Three-Dimensional Nanofabrication Utilizing Selective Etching of Silicon Induced by Focused Ion Beam Irradiation*

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A simple process of fabricating a three-dimensional nanostructure on a silicon surface was investigated in this study. The silicon surface area irradiated by focused ion beam (FIB) was selectively etched in HF, whereas the non-irradiated area was scarcely etched, and consequently, a concave nanostructure was fabricated on the irradiated area. To control the depth of the nanostructure, the depth dependence on ion irradiation parameters was investigated. As a result, it was found that the depth of the irradiated area can be controlled by changing ion irradiation parameters, such as dose and ion energy. Under a low-dose condition, the irradiated area was scarcely etched, due to the formation of an amorphous layer on the interior of silicon. Subsequently, it was etched in KOH to evaluate the mechanism of this phenomenon. In addition, the surface roughness dependence on ion irradiation parameters was investigated. Finally, three-dimensional nanostructures were fabricated on the basis of these results, suggesting that this method is a novel three-dimensional nanofabrication method.

Key Words: Three-Dimensional Nanofabrication, Ion Beam Lithography, Focused Ion Beam, Wet Chemical Etching, Single Crystal Silicon

1. Introduction

A photolithography technique has been used to fabricate semiconductor devices and has contributed to the advancement of large-scale integrated circuit technology. Nowadays, this technique is applied to various industrial fields that require micro/nanoscale structures, e.g., microelectromechanical system (MEMS) and micrototal analysis system (μ-TAS). However, there are a number of problems associated with this technique. Some problems include a high cost and a time-consuming step. In addition, this technique basically consists of a two-dimensional fabrication process and, therefore, it is difficult to fabricate a complex shaped three-dimensional structure.

Focused ion beam (FIB)-based lithography enables the fabrication of nanostructures by a simple and precise maskless method. The silicon surface area irradiated by FIB can withstand etching in KOH$^{(1)-(5)}$, $N_2H_4H_2O^{(6)}$, TMAH$^{(7)}$ and some other etchant solutions, whereas the non-irradiated area is susceptible to etching. Therefore, protruding nanostructures can be fabricated on the irradiated area. On the other hand, the ion-irradiated silicon surface can be selectively etched with hydrofluoric acid (HF)$^{(8)-(11)}$ and phosphoric acid $(H_3PO_4)^{(12)}$. In this case, a concave structure can be fabricated on the silicon surface. In these studies, it was shown that nanostructures with different shapes and sizes can be fabricated using FIB irradiation, by changing the irradiated ion dose, FIB spot size and scan field dimensions followed by the wet chemi-

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cal etching of silicon. However, there have been no studies that attempt to control the height and depth of structures with different irradiation parameters and to fabricate three-dimensional nanostructures.

Herein, we present a simple process of fabricating a three-dimensional nanostructure on a silicon surface using a combination of FIB irradiation and wet chemical etching. In this study, a selective etching method using HF was applied to fabricate structures. By using this method, a more precise structure with a low-amount-affected layer than that fabricated by direct ion milling was fabricated, because an amorphous layer in silicon and a reattachment causing a decrease in accuracy were selectively removed. To control the shape of a nanostructure, its height and shape dependences on FIB irradiation parameters were investigated. In addition, three-dimensional nanostructures were fabricated using the results obtained. From these results, a novel three-dimensional nanofabrication method using a combination of FIB irradiation and wet chemical etching was developed.

2. Experimental Methods

The experimental process of nanofabrication is illustrated schematically in Fig. 1. Ion irradiation experiments were conducted by employing a Hitachi high-technology FB-2000A FIB facility, which can irradiate a Ga^+ ion beam with an ion energy up to 30 keV.

An undoped silicon sample (surface roughness Ra: 0.89 nm) was rinsed in acetone and then pure water. The silicon sample was irradiated with Ga^+ ions at room temperature and then rinsed in pure water again. After the ion irradiation, the irradiated sample was etched in 46 mass% HF at 24°C. The etching was conducted with sonication in order to obtain a smooth surface. All measurements were conducted using an atomic force microscope (AFM: Shimadzu SPM-9500J2), and the effect of ion irradiation parameters on the shape of the structure was evaluated.

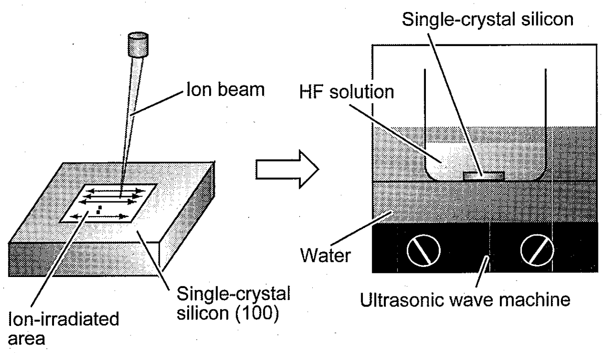

Fig. 1 Schematic diagrams of experimental process. (a) FIB irradiation using Ga^+ ions. (b) Wet chemical etching in HF with sonication

3. Results and Discussion

3.1 Nanofabrication using ion beam irradiation followed by wet chemical etching

A nanofabrication method using a combination of FIB irradiation and wet chemical etching is shown in Fig. 2. Figure 2 (a) shows an AFM topography image of a silicon surface area after 30 keV Ga^+ ion irradiation ($5 \times 5\,\mu m^2$ area) at a dose of 13.0 $\mu C/cm^2$. This image shows a minute protuberance on the irradiated area, which is only 1–2 nm in height. This phenomenon is considered to result from the formation of an amorphous layer induced by FIB irradiation. Figure 2 (b) shows an AFM topography image of the same area as that shown in Fig. 2 (a), after etching in 46 mass% HF for 20 min. The irradiated area is selectively etched in HF, whereas the non-irradiated area is scarcely etched[13]. Therefore a concave nanostructure with a depth of 33 nm is fabricated on the irradiated area. In this study, a three-dimensional nanofabrication technique is developed by controlling this technique.

3.2 Depth dependence on ion irradiation parameters

3.2.1 Depth dependence on ion dose To control the depth of the nanostructure, the depth dependence on the ion irradiation parameters was investigated. The silicon sample was irradiated with various doses of 30 keV Ga^+ ions, and subsequently etched in 46 mass% HF for 20 min. Figure 3 (a) shows an AFM topography image of the silicon surface area irradiated with 30 keV Ga^+ ions at doses of 0.2 to 27.1 $\mu C/cm^2$. It can be observed that the irradiated area is protruding at a height of 1–2 nm. However, the difference is less than 1 nm. Figure 3 (b) shows an AFM topography image of the same area after etching in 46 mass% HF for 20 min. Under a low-dose condition, the irradiated area is scarcely etched, whereas the irradiated area is etched under a high-dose condition and a concave structure is fabricated on the irradiated area. In addition, this image reveals that the depth increases with the dose.

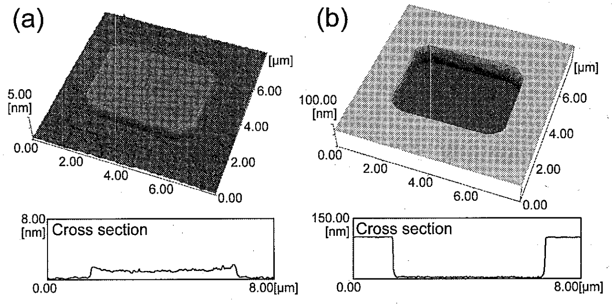

Fig. 2 Nanofabrication method using FIB irradiation followed by wet chemical etching. (a) AFM topography image of silicon surface after irradiation with 30 keV Ga^+ ions at dose of 13.0 $\mu C/cm^2$. (b) AFM topography image of same area after etching in 46 mass% HF for 60 min

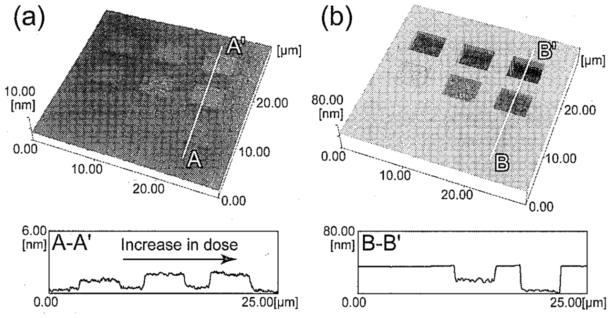

Fig. 3 Change in ion-irradiated area after etching in HF under low-dose condition. (a) AFM topography image of irradiated area at doses of 0.2 to 27.1 μC/cm^2. (b) AFM topography image of same area after etching in 46 mass% HF

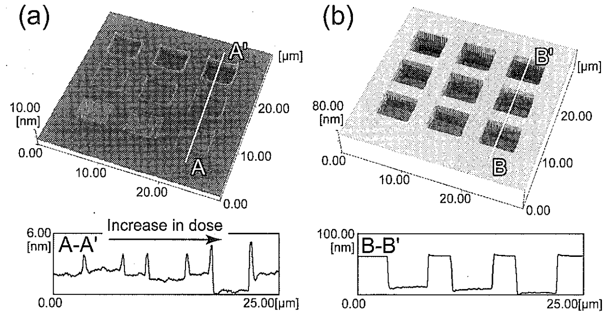

Fig. 4 Change in ion-irradiated area after etching in HF under high-dose condition. (a) AFM topography image of irradiated area at doses of 224.0 to 2 016.0 μC/cm^2. (b) AFM topography image of same area after etching in 46 mass% HF

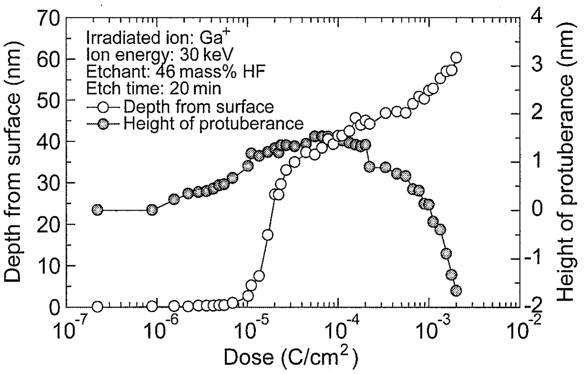

Fig. 5 Changes in depth of irradiated area at various doses. Silicon is irradiated with 30 keV Ga$^+$ ions and subsequently etched in 46 mass% HF for 20 min

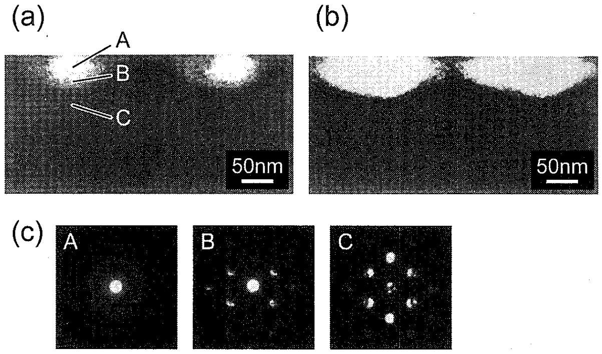

Fig. 6 Bright-field cross-sectional TEM images of silicon irradiated with 30 keV Ga$^+$ ions under (a) low- and (b) high-dose conditions. (c) Nanoelectron diffraction pattern of irradiated areas

Figure 4 (a) shows an AFM topography image of a silicon surface irradiated with 30 keV Ga$^+$ ions at doses of 224.0 to 2 016.0 μC/cm^2. The irradiated area is spattered, and a concave structure with a depth of 0.9 to 1.7 nm is fabricated after the irradiation. In addition, a burrlike structure is formed around the irradiated area, due to the reattachment of spattered ions. Under these conditions, the irradiated area is etched in HF, and concave structures are fabricated under all dose conditions, as shown in Fig. 4 (b). In addition, the burrlike structure is removed entirely, and a smooth surface is fabricated around the irradiated area.

A change in the depth of the irradiated area plotted as a function of dose is shown in Fig. 5. It can be observed that the irradiated area protrudes after the irradiation at a dose less than 896.0 μC/cm^2. For a dose more than over 1 120.0 μC/cm^2, the irradiated area is sputtered and a concave structure is fabricated after the irradiation. After the etching in HF, the irradiated area is scarcely etched in HF lower than 6.9 μC/cm^2 in dose. The depth of the irradiated area rapidly increases over this value, and a gradual increase is shown at a dose more than 20.4 μC/cm^2.

Figure 6 shows the cross-sectional transmission electron microscope (TEM) images and nanoelectron diffraction (Nano-ED) patterns of 30 keV Ga$^+$ ion irradiated areas at different doses. Under the low-dose condition, the amorphous layer, which has the same pitch as that of a dot, is formed on the silicon substrate, as indicated by the nano-ED image in Fig. 6 (c) showing a diffuse ring pattern, and the layer expands to a depth of approximately 70 nm, as can be observed in Fig. 6 (a). On the other hand, a thicker and wider amorphous layer is formed under the high-dose condition than under the low-dose condition, and the layer is formed from the surface, as shown in Fig. 6 (b).

Ion-irradiation-induced amorphization initially occurs near the most heavily damaged region where most of the irradiated ions have ceased and have low energies(14), (15). Continued irradiation increases the thickness of the generated amorphous layer. In addition, the projected range and straggling of 30 keV Ga$^+$ ions in silicon simulated by SRIM(16) are 26.9 nm and 9.3 nm, respectively. These indicate that the ion-beam-induced amorphous layer is formed near this region.

Under the low-dose condition, an amorphous layer is formed on the interior of silicon near the range of the irradiated ions and the surface is recrystalized and/or not transformed to an amorphous phase. Therefore, the irradi-

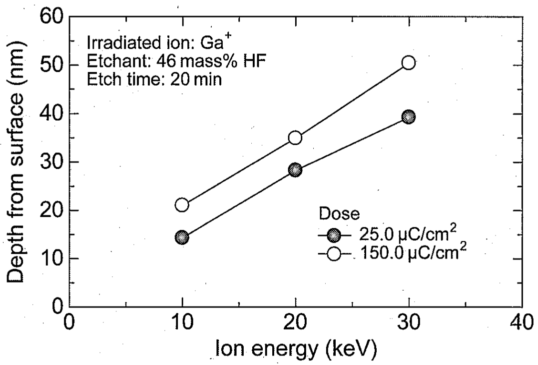

Fig. 7 Changes in depth of irradiated area at various ion energies. Silicon is irradiated with Ga$^+$ ions and subsequently etched in 46 mass% HF for 20 min

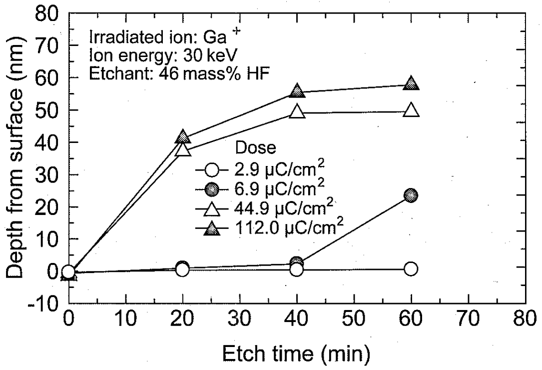

Fig. 8 Changes in depth of irradiated area at various doses plotted as function of etch time. Silicon is irradiated with Ga$^+$ ions and subsequently etched in 46 mass% HF

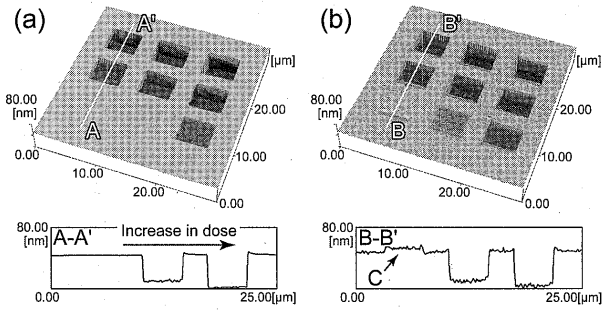

Fig. 9 Change in irradiated area after etching in KOH. (a) AFM topography image of silicon surface irradiated with 30 keV Ga$^+$ ions at doses of 0.2 to 27.1 μC/cm^2, followed by wet chemical etching in 46 mass% HF for 60 min. (b) AFM topography image of same area after etching in 10 mass% KOH for 90 s

ated area is scarcely etched in HF due to the surface crystalline layer. On the other hand, an amorphous layer is formed from the surface under the high-dose condition due to the expansion of the amorphous layer, resulting in the dissolution of the irradiated area in HF. In addition, a deep structure is fabricated when the dose increases because of the longitudinal expansion of the amorphous layer. This phenomenon is independent of the species of irradiated ions(8)–(12). Therefore, this phenomenon is caused not by the existence of irradiated ions, but by the formation of an amorphous layer.

3.2.2 Depth dependence on ion energy Figure 7 shows the changes in the depth of the irradiated area at various ion energies. Silicon was irradiated with Ga$^+$ ions at various ion energies and subsequently etched in 46 mass% HF for 20 min. It can be observed that the depth of the irradiated area is proportional to the ion energy under both dose conditions, and a deep structure with a depth of 51 nm is fabricated under the dose of 150.0 μC/cm^2 and ion energy of 30 keV. The project range of the irradiated ions increases with the ion energy, resulting in the formation of an amorphous layer at a deep region. Therefore, a deep structure is fabricated under a high-ion-energy condition. The project ranges at 10 and 20 keV simulated by SRIM(16) are 12.5 ± 4.8, 20.0 ± 7.2 nm, respectively. These values show a good agreement with the depths of the structure obtained in Fig. 7.

3.3 Depth dependence on etch time

Figure 8 shows the changes in the depth of the irradiated area at various doses plotted as a function of etch time. At a dose of 2.9 μC/cm^2, the irradiated area is scarcely etched because the surface layer is crystalline silicon due to a low defect density. The irradiated area is etched for more than 40 min at a dose of 6.9 μC/cm^2. In this case, the irradiated area is gradually etched when the etch time is lower than 40 min due to the surface crystalline layer. Then, the silicon etching reaches the amorphous layer existing on the interior of the substrate, and the depth is rapidly increased after 40 min. The depth, at a dose of more than 44.9 μC/cm^2, increases at the etch time of 20 min because the amorphous layer is formed from the surface, resulting in the dissolution of the amorphous layer for the short etch time.

3.4 Mechanism of increase in depth

From the results presented in Figs. 5 and 8, it was found that the depth of the structure can be controlled by the ion dose due to the change in the morphology of the amorphous layer. On the other hand, the irradiated area is scarcely etched under the low-dose condition due to the surface crystalline layer. To confirm this assumption, the fabricated structure was subsequently etched in KOH.

The change in irradiated area after etching in KOH is shown in Fig. 9. Figure 9 (a) shows an AFM topography image of the same silicon surface as that shown in Fig. 3 (a) obtained after etching in 46 mass% HF for 60 min. It can be observed that concave structures with depths of several tens of nanometers are fabricated on the irradiated area, whereas the irradiated area is scarcely etched when the dose is less than 3.5 μC/cm^2. Figure 9 (b) shows an AFM topography image of the same area obtained after etching in 10 mass% KOH for 90 s. The irradiated area at a dose of 3.5 μC/cm^2 withstands etching in

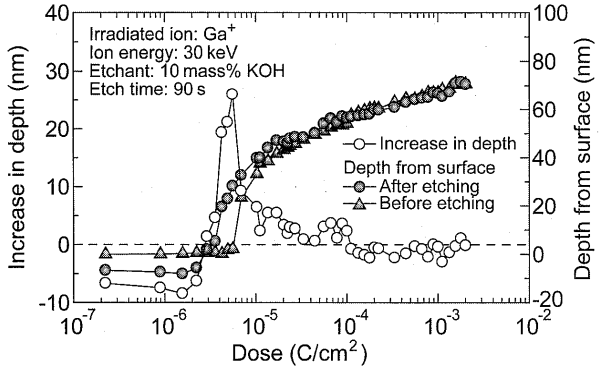

Fig. 10 Changes in depth of irradiated area at various doses. The ion-irradiated silicon sample is etched in 46 mass% HF for 60 min and subsequently in 10 mass% KOH for 90 s

KOH, whereas the non-irradiated area is etched and, consequently, a protruding structure with a height of 7 nm is fabricated on the irradiated area (marked C, Fig. 9 (b)).

The change in the depth of the irradiated area after etching in KOH is shown in Fig. 10. At a dose less than 2.2 μC/cm^2, the irradiated area withstands etching in KOH, and a protruding structure is fabricated on the irradiated area. This result indicates that the ion-irradiation-induced amorphous layer, which has corrosion resistance against KOH$^{(1)-(4)}$, does not dissolved in previous etching in HF, resulting in the formation of a protruding structure under the low-dose condition. The rate of increase in depth rapidly increases when the dose is more than 2.2 μC/cm^2. These phenomenons are attributed to the ion-beam-induced damaged layer, which causes an etching enhancement against KOH. The depth does not change after the etching under the high-dose condition because the amorphous layer is entirely removed in previous etching in HF.

3.5 Surface roughness dependence on ion irradiation parameters

To fabricate a precise structure, the effects of the ion irradiation parameters on the surface roughness were investigated. The silicon sample was irradiated with 30 keV Ga$^+$ ions at various dot pitches, at a dose per dot of 4.0×10^{-14} C, and subsequently etched in 46 mass% HF for 20 min.

Figure 11 shows the AFM topography images of silicon irradiated with different dot pitches after etching in 46 mass% HF for 20 min. At a dot pitch of 63 nm, a smooth surface is formed on the irradiated area. On the other hand, a concave-convex pattern, which has the same pitch as the dot pitch, is formed on the irradiated area at a dot pitch of more than 125 nm. Therefore, these results indicate that the surface roughness of the irradiated area strongly depends on the dot pitch of irradiated ions.

Changes in the surface roughness of the irradiated area at various dot pitches are shown in Fig. 12. It can be observed that a smooth surface is formed when the dot pitch is less than 125 nm. The surface roughness increases with the dot pitch when the dot pitch is more than 250 nm due to the formation of a concave-convex pattern, resulting in a rough surface. These results indicate that a smooth surface can be fabricated at a low dot pitch and can become significantly rougher at a dot pitch of more than 250 nm.

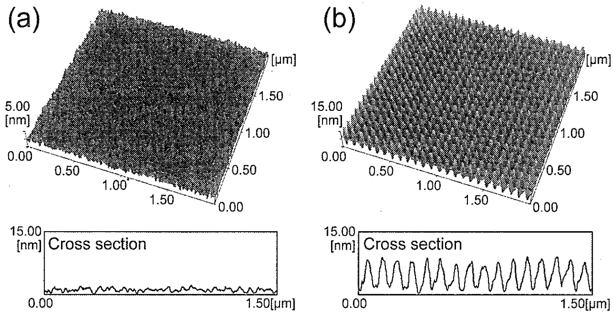

Fig. 11 AFM topography images of irradiated area at dot pitches of (a) 63 nm and (b) 125 nm. The silicon sample is irradiated with 30 keV Ga$^+$ ions at various dot pitches and subsequently etched in 46 mass% HF for 20 min

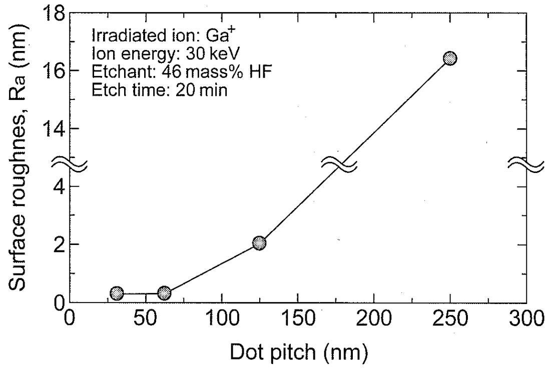

Fig. 12 Changes in surface roughness of irradiated area at various dot pitches. Silicon is irradiated with 30 keV Ga$^+$ ions and subsequently etched in 46 mass% HF for 20 min

3.6 Application to three-dimensional nanofabrication

From the results shown in Figs. 5 and 7, it was found that the depth of the structure can be controlled by ion irradiation parameters, such as dose and ion energy. Herein, a three-dimensional structure is fabricated on the basis of these results.

Figure 13 (a) shows an AFM topography image of the silicon surface irradiated with different doses. It can be observed that the irradiated area is protruding due to the formation of an amorphous layer. The height shows a marginal increase with an increase in dose. Figure 13 (b) shows an AFM topography image of the same area after etching in 46 mass% HF for 20 min. The depth increases with the dose, due to the change in the thickness

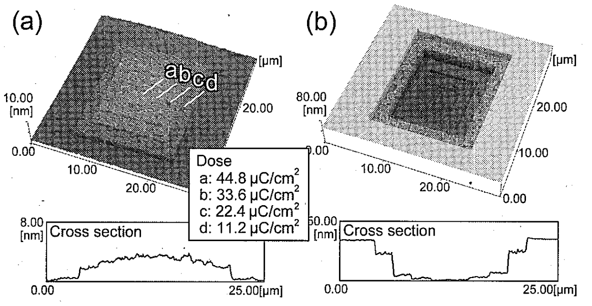

Fig. 13 Step structure fabricated using FIB irradiation followed by wet chemical etching. (a) AFM topography image of silicon surface irradiated at doses of 11.2 to 44.8 μC/cm^2. (b) AFM topography image of same area after etching in 46 mass% HF for 20 min

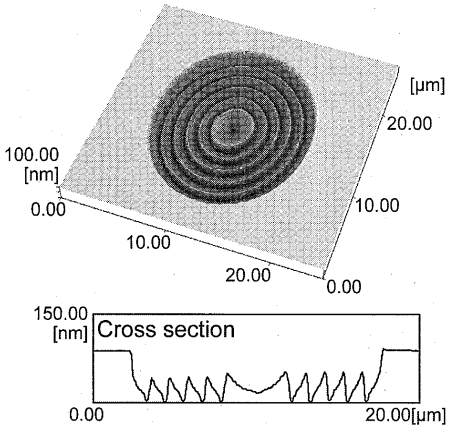

Fig. 14 AFM topography image of Fresnel lens pattern structure fabricated using ion beam irradiation followed by wet chemical etching. The structure is fabricated using ion beam irradiation at different ion doses and subsequently etched in 46 mass% HF for 20 min

of the amorphous layer, and consequently, a step structure, which has four different depths, is fabricated on the irradiated area.

Figure 14 shows an AFM topography image of a Fresnel pattern structure. The structure is fabricated with FIB irradiation by changing the dose at the dot pitch of 63 nm, followed by wet chemical etching in 46 mass% HF for 20 min. A three-dimensional structure with a smooth, curved surface can be fabricated by gradually changing the ion dose.

4. Conclusions

In this study, we demonstrate a method of three-dimensional nanofabrication on a silicon surface using a combination of FIB irradiation and wet chemical etching. An ion-irradiated silicon surface can be electively etched in HF, and a concave nanostructure can be fabricated by this method. The depth of the irradiated area can be controlled by ion irradiation parameters, such as dose and ion energy, due to the change in the morphology of the amorphous layer. In addition, the surface roughness dependence on ion irradiation parameters is investigated. Finally, three-dimensional nanostructure can be fabricated on the basis of these results, suggesting that this method is a novel three-dimensional nanofabrication method.

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