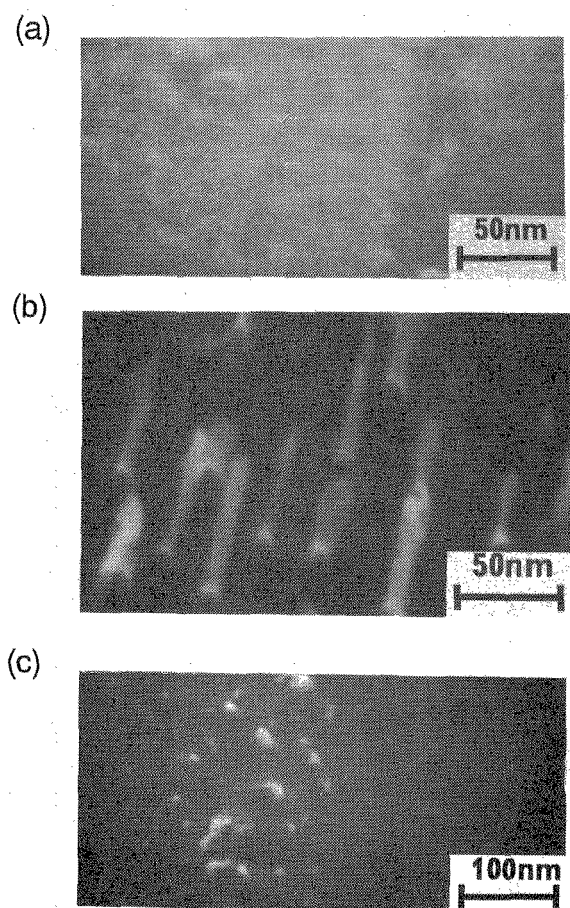


Fig.2 SEM micrographs of Si surfaces scratched with a tungsten needle and then ECR etched at (a)  $-140^{\circ}\text{C}$ , (b)  $-130^{\circ}\text{C}$ , and (c)  $-120^{\circ}\text{C}$ . The tilt angle is  $40^{\circ}$ . Pillars are observed only in (b).

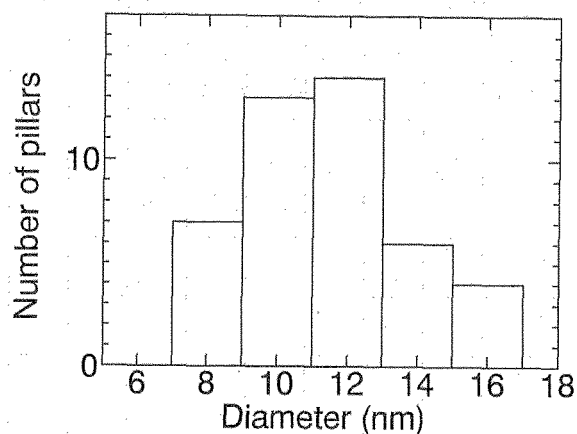


Fig.3 The diameter distribution of the fabricated Si pillars. The average diameter is 11 nm with a standard deviation of 2.5 nm.

fabricated Si pillars seen in fig.2 (b). A histogram for 45 pillars is shown in fig.3. The average of the pillar diameter is 11 nm and its standard deviation is 2.5 nm. This distribution is remarkably narrow although the fabrication process is very simple. This results agrees with the mechanism that the self-assembling phenomenon during the condensation process takes part in formation of the etching masks.

Finally, we confirmed by transmission electron microscope (TEM) observation that the fabricated pillars consist of single crystalline Si sculptured from the substrate. Figure 4 shows a lattice image of a fabricated Si pillars and its electron beam diffraction pattern. The diffraction pattern has two fold symmetry, indicating that the sample orientation is the (110). The lattice constant obtained is about 0.54 nm and is in good agreement with that of Si.

### 3. Conclusion

The self-assembling pattern formation has been found to occur during ECR plasma etching when the sample is cooled to a low temperature, at which condensation of the etch products or the etching gas starts to occur. We have also found that

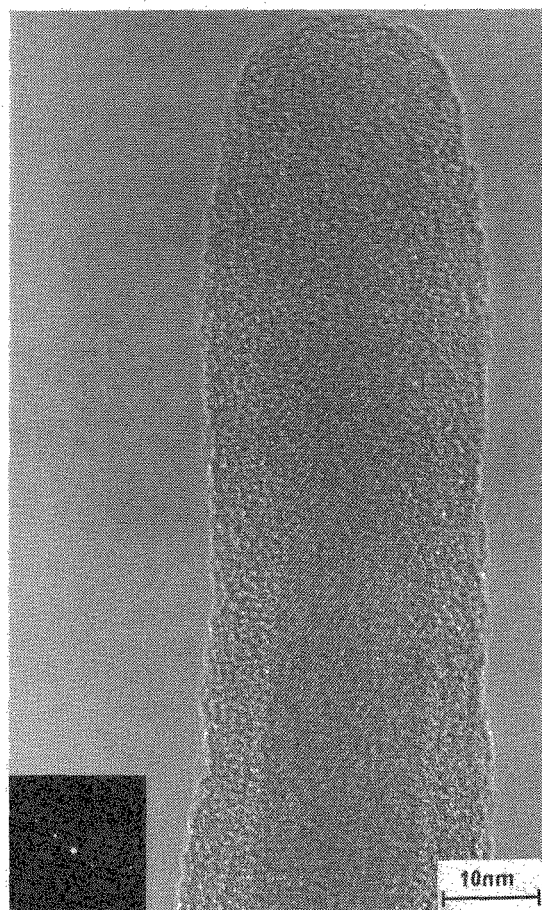


Fig.4 TEM micrograph of the fabricated pillar and its diffraction pattern. The diffraction pattern has two-fold symmetry corresponding to the (110) orientation. The estimated lattice constant corresponds to that of the Si crystal.

if nucleation sites are present on the surface, the condensation occurs preferentially on the nucleation sites and the resulting condensates act as etching masks, leading to the fabrication of Si nano-pillars.

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