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Nanoporous structure formations on germanium surfaces by focused ion beam irradiations

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Abstract

The formation of porous structures of nanometre size (nanoporous structures) on germanium (Ge) surfaces by focused ion beam (FIB) irradiations was investigated using various FIB conditions such as ion species, irradiation energies, total fluences, fluence rates, and incident angles. FIB-irradiated regions were observed using a scanning electron microscope and an atomic force microscope. It is found that, using a focused Ga ion beam (Ga FIB) at an energy of 100 keV, the irradiated Ge surface swelled up to ion fluence of 2×10^{17} cm^{-2} with nanoporous structures and then was etched for larger fluences. The shape of swollen nanoporous structures depended on the fluence rate and the incident angle of the Ga FIB. However, such porous structures were observed neither for low-energy (15–30 keV) FIB irradiations using Si and Au ions nor for high-energy (200 keV), heavy ion (Au) irradiation. These observations might be helpful in discussing the formation mechanisms of the nanoporous structures on Ge surfaces by ion beam irradiations. Fabrication of patterned structures at selected regions on the Ge surface was demonstrated without using any masks.

1. Introduction

Single-crystal germanium (Ge) surfaces swell and change to porous structures of nanometre size (nanoporous structures) after energetic ion beam irradiations. The form of the swollen region is something like a sponge of nanometre size and, therefore, it has very large surface area compared with its volume. In another words, a large number of holes of nanometre size are formed in the swollen region of Ge surfaces. Because of these remarkable characteristics, the nanoporous structures might be useful to, for example, form a nanofilter in biochips, sensor materials, low-dielectric constant materials, and so on.

The formation of swollen and/or nanoporous structures on Ge surfaces by ion implantation has been reported by several authors. Wilson investigated the effect of self-ion bombardment on the surface topography of single-crystal Ge using 30–500 keV Ge ions and reported the formation of cellular structures with a mean cell diameter of 120 nm at the maximum and a depth of the porous layer up to six times the projected range (R_p) [1]. Appleton *et al* reported the formation of surface craters on Ge(100) and (111) surfaces up to a depth of several hundreds of nanometres using Ge, In, Sb, Tl and Bi ions at energies of 70–280 keV [2]. Wang and Birtcher observed the change from small void-like cavities to sponge-like porous material of amorphous Ge surfaces by increasing Kr ion fluences at an energy of 1.5 MeV [3]. Bhatia *et al* reported the possibility of the formation of porous materials on Ge(111) by Ni, Ge and Ag ion irradiations at an energy of 75 MeV [4]. We have also reported the formation of swollen nanoporous structures on Ge(110) surfaces by Ga focused ion beam (Ga FIB) irradiation at an energy of 100 keV, and such a structure was found to be stable in water for at least 10 h [5]. In all these reports, rather high-energy ions from 30 keV to 75 MeV and heavier ions were irradiated on Ge surfaces.

In case of a Si surface, the swelling of the surface by ion implantation was reported by Lehrer *et al* [6] using 30 keV Ga ion implantations on Si surfaces at lower fluences, and the mechanism was explained by the volume change in the ion-implanted region of Si from a crystal to an amorphous state. However, because no porous structure was observed for the swollen Si surface, the mechanism cannot apply directly for Ge surfaces. Although the formation mechanisms of swollen and nanoporous structures on Ge surfaces are not known at present, it should be helpful to clarify the dependence of the shape of such structures on the ion irradiation conditions to discuss the formation mechanisms.

Using an FIB system with a mass separator, several kinds of ions can be irradiated on locally selected regions on the surface without using any masks, and the ion irradiation conditions such as fluence rate, as well as total fluence of ions and incident angle of ions, can be varied easily by scanning methods without changing the ion beam current. In the present paper, the shape of the swollen and nanoporous structures formed on Ge surfaces by Ga, Si or Au FIB irradiations for different conditions of ion energies, total fluences, fluence rates and incident angles was observed. To demonstrate an ability to fabricate local patterns on Ge surfaces in both swollen and etched shapes without using any masks, the Ga FIB was irradiated along lines comprising the word 'ION' with different fluences.

2. Experimental details

Single-crystal Ge(110) and (100) wafers were used in this study and the surfaces of the sample chips cut out from the wafers were etched using CP4 solvent before mounting on a sample holder for the FIB system. For high- and low-energy ion irradiations, FIB systems with an acceleration voltage of 100 kV and 15 kV were used, respectively. Because both systems have an $E \times B$ mass filter, Au^+, Au^{2+}, Si^+ and Si^{2+} ions can be separated from a common AuSi alloyed metal source. Ga^+ is obtained from another single Ga metal source. The FIB irradiation was performed on 5 μm × 5 μm (high-energy irradiation) or 10 μm × 10 μm (low-energy irradiation) areas on the Ge surfaces with ion fluences between 3×10^{15} and 4×10^{17} cm^{-2}, changing the repetition number of raster scan of each FIB. The beam current of 10–1200 pA and the dwell time of 1–128 μs were used to change the fluence rate of FIB irradiations.

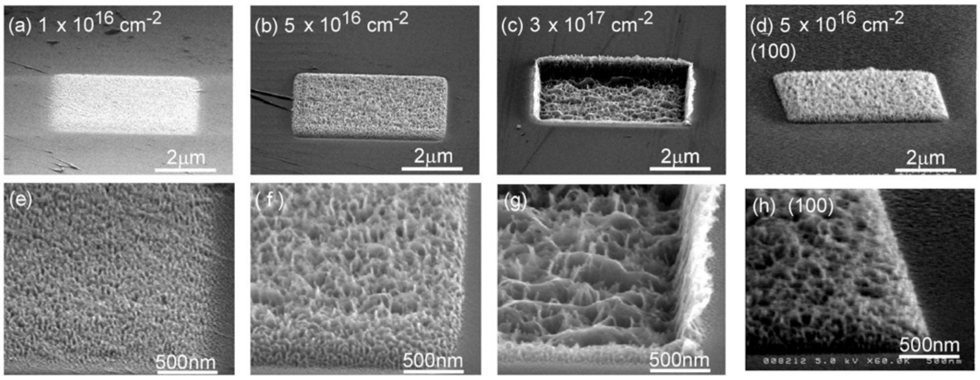

Figure 1. SEM images of 100 keV Ga FIB-irradiated Ge(110) ((a)–(c)) and (100) ((d)) surfaces at fluences shown. (e)–(h) are partly enlarged images corresponding to (a)–(d), respectively (viewing angle: 70° from the surface normal).

The beam diameter of the high-energy FIB was equal to the measured linewidth of the sputtered grooves delineated on the surface by changing fluences [7] and estimated to be about 90 nm [8]. That of the low-energy one was estimated to be several micrometres.

To form patterned structures on Ge surfaces, the Ga FIB at an energy of 100 keV was delineated along several lines 10 μm in length at a fluence of 1×10^{16} or 4×10^{17} cm^{-2}.

The surface topography of the FIB-irradiated regions was observed using a scanning electron microscope (SEM) and an atomic force microscope (AFM).

3. Results and discussion

3.1. Dependence on total fluences of 100 keV Ga FIB irradiations

Figures 1(a)–(c) show the SEM images of the Ga FIB-irradiated regions at an energy of 100 keV on a Ge(110) surface. Using a beam current of 60 pA and a dwell time of 1 μs, one raster scan produces a fluence of 7×10^{14} cm^{-2} in the present FIB condition used. By repeating the raster scan 14, 71 and 429 times, the total fluences were adjusted to 1×10^{16}, 5×10^{16} and 3×10^{17} cm^{-2}. Figures 1(d)–(f) show the partly enlarged SEM images corresponding to figures 1(a)–(c), respectively. Because the viewing angle of these SEM images was tilted 70° from the surface normal direction, it can easily be shown that the Ga FIB-irradiated regions at fluences of 1×10^{16} and 5×10^{16} cm^{-2} swelled and that nanoporous structures were formed. The height and the size of the holes in the nanoporous structure increased by increasing the fluence, but for larger fluence of 3×10^{17} cm^{-2}, the surface was etched.

As shown in figures 1(d) and (h), the swollen nanoporous structure was also observed on Ge(100) surface. Although the beam current used was 31 pA, the dwell time of 1 μs was same with that used for the Ge(110) surface. The feature of the structure was almost the same as those observed on the Ge(110) surface at the same fluence.

To investigate the dependence of the swelling or etching characteristics on the ion fluence, the height of the Ga FIB-irradiated regions on the Ge(110) surface was measured by AFM as a function of the ion fluence. The result is shown in figure 2. It is found that the height of the surface increased up to a fluence of about 8×10^{16} cm^{-2} and then decreased for larger fluences. As a result, the surface of the Ga FIB-irradiated regions swelled up to an ion fluence of about 2×10^{17} cm^{-2}, but the surface was etched by Ga FIB irradiations at ion fluences larger than about 2×10^{17} cm^{-2}.

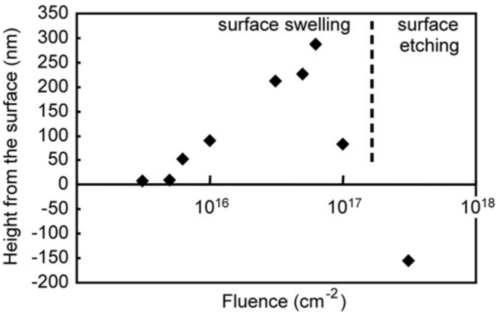

Figure 2. Ion fluence dependence of the height of the 100 keV Ga FIB-irradiated region on Ge(110).

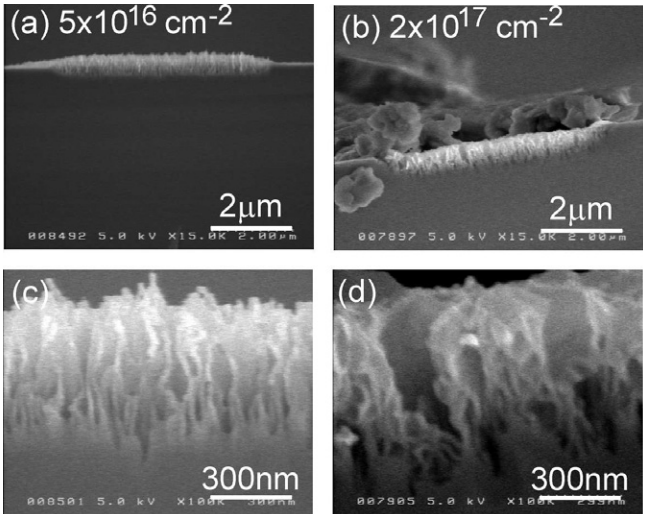

Figure 3. Cross-sectional SEM images of the 100 keV Ga-irradiated region on Ge(110) surface at the fluence shown. (c) and (d) are partly enlarged images of (a) and (b), respectively.

To obtain cross-sectional images for the swollen and etched regions, the sample chip was cleaved so as to intersect the Ga FIB-irradiated regions. SEM images of the cross section of the Ge(110) after the 100 keV Ga FIB irradiation are shown in figures 3(a) and (b) for the ion fluences of 5×10^{16} and 2×10^{17} cm^{-2}, respectively. It can be seen that the surface definitely swelled after the Ga FIB irradiation at the lower fluence, and that the influence was to a depth of about 600 nm below the surface, the value of which is 15 times that of the projected range of 100 keV Ga ions in (amorphous) Ge (40 nm) calculated by the TRIM code [9]. On the other hand, the height of the Ga FIB-irradiated surface at the fluence of 2×10^{17} cm^{-2} was almost unchanged, which agrees with the expectation from the result of figure 2. The region with a thickness of about 600 nm from the surface was also influenced by the Ga FIB irradiation. However, the features are different. Figures 3(c) and (d) show partly enlarged SEM images corresponding to figures 3(a) and (b), respectively. From figure 3(c), it is found that air holes with a shape like a winding column with a diameter of several tens of nanometres were formed from the bottom to the surface, constructing the nanoporous structures. On the other hand, although the lower half of the structure was almost the same as those formed

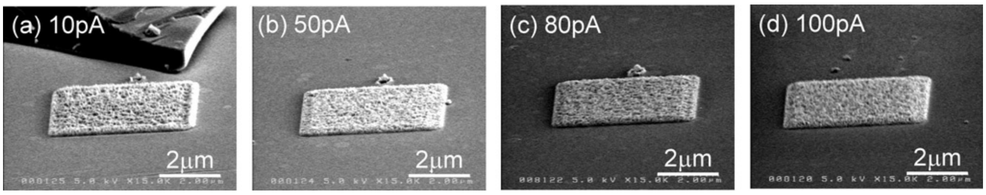

Figure 4. SEM images of 100 keV Ga FIB-irradiated region on a Ge(110) surface using the ion beam current shown. The total fluence was 1×10^{17} cm^{-2} in all irradiations (70° tilted).

by the Ga FIB irradiations at lower fluences, the upper half was changed to something like standing lamellae for the structure formed by Ga FIB irradiations at higher fluences, as shown in figure 3(d). Because the atomic density on a lamellar surface is rather high, sputtering by ion beam irradiation might easily be done. From an Auger electron spectroscopy (AES) measurement, no Ga-related AES signal was observed even for the etched surface formed by higher fluences [5], indicating that precipitation of implanted Ga is not the primary component of the lamellar structures. These results might suggest that because the surface was changed to dense lamellar structures, the surface etching might be advanced by the Ga ion irradiation for larger fluences, although the formation mechanisms of the lamellar structures, as well as those of swollen nanoporous structures, are not clear at present.

3.2. Dependence on fluence rates and incident angles of 100 keV Ga FIB irradiations

As mentioned in the previous subsection, it was found that the Ge surface swelled and changed to nanoporous structures after Ga FIB irradiations at an energy of 100 keV at fluences up to 2×10^{17} cm^{-2}, and that the surface topography strongly depended on the Ga ion fluences. Because the Ga FIB was used in the present study as an ion irradiation tool on Ge surfaces, there exists a new parameter of FIB scan speed, which is adjusted by the dwell time of the FIB. In this subsection, we report on the investigation of the FIB irradiation parameter dependence of the shape of the nanostructures formed on the Ge(110) surface by 100 keV Ga FIB at a constant total fluence of 1×10^{17} cm^{-2} by changing the ion beam current, dwell time and incident angle.

Figure 4 shows the SEM images of the Ga FIB-irradiated regions on the Ge surface using an FIB beam current of (a) 10, (b) 50, (c) 80 and (d) 100 pA, respectively. To make the total fluence 1×10^{17} cm^{-2}, raster scans having a dwell time of 1 μs were repeated 845, 169, 106 and 85 times, respectively. It is found that all of these regions swelled and changed to nanoporous structures. Although the total fluences were equal to each other, the result shown in figure 4(a) is a little bit different from others, showing a small tendency of etching.

Figure 5 shows the SEM images of the dwell time dependence of the structures formed. Using the dwell time and repetition of raster scans of (a) 1 μs, 169 times, (b) 8 μs, 21 times and (c) 128 μs, 1 time, the total fluence was 1×10^{17}, 1×10^{17} and 8×10^{16} cm^{-2}, respectively. Figures 5(d)–(f) are also partly enlarged SEM images corresponding to figures 5(a)–(c), respectively. Here swollen nanoporous structures were also observed in all regions. As shown in figure 5(c), however, the tendency of etching was observed for the irradiation condition of a dwell time of 128 μs and a single scan, although the total fluence was a little small as 8×10^{16} cm^{-2}, for which fluence the height should be the maximum according to the result shown in figure 2.

From these results, it might be said that if the smaller beam current and the larger repetition number were used or the larger dwell time and the smaller repetition number were used, the etching of the swollen surface started, although the total fluence was almost the same.

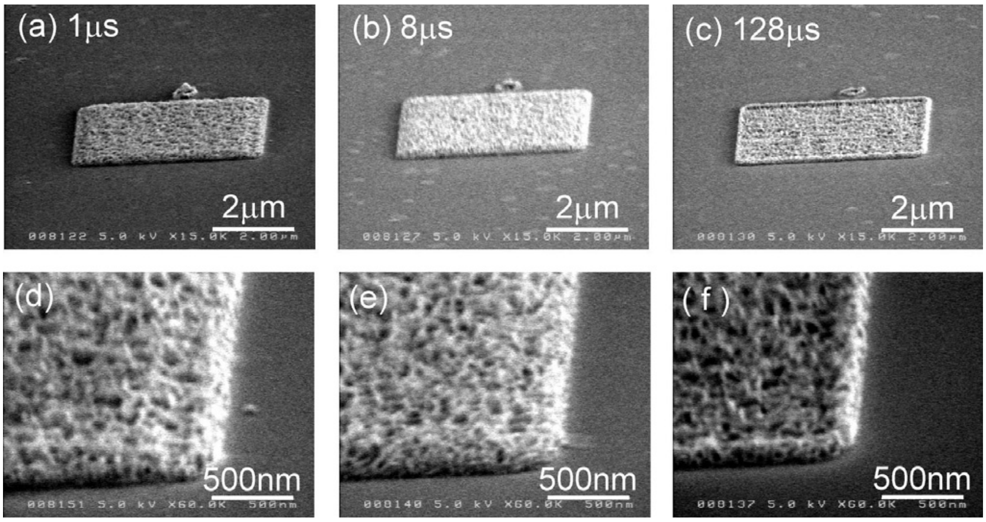

Figure 5. SEM images of 100 keV Ga FIB-irradiated region on Ge(110) surface using the dwell time shown. (d)–(f) show the partly enlarged images of (a)–(c), respectively. The total fluence was 1×10^{17} cm^{-2} in all irradiations (70° tilted).

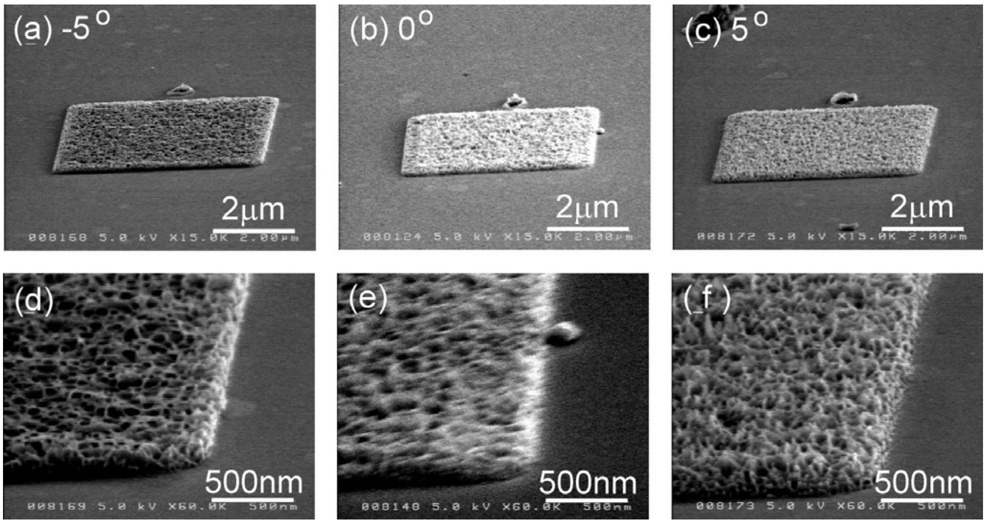

Figure 6. SEM image of 100 keV Ga FIB-irradiated region on a Ge(110) surface using the incident angle shown (viewing angle: 70°).

Figure 6 shows the swollen nanoporous structures formed by changing the incident angle of the Ga FIB. The incident angle of the FIB was able to change 5° in one direction from the surface normal direction, and 5° in the opposite direction. Although the orientation of the tilting angle on Ge(110) surface was not apparent, the topographies of the swollen nanostructure were different from each other; that is, net-like (figures 6(a) and (d)) and needle-like (figures 6(c) and (f)) structures can be obtained by tilting the incident angle of the Ga FIB in opposite directions.

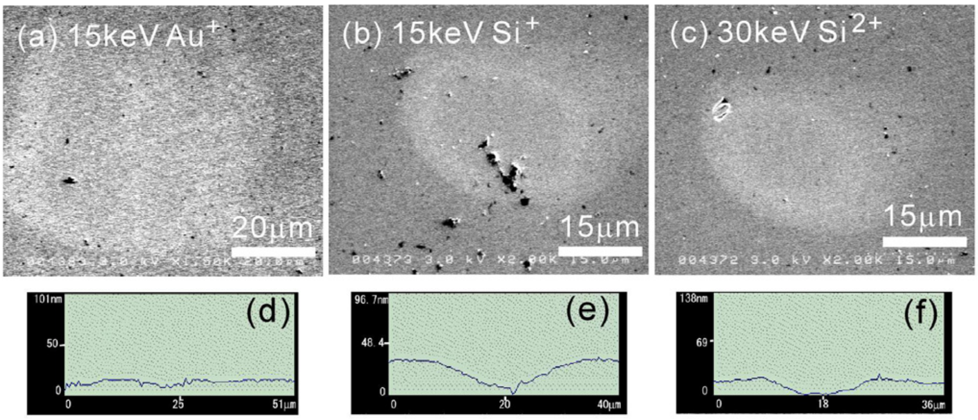

Figure 7. SEM images of low-energy Au and Si FIB-irradiated regions on Ge(110) surfaces. (d)–(f) show the AFM cross-sectional images along a line intersecting the FIB-irradiated region corresponding to (a)–(c), respectively. The total fluence was 1×10^{17} cm^{-2} in all irradiations.

(This figure is in colour only in the electronic version)

These results indicate that although the formation mechanisms of the swollen nanoporous structures are not known at present, the shape of such structures can be controlled by the Ga FIB irradiation conditions, such as total ion fluence, beam current and dwell time (that is, fluence rate), incident angle, and so on.

3.3. Dependence of ion species and irradiation energies

In this subsection, we report on another kind of energetic ions than the 100 keV Ga FIB that were used to investigate the irradiation effect on the Ge(110) surfaces. Au and Si ions were chosen as heavier and lighter elements, respectively, than Ga and Ge.

Figure 7 shows the SEM images of the Ge surfaces after FIB irradiation at the same fluence of 1×10^{17} cm^{-2} using (a) 15 keV Au^+, (b) 15 keV Si^+ and (c) 30 keV Si^{2+} ions. The beam current of each FIB was 1200, 80 and 350 pA, respectively. Figures 7(d)–(f) show the AFM cross-sectional images along a line intersecting the FIB-irradiated region shown in figures 7(a)–(c), respectively. It is found that the surface was smoothly etched with no porous structure for these low-energy irradiations. In the case of the 15 keV Si^+ irradiation, the sputtering rate was estimated to be about one, which is not a peculiar value compared to conventional ion sputtering. This result indicates that a certain level of energy of incident ions should be needed to form the swollen nanoporous structures on Ge surfaces by ion irradiations.

Higher-energy irradiation was also performed using 100 keV Au^+ and 200 keV Si^{2+} and Au^+ ions. The observed Ge surfaces after each FIB irradiation are shown in figures 8(b)–(d), respectively. For comparison, the result using 100 keV Ga^+ was also shown in figure 8(a). The beam current and the total fluence were 20 pA and 3×10^{16} cm^{-2} for 100 keV Ga^+, Au^+ and 200 keV Si^{2+} irradiations (figures 8(a)–(c), respectively) and 80 pA and 1×10^{16} cm^{-2} for 200 keV Au^{2+} irradiation (figure 8(d)). The dwell time was 1 μs in all FIB irradiations.

It is found that the surface swelled a little and needle-like nanoporous structures were formed after the 100 keV Au^+ and 200 keV Si^{2+} FIB irradiations. The projected range of 100 keV Au and 200 keV Si in (amorphous) Ge was calculated to be 22 and 180 nm, respectively, using the TRIM code. Although these projected ranges were one order different to each other, the shape of the surface structure formed was almost the same.

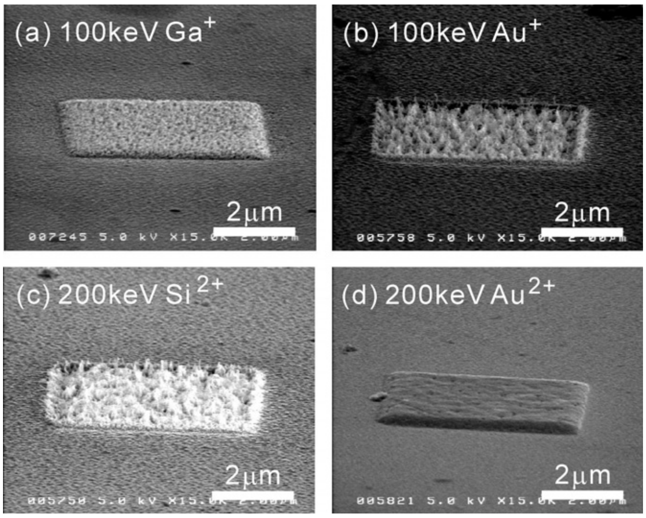

Figure 8. SEM images of high-energy FIB-irradiated region on Ge(110). The ion energy and species used are shown in each figure. The total fluence was 1×10^{17} cm^{-2} in all irradiations (70° tilted).

On the other hand, although surface swelling certainly occurred, no porous structure was observed for the 200 keV Au^{2+} irradiation. In addition, such swollen non-porous structures were observed at least up to a fluence of 1.6×10^{17} cm^{-2} in the case of using a 200 keV Au^{2+} FIB. In spite of the small difference in the projected ranges of 100 and 200 keV Au (calculated to 22 and 36 nm, respectively), the surface morphology was drastically changed, as shown in figures 8(b) and (d).

The reason why the different structures were formed on the Ge surface by different FIB irradiation conditions is not clear at present; these results might be helpful in a discussion of the formation mechanisms of the swollen nanoporous structures on Ge surfaces by ion beam irradiations.

3.4. Maskless patterning of Ge surfaces

From an application point of view, controlled local fabrication of nanostructures on a surface should be desired. Using an FIB, ion irradiations at selected areas on a surface with any patterns can be performed without using any masks. Even if the structure formed strongly depended on the ion fluences, it can easy to control the total fluences of ions. In this study, to demonstrate the abilities described above, the 100 keV Ga FIB was irradiated along lines which comprise the word 'ION' on a Ge surface using different fluences, resulting in the formation of both swollen and etched shapes.

Figure 9(a) shows the swollen pattern of the word 'ION' on the Ge(110) surface using a fluence of 1×10^{16} cm^{-2} and figure 9(b) shows the etched one using a fluence of 4×10^{17} cm^{-2}. As shown in the inset in figure 9(a), the surface swelled along a line with a width of about 300 nm using the lower fluence. Although the beam diameter of the present FIB system was estimated to about 90 nm, the swollen line was widened; this might be because of the beam tail of the FIB. The width of the etched groove was also widened to about 500 nm, especially because of the usage of a higher fluence, such as 4×10^{17} cm^{-2}.

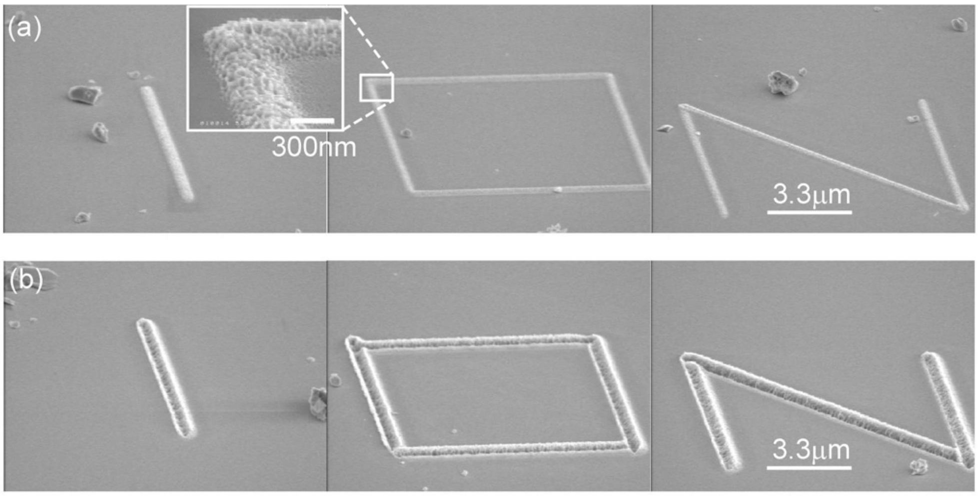

Figure 9. SEM images of patterned lines delineated by 100 keV Ga FIB scans on a Ge(110) surface at fluences of (a) 1×10^{16} and (b) 4×10^{17} cm^{-2} (70° tilted).

Although the size of the nanoporous structure is hard to control, it is demonstrated that the position and the area of the nanoporous structures, as well as etched structures, on a Ge surface can be controlled freely without using any masks.

4. Conclusions

To clarify the effects of ion irradiations on the shape of single-crystal Ge surfaces, Ga, Au and Si FIBs were irradiated on Ge(110) or (100) surfaces at energies between 15 and 200 keV with ion fluences between 3×10^{15} and 4×10^{17} cm^{-2}, changing the FIB scanning parameters. Using 100 keV Ga FIB irradiation, the Ge(110) surface swelled and nanoporous structures were formed up to an ion fluence of 2×10^{17} cm^{-2}, then the surface was etched for larger fluences. The effect of the ion irradiation was observed to a depth of 600 nm, which was 15 times the projected range of Ga in (amorphous) Ge. It is found that the shape of the swollen nanoporous structure was changed by the ion beam current, the dwell time and the incident angle of the FIB used. Swollen nanoporous structures were not observed on the Ge surfaces irradiated by low-energy (15–30 keV) Au and Si ions. For high-energy irradiation of Au and Si, the shape was drastically changed, especially for 100 and 200 keV Au ions. Although the formation mechanisms of swelling and nanoporous structures are not clarified at present, the present results might be helpful in a discussion of the formation mechanisms of them by ion beam irradiations. Finally, maskless formation of patterned structures on a Ge surface was demonstrated using a 100 keV Ga FIB.

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