Nanoporous structure formation on the surface of Ge by ion beam irradiation

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Abstract: The ion beam induced formation of nanoporous structures on the surface of Ge under controlled conditions of ion dose, flux, and irradiation angle using a focused ion beam was investigated by electron microscopy. The formation of large-scale nanoporous structures on the surface of the Ge specimens with increasing ion dose and increasing flux was observed via nanostructural characterization using scanning electron microscopy and transmission electron microscopy (TEM). Compared with the structure formed under irradiation at 0°, that formed under irradiation at 45° was tilted and large-scale. These results suggest that the number of point defects per unit volume of surface is important for the formation of a nanoporous structure. TEM observations revealed that the nanoporous structural features formed during the initial process were not voids but surface roughness. This mechanism differs from the nanoporous structure formation mechanism of GaSb and InSb. The growth of the nanoporous structure in the vertical direction was promoted until the ion dose was 1 × 10¹⁷ ions/m² or greater. At ion doses greater than 1 × 10¹⁸ ions/m², the growth was saturated. The wall thickness remained almost constant with increasing ion dose.

1. Introduction

Ge (Eg = 0.66 eV indirect at 300 K) was used for the first transistor reported in 1947. Recently, Ge has been used in diodes and γ-ray detectors. The electrical properties of Ge include an electron mobility of 3900 cm²/(V·s) and a hole mobility of 1900 cm²/(V·s). The electron transport properties of Ge are better than those of Si, which has an electron mobility and a hole mobility of 1400 and 450 cm²/(V·s), respectively. Ge has thus been receiving renewed attention as an alternative semiconductor to Si.

The formation of nanoporous structures on the surface of Ge via ion beam irradiation has been reported. Similar nanoporous structures have been formed on the surfaces of GaSb and InSb. A nanoporous structure formation behavior in Si₁₋ₓGeₓ and GaAs₁₋ₓSbₓ irradiated alloys has also been reported. By contrast, a nanoporous structure is not formed on the surface of Si.

The details of the nanoporous structure formation mechanism of Ge differ from those of GaSb and InSb. In the case of Ge, an amorphous structure first forms on the surface, followed by growth of a nanoporous structure. By contrast, in the cases of GaSb and InSb, a nanoporous structure first forms on their surface, followed by the formation of an amorphous structure. The initial stage of nanoporous structure formation in GaSb and InSb is void formation. Voids form first, followed by growth of a nanoporous structure. The initial stage of formation of the nanoporous structure in Ge was investigated by Koffel et al., who irradiated Ge wafers with 150 keV Ge⁺ ions. The nanoporous structure rapidly grew in the vertical direction under doses ranging from 1 × 10¹⁷ to 5 × 10¹⁹ ions/m². However, the nanoporous structure formation sequence under low doses has not been studied in detail.

Semiconductors with nanoporous structures on their surface have a strong potential for application as electric and photonic materials (e.g., quantum dots and photonic crystals) and in devices such as thin-film transistors. In this study, the formation of nanoporous structures with different densities of point defects by ion irradiation of Ge surfaces using a focused ion beam (FIB) at various ion doses, fluxes, and irradiation angles was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Additionally, the initial stage of nanoporous structure formation on Ge was confirmed by TEM observation.

2. Experimental procedure

Mirror-polished single-crystal Ge wafers with (001) orientation were used for ion beam irradiation. FIB irradiation was carried out using an FEI Quanta 3D 200i. The ion species was Ga⁺, and the ion beam irradiation was performed at room temperature. The accelerating voltage was 30 kV, the chamber pressure was ~4 × 10⁻⁴ Pa, and the irradiation angle was 0 or 45°. The Ga⁺ ion irradiation was conducted in image scanning mode, where Ge was irradiated in a 512 × 441 dot array over a 12.5 × 10.8 µm² area under 0°-angle irradiation and over a 12.5 × 15.3 µm² area under 45°-angle irradiation of the surface in a single scan. The total ion beam dose ranged from 1 × 10¹⁸ to 3 × 10²¹ ions/m². The ion beam flux ranged from 1.5 × 10¹⁸ to 2.8 × 10¹⁹ ions/(m²·s). Two methods were used to vary the beam flux: changing the ion beam current and changing the dose per scan.

Changes in the surface morphology resulting from ion beam irradiation were observed by SEM (JEOL JSM-7401F). The electron accelerating voltage was 5 kV. Cross-sectional observation was carried out by TEM (JEOL JEM-2100F) at an electron accelerating voltage of 200 kV. TEM specimens smaller than 100 nm were prepared via a microsampling method using FIB. Bright-field images (BFIs) and selected-area electron diffraction (SAED) patterns were obtained by TEM. The detector used to collect TEM data was a camera (GATAN Orius SC200D).

3. Results and discussion

Figure 1 shows surface SEM images of Ge irradiated with a 30-kV Ga⁺ ion beam at room temperature. The irradiation angles were (a)–(f) 0° and (g)–(l) 45°. The scanning doses were 1 × 10¹⁸ ions/m² per one scan (0°) and 0.7 × 10¹⁸ ions/m² per one scan (45°). The ion beam fluxes were (a)–(c) 1.6 × 10¹⁸ ions/(m²·s), (d)–(i) 5.3 × 10¹⁸ ions/(m²·s), (g)–(i) 1.7 × 10¹⁸ ions/(m²·s), and (j)–(l) 5.3 × 10¹⁸ ions/(m²·s). A nanoporous structure was not observed on the surface of all of the samples.
In cases where a nanoporous structure was not observed, we considered that the number of point defects was insufficient for the formation of a nanoporous structure at the given ion beam irradiation dose. A nanoporous structure was also not observed on samples irradiated at 45°.

Figure 2 shows surface SEM images of Ge irradiated with a 30-kV Ga⁺ ion beam at room temperature. The irradiation angles were (a)–(s) 0° and (t)–(aa) 45°. The scanning doses were 1 × 10¹⁹ ions/m² per one scan (0°) and 0.7 × 10¹⁸ ions/m² per one scan (45°). The ion dose per scan was 10 times greater than that applied to the samples shown in Fig. 1. The fluxes of ion beam were (a)–(e) 1.6 × 10¹⁸ ions/(m²·s), (f)–(j) 2.8 × 10¹⁸ ions/(m²·s), (k)–(o) 5.3 × 10¹⁸ ions/(m²·s), (p)–(t) 2.8 × 10¹⁹ ions/(m²·s), (u)–(x) 1.7 × 10¹⁸ ions/(m²·s), and (y)–(bb) 5.3 × 10¹⁸ ions/(m²·s). The inset is an enlarged view of the SEM image. The nanoporous structure was not observed on the surface of the sample irradiated at 0° at a low dose (1 × 10¹⁹ or 5 × 10¹⁹ ions/m²). With increasing ion dose, surface roughness was observed. Holes were first observed at a dose of 1.5 × 10²⁰ ions/m². Large nanoporous structures with a wave-like shape were formed on the surface at the maximum dose (1 × 10²¹ ions/m²). The porous structures formed under high-flux irradiation were larger than those formed under low-flux irradiation at the same ion dose. The introduction of point defects caused coalescence within the ion dose range for the formation of clusters. Apparently, a high density of point defects (formed under high-flux irradiation) leads to easy...
aggregation and to the formation of large porous structures. The samples irradiated at 45° and at the lowest dose (1 \times 10^{19} \text{ ions/m}^2) did not show a nanoporous structure on their surface; however, tilted nanoporous structures were formed on their surface at high doses. By contrast, nanoporous structures were not formed on the surface of samples irradiated at 0° and at a low dose. These results show that point defects were distributed near the surface of samples irradiated while tilted.

The ion range and vacancy distribution of Ge irradiated with a Ga+ ion beam were calculated using SRIM simulations. SRIM is a Monte Carlo simulation of ion beam collisions in solids. The number of calculated Ga+ ions was 10,000. We adopted displacement threshold energy values reported by Andersen and Ziegler (15 eV for Ge). According to the SRIM simulations, the projected depth and number of vacancies per ion were 18 nm and 1076, respectively, under 0° irradiation and 14 nm and 1043, respectively, under 45° irradiation. The ion range under 45° irradiation was shorter than that under 0° irradiation. Therefore, the formed point defects were densely distributed near the surface of the samples irradiated at 0°, confirming the nanoporous structure formation observed under low-dose irradiation.

Figure 3 shows surface SEM images of Ge irradiated with a 30-kV Ga+ ion beam at room temperature. The irradiation angles were (a)–(p) 0° and (q)–(x) 45°. The scanning doses were 1 \times 10^{20} \text{ ions/m}^2 per one scan (0°) and 0.7 \times 10^{20} \text{ ions/m}^2 per one scan (45°). The ion dose per scan was 10 times greater than that applied to the samples shown in Fig. 2. The fluxes of ion beam were (a)–(d) 1.5 \times 10^{18} \text{ ions/(m}^2 \text{s}), (e)–(h) 2.8 \times 10^{18} \text{ ions/(m}^2 \text{s}), (i)–(l) 5.4 \times 10^{18} \text{ ions/(m}^2 \text{s}), (m)–(p) 2.8 \times 10^{18} \text{ ions/(m}^2 \text{s}), (q)–(t) 1.7 \times 10^{18} \text{ ions/(m}^2 \text{s}), and (u)–(x) 5.3 \times 10^{18} \text{ ions/(m}^2 \text{s}).

Cross-sectional TEM images (BFIs) and SAEDs of Ge irradiated with a 30-kV Ga+ ion beam at room temperature are shown in Fig. 4. Like the samples shown in Fig. 2, the samples in Fig. 4 were subjected to a scanning dose of 1 \times 10^{19} \text{ ions/m}^2 per one scan. The fluxes of ion beam were (a) 2.6 \times 10^{18} \text{ ions/(m}^2 \text{s}), (b) 2.2 \times 10^{18} \text{ ions/(m}^2 \text{s}), (c) 2.4 \times 10^{18} \text{ ions/(m}^2 \text{s}), (d) 2.6 \times 10^{18} \text{ ions/(m}^2 \text{s}), (e) 2.6 \times 10^{18} \text{ ions/(m}^2 \text{s}), (f) 2.4 \times 10^{18} \text{ ions/(m}^2 \text{s}), (g) 2.6 \times 10^{18} \text{ ions/(m}^2 \text{s}), (h) 2.8 \times 10^{18} \text{ ions/(m}^2 \text{s}), (i) 2.4 \times 10^{18} \text{ ions/(m}^2 \text{s}), (j) 2.9 \times 10^{18} \text{ ions/(m}^2 \text{s}), and 2.4 \times 10^{18} \text{ ions/(m}^2 \text{s}). The irradiation angle was 0°. Amorphous halo rings are observed in the SAEDs of all of the samples, indicating that the structures were not crystalline. Sharp spots are diffractions explained by no irradiated region. A horizontally long void and a
The black contrast of the surface roughness were first observed in the amorphous layer. When the ion dose was increased to $8 \times 10^{18}$ ions/m$^2$, the voids formed in parts. At a dose of $9 \times 10^{18}$ ions/m$^2$, the rough surface formed, and voids were not observed. With increasing ion dose, structures remarkably grew perpendicular as the starting point of surface roughness. The remarkable growth was not observed at doses between $1 \times 10^{21}$ and $3 \times 10^{21}$ ions/m$^2$. In these experiments, the ion range projected by SRIM simulations was 18 nm. The structure formed at the maximum dose was almost 10 times larger than the projected ion range of 18 nm. This difference indicates that the structure growth resulted from interstitial atoms migration. Vacancies migration was short in this system.

Amorphous layers were observed for all samples under the wall. The size of the amorphous layer was constant until the ion dose exceeded $5 \times 10^{20}$ ions/m$^2$. At ion doses greater than $5 \times 10^{20}$ ions/m$^2$, the amorphous layer exhibited roughness. Black contrast lines were observed between the amorphous layer and the substrate crystal in all of the samples. We speculated that the samples exhibited a lattice strain because of nanoporous structure formation.

In GaSb, voids are first formed on the surface; as these voids grow perpendicular to the surface, the nanoporous structure grows via void formation.\textsuperscript{16} The Ge nanoporous structure formation mechanism is not the same as that of GaSb. In the case of Ge, surface roughness forms instead of voids, and surface roughness subsequently increases. These results represent a new finding for the formation mechanism of Ge nanoporous structures. The surface roughness in Ge surface will be an influence on the size of nanoporous structure.

Cross-sectional TEM images (BFIs) and SAEDs of Ge irradiated with a 30-kV Ga$^+$ ion beam at room temperature are shown in Fig. 5. The scanning dose was $1 \times 10^{19}$ ions/m$^2$ per one scan. The ion beam fluxes were (a) $2.6 \times 10^{18}$ ions/(m$^2$·s), (b) $2.2 \times 10^{18}$ ions/(m$^2$·s), (c) $2.4 \times 10^{18}$ ions/(m$^2$·s), (d) $2.6 \times 10^{18}$ ions/(m$^2$·s), (e) $2.6 \times 10^{18}$ ions/(m$^2$·s), (f) $2.8 \times 10^{18}$ ions/(m$^2$·s), (g) $2.6 \times 10^{18}$ ions/(m$^2$·s), (h) $2.8 \times 10^{18}$ ions/(m$^2$·s), (i) $2.4 \times 10^{18}$ ions/(m$^2$·s), (j) $2.9 \times 10^{18}$ ions/(m$^2$·s), and $2.4 \times 10^{18}$ ions/(m$^2$·s). The irradiation angle was 0°.
low-flux irradiation experiments [Fig. 4(i), $1 \times 10^{21} \text{ions/m}^2$ (scan 100) and (j) $2 \times 10^{21} \text{ions/m}^2$ (scan 200)], which are the same irradiation doses as those used in Fig. 5] reveals that the perpendicular growth was not remarkable. In addition, the structure was disorganized compared with those formed under low-flux irradiation conditions. The high density of introduced point defects (high-flux irradiation) led to easy aggregation and to the formation of poorly organized porous structures.

Figure 6 shows the structure sizes (depth and wall thickness) of Ge, as obtained from the TEM micrographs in Figs. 4 and 5, plotted as a function of irradiation dose. The wall thickness was almost constant with increasing ion dose. It was showed that the size of surface roughness had an influence on the size of nanoporous structure. By contrast, the depth increased rapidly with increasing dose until the dose reached $1 \times 10^{21} \text{ions/m}^2$, at which point the vertical growth became saturated. The depth was 10 nm at a dose of $9 \times 10^{19} \text{ions/m}^2$ and 147 nm at a dose of $1 \times 10^{21} \text{ions/m}^2$. In the first stage of structure formation, the vertical and horizontal sizes were approximately the same. The growth in the vertical direction became remarkable with increasing ion dose. The maximum aspect ratio between the wall thickness and the depth was 12 at a dose of $2 \times 10^{21} \text{ions/m}^2$.

Figure 7 shows the structure sizes (void diameter and thickness of the amorphous layer) of Ge, as obtained from the TEM micrographs in Figs. 4 and 5, plotted as a function of irradiation dose. The initial process, voids were not formed on the surface; rather, surface roughness was observed. The growth of the nanoporous structure in the vertical direction was promoted above a dose of $1 \times 10^{21} \text{ions/m}^2$. The wall thickness with increasing ion dose was approximately constant.

4. Conclusions

Ion beam irradiation of Ge was carried out under different ion beam conditions. Large-scale nanoporous structures formed at high-ion doses and under high-flux irradiation were evaluated. TEM observations provided details of the initial process of formation of Ge nanoporous structures. In the initial process, voids were not formed on the surface; rather, surface roughness was observed. The growth of the nanoporous structure in the vertical direction was promoted above a dose of $1 \times 10^{21} \text{ions/m}^2$. The wall thickness with increasing ion dose was approximately constant.

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