

Low-Temperature Fabrication of Ion-Induced Ge Nanostructures: Effect of Simultaneous Al Supply

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SUMMARY Ge surfaces were irradiated by Ar⁺ ions at 600 eV with and without simultaneous supply of Ge or Al at room temperature. The surfaces ion-irradiated without any simultaneous metal supply were characterized by densely distributed conical protrusions. By contrast, various kinds of nanostructures were formed on the Ge surfaces ion-irradiated with a simultaneous metal supply. They featured cones and nanobelts with a flattened top for Ge supply cases, whereas they were characterized by the nanorods, nanobelts and nanowalls for Al supply cases. Very interestingly, most of the nanorods and nanobelts formed with an Al supply possessed a bottleneck structure. Thus, the Ge nanostructures were controllable in morphology by species and amount of simultaneously supplied metals.

key words: nanomaterial, nanostructure, nanorod, ion irradiation, Ge

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], one-dimensional (1-D) nanomaterials have attracted a great attention in materials science. Many approaches have been reported for their synthesis [2], [3]. In general those approaches include a gas phase process at high temperatures. However, for a wider range of applications, a lower-temperature process, ideally room-temperature process, should be developed to fabricate 1-D nanomaterials.

As well-known, ion irradiation to a solid surface entails changes in crystalline structure and morphology even at room temperature. This may imply that the ion irradiation is promising as a basic technique to fabricate nanostructures at low temperatures. In fact, nanostructure fabrication using ion irradiation has been reported for various materials [4]–[6]. In our previous papers, for instance, we demonstrated that oblique Ar⁺ ion irradiation to bulk carbon and carbon-coated substrates induced a 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 [7].

Ge is a group IV material, similar to C. Is it possible to fabricate 1-D nanostructures by ion irradiation for group IV materials at low temperatures? For Ge, 1-D nanostructures, such as nanowires, have been synthesized mainly by vapor-liquid-solid (VLS [8], [9]), solution-liquid-solid (SLS

[10]) and laser ablation methods [11]. These methods, however, require high temperature, high pressure, catalysts and long growth duration for their growth. If low-temperature fabrication of 1-D nanostructures can be achieved by ion irradiation for semiconductors, it will be very fascinating.

For ion-induced CNFs, redeposition of sputtered carbon atoms onto a side wall of cones plays an important role in the CNFs growth [7]. Based on this fact, we tried an intentional Ge supply to the sample surfaces during Ar⁺ ion irradiation [12]. On the surfaces, the formation of several kinds of nanostructures such as cones, nanobelts and nanowalls were observed, while only conical structures were formed by Ar⁺ ion irradiation without a simultaneous Ge supply [12]. In this work, we tackled the fabrication of further variation of nanostructures using Ar⁺ ion irradiation to Ge surfaces with a simultaneous supply of Al. Since Al is known to act as a catalyst for the synthesis of Ge nanowires in the SLS method [13], slender Ge nanostructures may be expectable by Ar⁺ ion irradiation at low temperature.

2. Experimental

Samples employed were platelets of single crystalline Ge (100), ~ 15 × 10 mm² in size. Ar⁺ ions were irradiated to the samples using Kaufman-type ion gun (Veeco Ion-tech.; Model 15-1500-500) at room temperature. Since an oblique Ar⁺ bombardment is known to be suitable for the ion-induced CNFs growth [14], incidence angle of the ion beam was set at 45° from the normal to the surface (Fig. 1). The diameter, accelerating voltage of the ion beam and ion irradiation time were 100 μm, 600 eV and 60 min, respectively. The total ion doses for respective samples were 5.8 × 10¹⁸ cm⁻². In order to enhance the formation of Ge nanostructures, Ge or Al were supplied during the ion irradiation. To investigate the effects of their supply rate, Ge was supplied at 0.7, 1.3 and 2.6 nm/min, and Al was supplied at

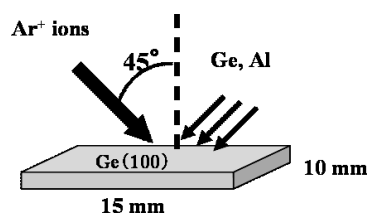


Fig. 1 Schematic representation of experimental setup.

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0.5, 1.3 and 2.2 nm/min. The basal and working pressures were 2.0×10^{-4} Pa and 1.6×10^{-2} Pa, respectively. After the ion irradiation, morphological structures of the surfaces were observed by a scanning electron microscope [SEM (JEOL; JSM-5600)]. In order to investigate the early stage of the nanostructure formation, the surfaces ion-irradiated for 5 min were observed by atomic force microscopy [AFM (JEOL; JSPM-5200TM)] in the tapping mode using a CNF probe [15].

3. Results and Discussion

Figure 2 shows a SEM image of a sample surface ion-irradiated without any simultaneous material supply. Conical protrusions (cones), which are typical surface projections commonly observed on ion-irradiated surfaces, were formed. The cones formed were $\sim 1 \mu\text{m}$ in stem diameter, $\sim 3 \mu\text{m}$ in length, and cones pointed in the ion-beam direction. The formation of conical protrusion is, in general, ascribed to the dependence of sputtering yield (S) on the incidence-angle of ion-beam (θ). S increases with θ up to a critical angle θ_m and then decreases rapidly with a further increase in θ . Due to this S - θ variation, cones formed by ion-erosion process are known to possess the apex angle of $2(90^\circ - \theta_m)$. Since θ_m is, in general, known to be 70 – 75° for Ar^+ sputtering at a keV range [16], the apex angle of cones should be in the range of 30° – 40° . The apex angles of the Ge cones observed here were in this range, $\sim 30^\circ$, suggesting that the Ge cones were formed mainly due to the ion-erosion process (S - θ dependence).

Figure 3 shows SEM images of sample surfaces when ion-irradiated with a simultaneous Ge supply at 0.7, 1.3 and 2.6 nm/min [Figs. 3(a), (b) and (c), respectively]. Compared with the cones fabricated without Ge supply [see Fig. 2],

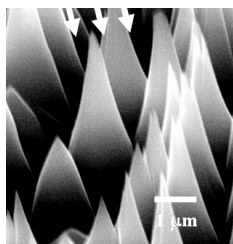


Fig. 2 SEM image of a Ge surface after ion irradiation without a simultaneous material supply. The arrows indicate the direction of Ar^+ ions.

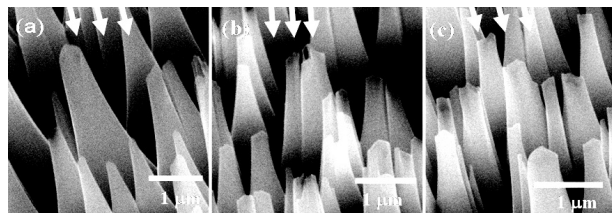


Fig. 3 SEM images of (a), (b) cones with an obtuse tip and (c) nanobelts. The Ge supply rate: (a) 0.7, (b) 1.3 and (c) 2.6 nm/min. The arrows indicate the direction of Ar^+ ions.

nanostructures formed with Ge supply featured obtuse or flattened top. For example, nanostructures formed with Ge supply at 2.6 nm/min were characterized by nanobelts with a flattened top and their widths were typically 200–400 nm [Fig. 3(c)]. These nanostructures which are different from conical structures, strongly suggested that their formation mechanism was not explicable in terms of ion-erosion process alone, and that deposited (supplied) Ge particles played an important role in the formation of nanostructures. The continuously-supplied Ge would be deposited onto the sides and valleys of cones, and subsequent surface diffusion of Ge would enhance the coalescence of the cones to form nanobelts [12].

Figure 4 shows SEM images of sample surfaces when ion-irradiated with an Al supply at 0.5, 1.3 and 2.2 nm/min [Figs. 4(a), (b) and (c), respectively]. Nanostructures formed at a low Al supply rate (0.5 nm/min) possessed a flattened top. Very interestingly, they were characterized by nanorods with bottleneck structures of 50–100 nm in width at the top and 40–80 nm in width at the constricted part. At an Al supply rate of 1.3 nm/min, nanobelts (250–500 nm in width) and nanowalls which are larger in width (500–700 nm) than nanobelts were observed [Fig. 4(b)]. At an Al supply rate of 2.2 nm/min, the whole surface was covered with nanowalls in high density [Fig. 4(c)]. On the top of them, nanorods with bottleneck structures were observed sometimes.

As described above, Ge nanostructure formed by ion-irradiation strongly depended on particle species simultaneously supplied. In order to elucidate their formation mechanism, an initial stage of their formation was observed by AFM. Figure 5 shows AFM images of the sample surfaces when ion-irradiated for 5 min with a simultaneous Ge [Fig. 5(a)] and Al [Fig. 5(b)] supplies at 1.3 nm/min. In the Ge supply case, the surface was relatively flat with an av-

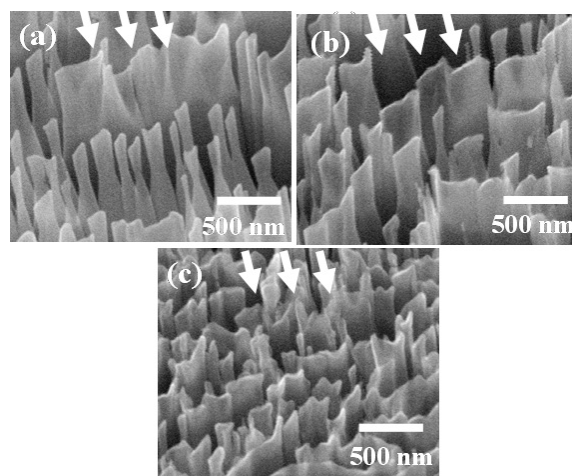


Fig. 4 SEM images of (a) nanorods with bottleneck structures, (b) nanobelts and nanowalls and (c) nanowalls. The Al supply rate: (a) 0.5, (b) 1.3 and (c) 2.2 nm/min. The arrows indicate the direction of Ar^+ ions. For convenience, we defined the nanorod, nanobelt and nanowall as the nanostructures of ~ 100 , < 500 and > 500 nm in width, respectively.

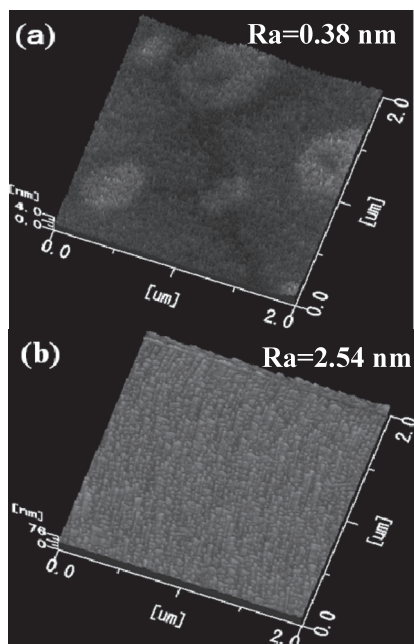


Fig. 5 AFM images of sample surfaces ion-irradiated for 5 min with simultaneous (a) Ge and (b) Al supply at 1.3 nm/min.

erage roughness of the surface (R_a) of 0.38 nm. This may be due to the isotropic surface diffusion of the deposited Ge particles. On the other hand, in the Al supply case, R_a measured 2.54 nm, being much larger than that of the Ge supply case (0.38 nm). As well-known, the surface impurities often enhance the formation of ion-induced nanostructures [17]. In the Al supply case also, deposited Al would act as a “seed” to enhance the nanostructure formation. If so, nanostructures formed at an early stage of the ion irradiation should depend on the Al supply rate.

The effect of the Al supply rate was further investigated in detail at 2.2 and 0.5 nm/min. Figure 6 shows the corresponding AFM images with typical line profiles. It should be noted that the higher the Al supply rate, the larger the R_a values. As described above, after prolonged sputtering (60 min), the surfaces supplied with Al at 2.2 and 0.5 nm/min were characterized by nanowall and nanorod structures, respectively. From these facts, the final morphology of nanostructures after prolonged irradiation is thought to be strongly influenced by the initial surface morphology formed at an early stage of ion irradiation.

The higher the Al supply rate (namely, the number density of the deposited Al), the easier coalescing of the Al particles would be. The coalesced Al clusters would be large enough to form nanowalls after prolonged sputtering with an Al supply at a high rate, whereas they would be small to form nanorod structures for the case of low Al supply rate.

4. Conclusion

Ge surfaces were irradiated by Ar^+ ions with and without a simultaneous Ge or Al supply at room temperature. The si-

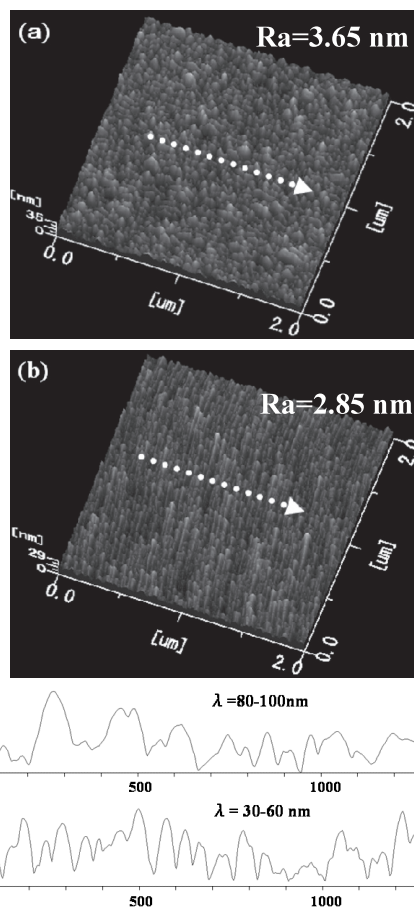


Fig. 6 (a), (b) AFM images of the sample surfaces ion-irradiated for 5 min with a simultaneous Al supply. The Al supply rate: (a) 2.2 and (b) 0.5 nm/min. (c), (d) Line profiles of the areas indicated by dotted lines in (a) and (b), respectively.

multaneous particle supply provided a variety of nanostructure such as cones, nanobelts, nanowalls and nanorods with bottleneck structure, while only conical structures formed on the Ar^+ -irradiated surfaces without any particle supply. On the Al-supplied surfaces, the formation of nanorods with bottleneck structure and nanobelts were prominent. So, the elucidation of the dependence of ion-induced nanostructures on the supplied metal species will be interesting. This subject will be dealt with in forthcoming papers.

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materials based on the ion-solid interactions, especially the room-temperature growth of carbon nanofibers and the low-temperature fabrication of ZnO nanoneedles, and their applications.



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