Transactions of the Materials Research Society of Japan 33[4] 1015-1018 (2008)

Low-temperature fabrication of Ge nanostructures by ion irradiation

A. Miyawakil[1]*, Y. Sugita[1], K. Yamaguchi[1], T. Hayashi[1], Y. Hayashi[1], T. Tokunaga[2] and M. Tanemura[1]

1 Department of Environmental Technology, Graduate School of Engineering, Nagoya. Inst. Technol., Gokiso-cho, Showa-ku, Nagoya, Japan
2 Department of Quantum Engineering, Nagoya University, Nagoya, Japan
Fax: 81-52-735-5379, e-mail: 17513007@stn.nitech.ac.jp

Ge surfaces were irradiated by Ar^+ ions of 600 eV with and without a simultaneous Ge supply at various temperatures up to 200°C. The surfaces ion-irradiated without a Ge supply were characterized by conical protrusions, independent of the fabrication temperature. By contrast, densely distributed cones, nanobelts and nanowalls were formed on the surfaces ion-irradiated with a simultaneous Ge supply even at room temperature. Because the formation of those nanobelts and nanowalls was specific to sputtering with a Ge supply and enhanced by sample heating, it was concluded that the surface diffusion of the supplied Ge atoms played an essential role in their formation. Thus, it was believed that the ion irradiation method would open up a new route to fabricate low-dimensional nanostructures of semiconductors at low temperatures.
Key words: Nanomaterial, Nanostructure, Nanowire, Nanorod, Ion Irradiation, Ge

1. Introduction

Low-dimensional nanostructures, such as carbon nanotubes, nanowalls and nanowires, have attracted great attention in materials science and nanotechnology fields. Especially, semiconductor nanowires and nanorods are expected to lead to improvement in the performance of electronic devices, due to their quantum confinement effect originating from their nanodimensionality. [1]

Since nanowires of Ge, for instance, were first reported by Heath and LeGoues in 1993 [2], various fabrication methods have been proposed for their expected better performance in electronic devices. These include chemical vapor deposition (CVD [3]), the vapor-liquid-solid growth (VLS [4, 5]), the solution-liquid-solid growth (SLS [6]), deposition of Ge^+-ions [7] and the laser ablation method [8]. Such methods generally require high temperature, high pressure, catalysts or long growth duration for the growth of Ge nanowires.

In previous papers, we demonstrated that oblique Ar^+ ion irradiation of bulk carbon and carbon-coated substrates induced formation of conical protrusions, and single carbon nanofibers (CNFs), 20 - 50 nm in diameter and 0.2 - 10 μm in length, grew on the cone top without any catalyst even at room temperature [9]. This implies that oblique Ar^+ ion irradiation may be promising as a basic technique for catalyst-free fabrication of low-dimensional nanomaterials at low temperatures [9-10]. In this research, we tackled the nanostructure fabrication of Ge at low temperatures without a catalyst. If successful, this technique will provide a promising new way for applications to solar cells and thermoelectric devices.

2. Experimental

The samples employed were platelets of mirror-polished single crystalline Ge (100). Ar^+ ions were irradiated to the samples, ~15 x 10 mm^2, using Kaufman-type ion gun (Iontech. Inc. Ltd., Model 15-1500-500). Since oblique Ar^+ bombardment is known to be suitable for ion-induced CNF growth, compared with ion irradiation at normal incidence [10], the incidence angle of the ion beam was set at 45° from the normal to the surface. The diameter and accelerating voltage of the ion beam employed were 100 mm and 600 eV, respectively. In order to investigate the effects of the ion irradiation time and the fabrication temperature on the ion-induced nanostructures, ion irradiation was done for 20, 60 and 120 min at room temperature, at 100°C and 200°C. In ion-induced CNF growth, carbon atoms which are sputter-ejected and deposited onto protrusions play an important role in CNF growth [9]. In order to enhance the deposition of Ge atoms onto the nanostructures, and hence enhance the Ge nanostructure formation, a Ge "wall" (10 x 5 mm^2) mounted near the sample was co-sputtered with the samples in several ion irradiation experiments (Fig. 1).

The basal and working pressures were 2.0 x 10^{-4} Pa and 1.6 x 10^{-2} Pa, respectively. After ion irradiation, the surface morphological structures were observed by scanning electron microscope [SEM (JEOL; JSM-5600)].

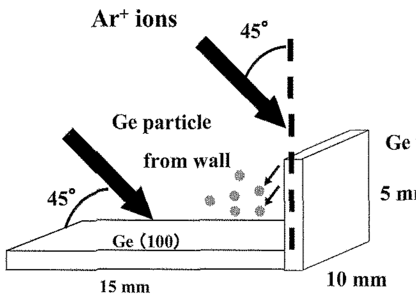

Fig. 1 Schematic representation of experimental setup.

3. Results and Discussion

3.1 Effect of ion-irradiation time

Figure 2 shows an SEM image of a sample surface ion-irradiated at room temperature without a simultaneous Ge supply. Conical protrusions, which are typical surface projections observed on the ion-irradiated surfaces, covered the whole sample surface ion-irradiated for 20 min [Fig. 2]. The cones formed were 660 – 750 nm in stem diameter, 1 – 2 μm in length and 3 x 10^6 mm^{-2} in number density. Cones were increased in size and decreased in number density with an increase in the ion-irradiation time (Table I), and those formed after the ion irradiation for 120 min reached 2 – 3 μm in stem diameter and ~5 μm in length. In every case, the cones pointed in the ion-beam direction. Thus, the ion-irradiated surfaces without a simultaneous Ge supply were characterized by the well-aligned conical structures.

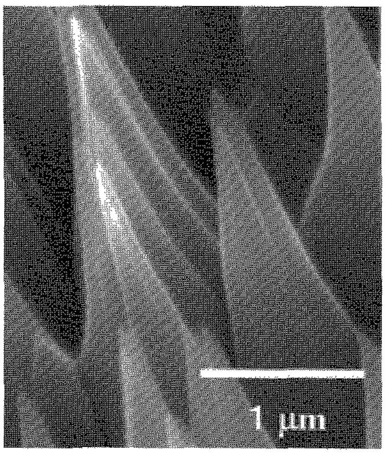

Fig. 2 SEM image of surface morphology after ion irradiation without a simultaneous Ge supply for 20 min.

Table I: Comparison of sizes of cones formed with various ion irradiation times.

ion irradiation time	stem diameter	length (μm)	density (mm^{-2})
20 min	660 ~ 750 nm	1 ~ 2	3 x 10^6
60 min	1 μm	3	3 x 10^5
120 min	2 ~ 3 μm	~ 5	2 x 10^5

Figure 3 shows SEM images of sample surfaces ion-irradiated at room temperature with a simultaneous Ge supply. After the ion irradiation for 20 min, the surface was covered with densely distributed cones [Fig. 3(a)]. Compared with the surface ion-irradiated without a Ge supply [see Fig. 2], cones formed on the Ge-supplied surface were smaller in size (500 – 650 nm in stem diameter), higher in number density (4 x 10^6 mm^{-2}) and sharper in apex angle. The surface ion-irradiated for 60 min [Fig. 3(b)] was characterized by the nanobelts, which were much different from the cones in morphology. They were two-dimensional structures with flattened tops, 350 - 500 nm in nanobelt width, 1 – 2 μm in height and 4 x 10^6 mm^{-2} in number density. These nanobelts were aligned almost parallel to the Ge wall. After a prolonged ion irradiation (120 min), the surface featured nanowall structures, which seem to consist of coalesced nanobelts [Fig. 3(c)]. The width of nanowalls measured ~1 μm, and nanorods (~90 nm in diameter and ~450 nm in length) sometimes grew on top of the nanowalls. From these results, it was concluded that the simultaneous Ge supply during the ion irradiation was essential for the ion-induced formation of various kinds of Ge nanostructures.

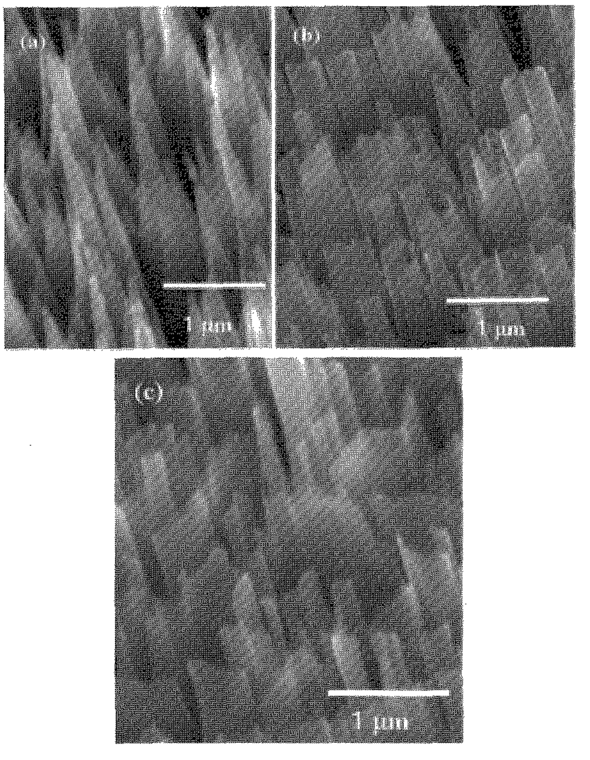

Fig. 3 SEM images of surface morphology after ion irradiation with a simultaneous Ge supply for (a) 20 min, (b) 60 min and (c) 120 min.

3.2 Effect of fabrication temperature

The effect of the fabrication temperature on the ion-induced surface morphology was further investigated in detail. Taking into account of unique morphological structures formed after ion-irradiation for 60 min with the Ge supply, the ion irradiation was carried out for 60 min at 100°C and at 200°C with and without a simultaneous Ge supply.

The surfaces ion-irradiated without Ge supplied was characterized by well-aligned cones, independent of the substrate temperature, as typically shown in Fig. 4. The cones were decreased in size and increased in the number density with the substrate temperature [see Table II]. The cones formed at 200°C, for instance, measured 500-660 nm in stem diameter and 1.5 μm in length. In general, the cones are not increased in size monotonously during ion irradiation [11], and the developed cones are finally shrunk and disappear. The sample heating would accelerate this process, so that the shrunk cones were observed for samples ion-irradiated at elevated temperatures.

Table II: Comparison of sizes of cones formed at various fabrication temperatures.

fabrication temperature	stem diameter	length (μm)	density (mm^{-2})
RT	1 μm	3	3×10^5
100 °C	510 ~ 750 nm	2	1.6×10^6
200 °C	500 ~ 660 nm	1.5	1.8×10^6

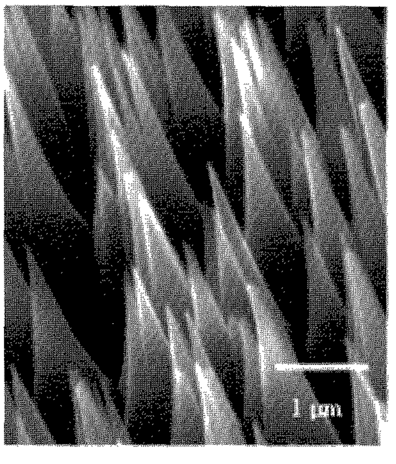

Fig. 4 SEM image of surface morphology after ion irradiation without a simultaneous Ge supply at 100°C. Ion irradiation time: 60 min.

Figure 5 shows the surface morphology attained by ion irradiation at 100°C with a Ge supply, revealing that the whole surface was covered with nanowalls similar to those formed on the surface ion-irradiated with a Ge supply at room temperature for 120 min [see also Fig. 3(c)]. In addition, nanorods, 50 – 80 nm in diameter and 300 – 400 nm in length, also formed on the nanowalls, similar to the prolonged ion irradiation case with a Ge supply at room temperature. Thus, the formation of nanowalls was enhanced by the ion irradiation at elevated temperatures.

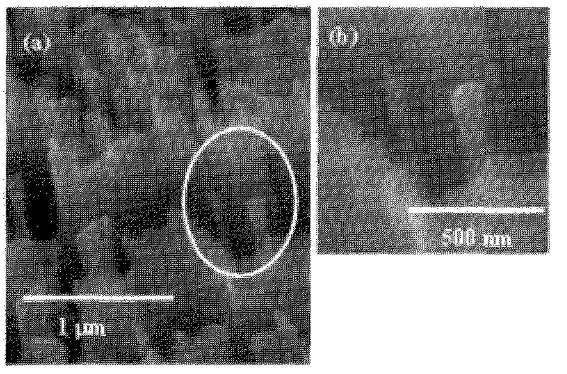

Fig. 5 SEM image of surface morphology after ion irradiation with a simultaneous Ge supply at 100 °C. (b) Enlarged image of encircled area in (a). Ion irradiation time: 60 min.

Figure 6 shows an SEM image of nanostructures formed after ion irradiation at 200°C with a Ge supply, showing that the surface was characterized by nanoflake-like structures. Different from the nanowalls possessing the smooth and continuous wall surfaces, the nanoflake-like structures seemed to consist of grains [compare Fig. 6 with Figs. 3(c) and 5]. In general, recrystallization is known to start at a temperature around one-third to one-half of the melting point. Since the melting point of Ge is 937.4°C (1210.4 K), the recrystallization and hence the polycrystallization process may have taken place during the ion irradiation at 200°C. The transmission electron microscope (TEM) observation of this recrystallization will be the subject of a forthcoming paper.

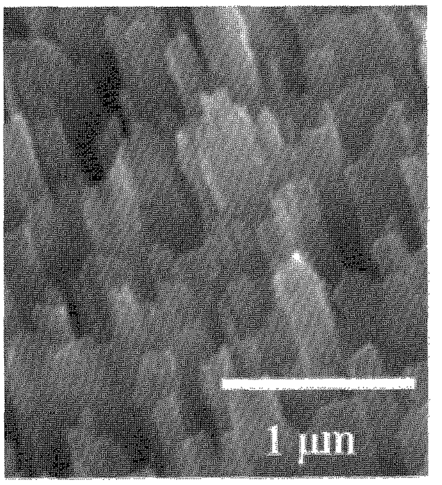

Fig. 6 SEM image of surface morphology after ion irradiation with a simultaneous Ge supply at 200 °C. Ion irradiation time: 60 min.

From a comparison of the results obtained with and without Ge supply (compare Fig. 2 with Fig. 3), it was concluded that the external Ge supply was essential for the formation of nanobelts and nanowalls. In addition, their formation was enhanced by the sample heating (compare Fig. 3(b) with Figs. 5 and 6). Because the diffusion is the well-known process which is enhanced at elevated temperatures, the surface diffusion of the supplied Ge is thought to play an important role in their formation. Thus, the formation mechanism of the Ge nanobelts and nanowalls is thought to be as follows: The continuously-supplied Ge atoms would deposit onto the sides and valleys of cones formed at the early stage of ion irradiation, and the subsequent surface diffusion of Ge would enhance the coalescence of the cones to form nanobelts with a short belt width. Further ion irradiation would induce the further coalescence of the nanobelts to form nanowalls. The formation of nanorods on the nanowalls (see Figs. 3(c) and 5) would be the evidence that the surface diffusion of Ge tends to occur towards the nanowall top. Similar to the growth mechanism of ion-induced CNFs, in which the surface diffusion of carbon atoms towards the protrusion top is responsible for the CNF growth [9], the surface diffusion of Ge atoms is considered to play an essential role in the formation of nanobelts and nanowalls.

In order to confirm the proposed formation mechanism of Ge nanostructures, the elucidation of their crystalline structure by TEM will be important. In addition, if the highly crystallized low-dimensional Ge nanostructures are successfully formed at low temperatures, they would be promising for electrical device applications. Investigations along these lines are now being undertaken, and the results will be dealt with in a forthcoming paper.

4. Conclusion

Ge surfaces were ion-irradiated with and without a simultaneous Ge supply at low temperatures. Depending on the ion-irradiation conditions, various kinds of Ge nanostructures, such as cones, nanobelts, nanowalls and nanoflakes, were formed on the ion-irradiated surfaces. Thus, the ion-irradiation method offers a promising new way to fabricate low-dimensional nanostructures of semiconductors at low temperatures without any catalyst.

Acknowledgement This work was partially supported by the Japan Society for the Promotion of Science (JSPS), and a Grant-in-Aid for Exploratory Research, No. 19656008.

References

[1] J. Hu, T.W. Odom, and C.M. Liber Acc. Chem, Res. **32** 435-445(1999).
[2] J.R. Heath, F.K. Legoues, Chem. Phys. Lett. **208** 263-268 (1993) .
[3] D. Wang, H. Dai, Angew. Chem. , Int. Ed. **41** 4783-4786 (2002).
[4] Z. W. Pan, S. Dai, D. H. Lowndes, Solid State Commun. **134** 251-255 (2005).
[5] Y. Wu. Pan, P. Yang, Chem. Mater. **12** 605-607 (2000).
[6] T. Hanrath, B.A. Korgel, J. Am. Chem. Soc. **124** 1424-1429 (2002).
[7] T. Muller, K. H. Heinig, B. Schmidt, Nucl. Instr. and Meth. **B 175-177** 468-473 (2001).
[8] A.M. Morales and C. M. Lieber, Science **279** 208-211 (1998).
[9] M. Tanemura, T. Okita, H. Yamauchi and S. Tanemura Appl. Phys. Lett. **84** 3831-3833(2004).
[10] M. Tanemura, J. Tanaka, K. Itoh, Y. Fujimoto, Y. Agawa, L. Miao and S. Tanemura Appl. Phys. Lett **86** 113107 (2005).
[11] O. Auciello and R. Kelly (eds.), "Ion bombardment modification of surfaces," Elsevier Science Publishing (1984) p. 5.

(Recieved December 8, 2007. ; Accepted June 30, 2008)