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Simple Fabrication of Nanopyramid Array (NPA) on Si Surface by Means of Focused Ion Beam Patterning and Wet Etching

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Abstract

We propose a simple process to fabricate nanopyramid array (NPA) on Si surface by utilizing a newly found phenomenon, that is, retarded etch rate of ion-beam-exposed Si by hydrazine. Two dimensional arrays of dots and lines were written directly on Si substrate with 60-keV focused Si and P ion beam at doses of 10^{13}–10^{15} cm^{-2}. Then Si substrate was dipped in hydrazine solution, where unexposed region was selectively etched by hydrazine. By using these simple processes, 100-nm pyramid arrays with 200-nm interval and 40-nm pyramidal etchpit arrays with 150-nm interval can be fabricated easily. The cause of the retarded etch rate of ion-beam-exposed Si by hydrazine is discussed comprehensively.

1. Introduction

Fabrication of two-dimensional (2-D) nanopyramid array (NPA) with nm interval is essential for tera-bit memory and high density field emitter array (FEA). The approaches to nanostructure fabrication have been generally done with the resist patterning by electron beam (EB) and the subsequent dry etching. However, fabrication of NPA by these processes is not so easy because of the proximity effects during EB exposure on the resist and narrow process window in dry etching [1].

In this work, we have found that the retarded etch rate (ER) of ion-beam (IB)-exposed Si by hydrazine solution in contrast to previously reported ion-bombardment-enhanced etching [2]. This paper describes that the newly found phenomenon, that is, ion-bombardment-retarded ER, makes it possible to easily fabricate the NPA on Si surfaces by using focused ion beam (FIB) patterning and wet etching.

2. Experimental

The 2-D NPAs are fabricated by only two step processes of the FIB patterning and the subsequent wet etching as illustrated in Fig. 1. We used n-type Si(100) wafers with the resistivity of 60 Ωcm. 10-nm thick oxides were grown to avoid the influence of the contamination due to IB exposure. Si or P ions were irradiated through 10-nm thick oxides at doses of 10^{13}–10^{15} cm^{-2} at 60 keV by using the FIB system [3] (for Si) and a conventional implanter (for P). Beam spot size of the FIB was about 50 nm. Base pressure during IB exposure was kept at below 10^{-8} Torr. Then the samples were exposed to O_2 plasma to perfectly remove the contamination. After the oxide stripping by 1% HF dipping, the wafers were patterned by dipping in hydrazine anisotropic etchant ($N_2H_4H_2O$) for 15 seconds at 115°C. Since hydrazine contains no contaminants, it is very suitable for Si device process.

3. Results and Discussion

The NPAs processed by the dot exposure of 60 keV Si FIB are shown in Fig. 2. At a dose of 5×10^{14} cm^{-2}, the IB-exposed regions definitely serve as etch masks and NPAs can be fabricated successfully, while the pyramids are incompletely structured at a lower dose (Fig. 3). The minimum size of the pyramids and the minimum interval are determined by the top size of pyramid, that is, the size of the region damaged by FIB exposure. The nanoetchpit arrays processed by the line exposure of 60 keV Si FIB are shown in Fig. 4. It can be observed in Fig. 4 that the pyramidal etchpit arrays are completely fabricated by etching of unexposed region surrounded by the lines. In this case, the minimum size of the pyramids and the minimum interval are determined by the controllability of FIB writing (about a few 10 nm for our system) and the size of the region damaged by FIB exposure, respectively.

From now we discuss the reason for ion-bombardment-retarded etch rate (ER) of Si by hydrazine. Fig. 5 shows the dependence of the ER of Si by hydrazine on the ion dose. Si(100) substrates with and without 10-nm thick oxides were exposed to 60 keV P ions to investigate the influences of oxide-through exposure. After the oxides were completely stripped by 1% HF dipping, the wafers were dipped in hydrazine. The ER markedly decreases as the ion dose increases, regardless of oxide-through exposure. This result suggests that neither knock-on oxygen nor contamination due to IB exposure cause the retarded ER of Si by hydrazine. We have confirmed also that the fabricated nanopyramids are etched by hydrazine after recrystallizing the damaged region by annealing in N_2 at 850°C for 2 min as can be seen in Fig. 6. So far it has been reported that hydrazine dissolves Si substrates electrochemically, so that the ER can be affected by the type, resistivity and electrical potential of Si substrates [4]. Koyama et al. [5] have reported that the resistivity of irradiated Si by 75 keV Ar ions increases by two order of magnitude. Based on our results and their reports, it is concluded that the retarded ER of Si by hydrazine originates in the difficulty of the electron transfer between Si and hydrazine solution due to the increase in the resistivity of Si induced by ion irradiation. Thus this phenomenon depends on not ion species but the damage introduced by ion irradiation. This is fairly good news especially for FEA [6], because we can easily control the electrical property of the top of the nanopyramids by FIB irradiation of dopants.

4. Summary

We found that etch rate of ion-beam-exposed Si by hydrazine is retarded drastically. It was demonstrated that nanopyramid arrays can be fabricated easily by utilizing this phenomenon.

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Reference

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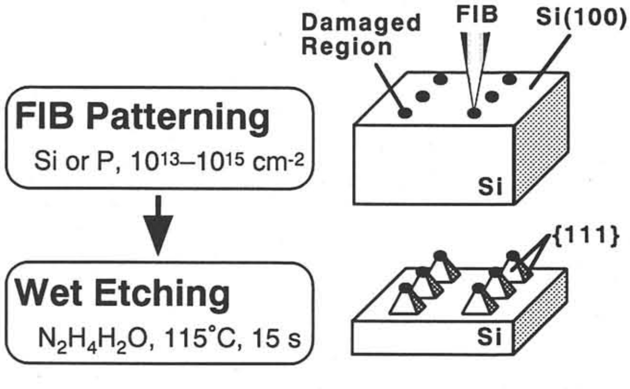

Fig.1 Nanopyramid array fabrication process flow

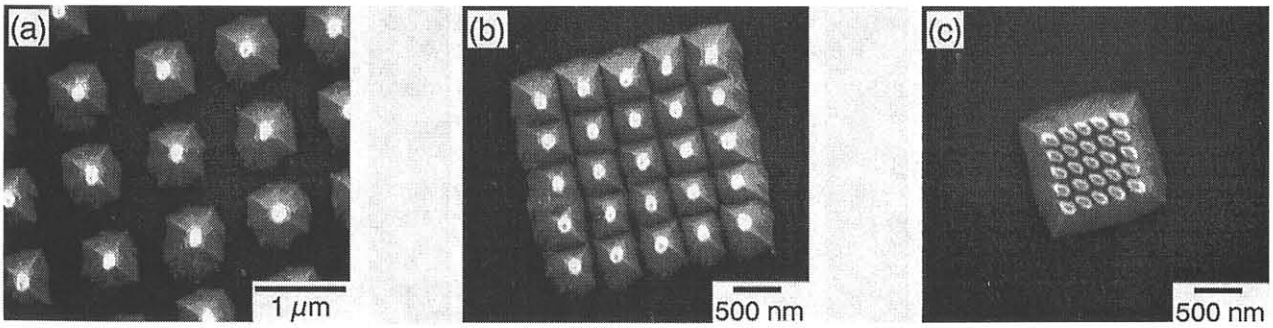

Fig.2 SEM images of nanopyramid arrays processed by the dot exposure of 60 keV Si FIB at a dose of $5x10^{14}$ cm^{-2} with interval of (a) 1μm, (b) 500 nm and (c) 200 nm.

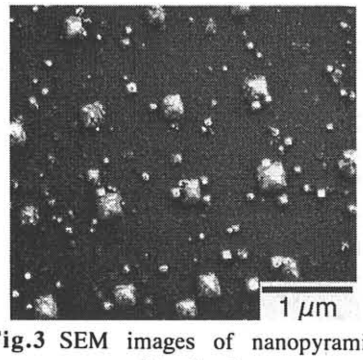

Fig.3 SEM images of nanopyramid arrays processed by the dot exposure of 60 keV Si FIB at a dose of $5x10^{13}$ cm^{-2}.

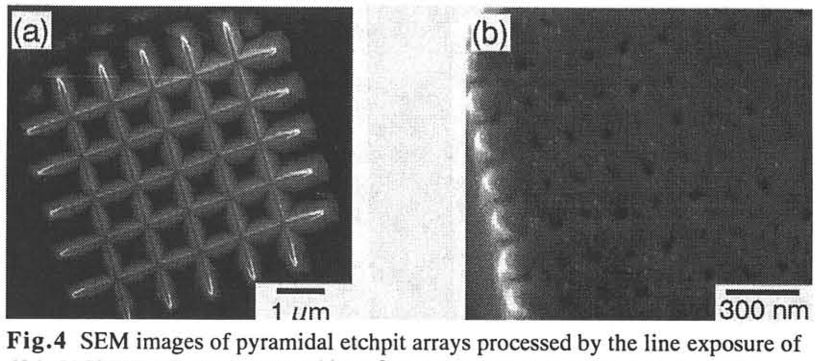

Fig.4 SEM images of pyramidal etchpit arrays processed by the line exposure of 60 keV Si FIB at a dose of $5x10^{14}$ cm^{-2} with interval of (a) 1μm and (b) 150 nm.

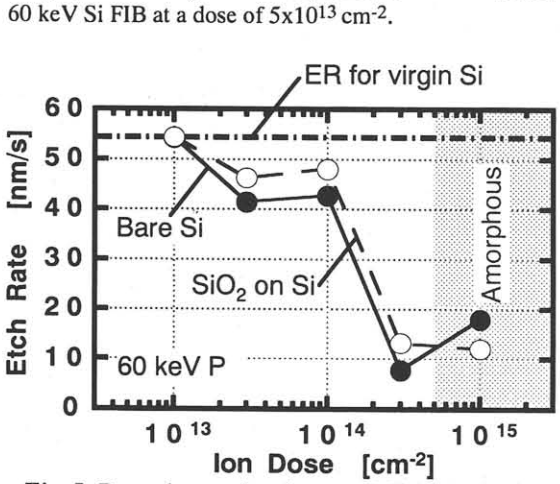

Fig.5 Dependence of etch rate of Si by hydrazine on the ion dose.

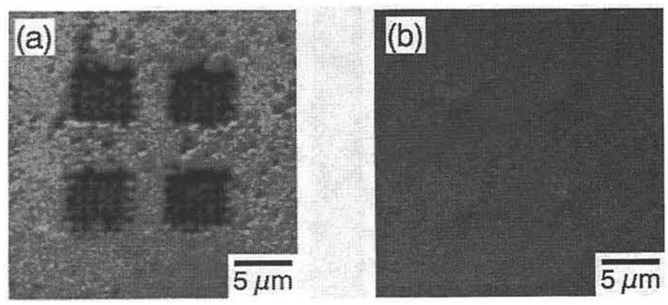

Fig.6 Optical micrograph of pyramidal etchpit arrays (a) after annealing for recrystallization in N_2 at 850°C for 2 min and (b) after the subsequent dipping in hydrazine solution for 15 s at 115°C.