I. INTRODUCTION

Silicon carbide (SiC) is expected as a semiconductor material for fabricating high-power, high-temperature and high-frequency devices, due to its wide band gap, high saturation electron mobility and stability at high temperatures [1]. SiC is also an attractive material in the characterization of atomic structure on the surface. SiC surfaces are graphitized or carbonized by annealing at high temperatures under decreased pressures [2,3] or under oxygen molecules [4]. This is due to evaporation of Si from SiC surfaces caused by annealing in the decreased pressures. On the other hand, periodic structures are formed by annealing SiC surfaces in ultra high vacuum (UHV), especially by annealing in a Si-rich environment to prevent the surface graphitization. Depending on polytypes, polarity and sample preparation procedures, various surface structures have been reported [3, 5-8].

Among them, graphitized structures produced on SiC surfaces are now noticed. It is known that carbon nanotubes, a new material for mechanical and electronic applications, are produced on 6H-SiC(0001) C-terminated surfaces in the direction perpendicular to the surfaces [9]. It has also been found that, on 6H-SiC(0001) Si-terminated surfaces, graphite layers or carbon nanotubes with shorter length than that on the C-terminated surfaces are produced depending on sample preparation procedures [10]. Previously, we have found that string-shaped structures consisting of graphite structure are produced along step edges on 6H-SiC(0001) Si-terminated surfaces by annealing in UHV [3]. Recently, Derycke, et al. have determined string-shaped structures on 6H-SiC(0001) Si-terminated surfaces to be carbon nanotubes produced in the direction parallel to the surfaces [11]. They also have found that a network of carbon nanotubes is developed on the Si-terminated surface. A network of carbon nanotubes developed on surfaces has a lot of possibility for industrial applications such as electronic devices. In order to control the development of the network, it is important to understand mechanisms of the network development.

In this study, we observe the graphitization processes of SiC for both (0001) Si- and (0001) C-terminated surfaces by scanning tunneling microscopy (STM) and reflection high-energy electron diffraction (RHEED). The SiC surfaces with offset angles are used to enhance growth of string-shaped structures along step edges. The development of the network on the SiC surfaces is investigated, and we propose the models for the generation of string-shaped structures.

II. EXPERIMENT

Samples used were 8° off-axis 4H-SiC(0001) Si- and (0001) C-terminated wafers (Cree Research Inc.), nitrogen-doped n-type wafers with a dopant concentrations of ~ 10^{16} cm^{-3}. Specimens were cut to the size of 1 × 7 × 0.26 mm³, cleaned in acetone by an ultrasonic cleaner for 5 min, dipped into concentrated HF (49%) for 5 min, rinsed in deionized water for 10 min and blown dry with N₂ gas. The experiment was carried out in a UHV system consisting of a treatment chamber and a main chamber with base pressures of 2 × 10^{-10} Pa and 2 × 10^{-8} Pa, respectively. The specimens were resistively annealed in the treatment chamber, and the surfaces of the specimens were observed in the main chamber by STM (JSTM-4500VT, JEOL) and RHEED at room temperature. After pre-heating at several hundreds degree C (24 hrs), the specimens were successively annealed at 1000°C (10 min), 1400°C (1 min), 1700°C (1 min) and 1800°C (10 min). The temperatures were measured by an IR thermometer (TR-630, Minolta). STM images were recorded using tungsten tips by a constant-current or a variable-current mode, with a tunneling current of 0.3 nA and sample bias voltages between -8.0 and +5.2V. RHEED patterns were taken with the beam energy of 10 keV in
FIG. 1: STM images of the 4H-SiC(0001) Si-terminated surfaces obtained in the series of the annealing process, after the pre-heating (a)(b), after annealed up to 1000°C (c)(d), 1400°C (e)(f), 1700°C (g)(h), 1800°C (i)(j). Sample bias voltages are -8.00 V (a)-(d) and 5.20 V (e)-(j). Tunneling current is 0.30 nA for all the images.
FIG. 2: STM image by a constant-current mode at the same area as Fig. 1(f), and the corrugation of string-shaped structures along step edges. Widths and heights of them are about 5 nm and 0.5 nm, respectively.

FIG. 3: STM image by a constant-current mode at the same area as Fig. 1(h), and the corrugation of string-shaped structure perpendiculars to step edges. Widths and heights of them are similar to that along step edges.

III. RESULTS

Figure 1 shows STM images of the 4H-SiC(0001) surfaces obtained in the series of the annealing process. STM images for the surface after the pre-heating are shown in Figs. 1(a) and (b). As shown in Fig 1(a), the surface has many straight steps perpendicular to the [11\(\overline{2}0\)] direction over 200 nm. Step edges separated into branches are observed clearly. Detailed observation of the surface shows that the surface has many protrusions as shown in Fig. 1(b). The plan view of the protrusion is round with a diameter of about 1 nm. It is reported that carbon nanotubes grow not only on (0001) surfaces but also on (0001) surfaces, when the native oxide is removed enough by HF treatment [10]. As the specimens used in this experiment are also treated by HF, it seems that the protrusions are the ends of carbon nanotubes in the initial stage growing on (0001) surfaces.

The surface after annealed up to 1000°C also has many straight steps perpendicular to the [11\(\overline{2}0\)] direction over 200 nm as shown in Fig. 1(c). The branches of step edges observed in Fig 1(a) have disappeared, and straight steps are arranged periodically. The periodicity of the straight steps is about 20 nm. Figure 1(d) shows the magnified STM image of Fig. 1(c). Diameters of protrusions are larger than that in Fig 1(b), which suggests the growth of carbon nanotubes by the successive annealing. Step edges are difficult to be detected due to the growth of the protrusions.

Figure 1(e) shows an STM image of the surface after annealed up to 1400°C. Surface structures have drastically changed from that in Fig. 1(c). Shapes of bunched steps are complicated. Figure 1(f) shows the magnified STM image of Fig. 1(e). The protrusions observed in Figs. 1(b) and (d) have disappeared, and terraces are rather flat. It is noted that mounds are formed at step edges by the annealing up to 1400°C. This is consistent with our previous result, that string-shaped structures are generated along step edges by annealing 6H-SiC(0001) on-axis surfaces at 1450°C [3]. We also call the mounds observed in this study as string-shaped structures. Figure 2 shows the STM image by a constant-current mode at the same area as Fig. 1(f). The profile shows the corrugation of step edges in Fig. 1(f). Widths and heights of string-shaped structures along step edges are about 5 nm and 0.5 nm, respectively.

Figure 1(g) shows an STM image of the surface after an-
nealed up to 1700°C. Complicated bunched steps in Fig. 1(e) have changed into straight ones, and larger terraces are formed. String-shaped structures along step edges still remain. The most noticeable feature is that string-shaped structures perpendicular to step edges are also generated. The magnified STM image of the surface is shown in Fig. 1(h). Most of the string-shaped structures are in terraces as shown by an arrow α. On the other hand, some structures grow across step edges as shown by an arrow β. Hereafter, we call string-shaped structures along step edges as type A structures, and that perpendicular to step edges as type B structures.

Figure 1(i) shows an STM image of the surface after annealed up to 1800°C. Compared to the STM image shown in Fig. 1(g), type A structures are straight, and type B structures have grown across bunched steps. Both structures are arranged in a row, especially in the case of type B structures. Figure 3 shows the STM image by a constant-current mode at the same area as Fig. 1(h). The profile shows the corrugation of type B structures. Widths and heights of type B structures are about 5 nm and 0.5 nm, respectively, which are similar to that of type A structures shown in Fig. 2.

String-shaped structures in STM images of the surface after annealed up to 1800°C are unstable. Figure 4 shows successive STM images obtained by scanning the same area of the surface after annealed up to 1800°C. Positions of string-shaped structures are different between Fig. 4(a) and Fig. 4(b), in spite of the successive scanning at the same area. Moreover, the STM image shown in Fig. 1(i) is considered to contain ghost images due to the double tip. The instability of string-shaped structures in the STM images may be caused by the interaction between the STM tip and string-shaped structures. Derycke et al. reported that the carbon nanotubes on the SiC(0001) surfaces, which correspond to string-shaped structures in our study, are possible to be bent or moved by AFM manipulations. Considering their results, the movement of string-shaped structures may disturb the tunneling current between the tip and the surface.

Figure 5 shows AFM images of the surface after annealed up to 1800°C. As shown in Fig. 5(a), a network of string shaped structures is developed on the surface. Distances between two strings of type A are about 50 to 100 nm, and that between two strings of type B are about 200 to 500 nm. Type B structures have grown across several bunched steps, and their lengths are about several hundreds nm. Type B structures with lengths less than 100 nm observed by STM were not detected by AFM. Figure 5(b) shows the AFM image with a scanning direction rotated by 90° with respect to that of Fig. 5(a). The images of type B structures drift when scanned along step edges. The drift suggests the possibility that type B structures are movable by AFM manipulations.

The graphitization process of 4H-SiC(0001) C-terminated surfaces with an offset angle of 8° was also observed in order to compare with the Si-terminated surfaces. Figure 6 shows STM images of the C-terminated surfaces obtained in the series of the annealing process. Different from the results on the Si-terminated surfaces, bunched steps are not observed clearly on the surface after the pre-heating as shown in Fig. 6(a). The magnified STM image shown in Fig. 6(b) reveals that the surface has many protrusions, which corresponds to the ends of carbon nanotubes. Straight steps in the direction perpendicular to the [11\(\overline{2}0\)] direction are slightly observed on the surface annealed up to 1000°C as shown in Fig. 6(c). Periodic structures are also formed on the surface as shown in Fig. 6(d). The periodicity of the periodic structures is 0.95 nm, which corresponds to the 3×3 structures. After annealed up to 1400°C, many bunched steps have appeared as shown in Fig. 6(e) and mounds are also formed at step edges as shown in Fig. 6(f). This phenomenon is the same as that observed on the Si-terminated surface. Terraces are narrower and step edges are wandering more than those observed on the Si-terminated surface.
FIG. 5: AFM images of the Si-terminated surface after annealed up to 1800°C with scanning directions (a) along and (b) perpendicular to step edges. A network of string-shaped structures is developed on the surface. Note that the images of string-shaped structures perpendicular to step edges in Fig. 5 drift.

Protrusions in Figs. 6(i) and (j) are observed clearly than that observed in Figs. 6(g) and (h), which means the growth of carbon nanotubes. AFM observations of the surface after annealed up to 1800°C were carried out to obtain wide range images. The AFM images reveal that the surface is very rough. String-shaped structures were not detected on the surface.

IV. DISCUSSION

Now we discuss about the generating process of string-shaped structures on the Si-terminated surfaces. Figure 7 shows RHEED patterns obtained in the series of the annealing process. Only the diffraction spots related to the SiC are observed in Figs. 7 (a), (b) and (c). New diffraction spots have appeared in the RHEED pattern from the surface annealed up to 1400°C, when type A structures are generated, as shown in Fig. 7 (d). The intense diffraction spot indicated by an arrow corresponds to the spot of the (10) rod for the graphite lattice rotated by 30° with respect to the SiC lattice. The weak diffraction spots indicated by arrows correspond to the double diffraction spots between the SiC lattice and the graphite lattice rotated by 30° with respect to the SiC lattice [3]. Diffraction spots from the graphite lattice remain even after annealed at 1800°C as shown in Figs. 7(e) and (f).

Taking into account the results that string-shaped structures are generated when the graphite spots appear in the RHEED pattern, and no other structure is detected from the RHEED pattern obtained after the successive annealing, we believe that the structures consist of graphite. It is reasonable to assume that graphitized string-shaped structures are generated in the process of a sublimation of Si from SiC surfaces at step edges. The surfaces after the annealing up to 1000°C have many steps perpendicular to the [11\overline{2}0] direction. As Si atoms sublime in two directions at step edges, it is expected that effect of graphitization at step edges is larger than that on terraces. The promotion of the graphitization at step edges leads to the generation of type A structures.

However, the generation of type B structures is not explained by the promotion of the graphitization at step edges. One possible explanation for the generation of type B structures is folding of graphite layers. Watanabe, et al. proposed the mechanism for the initial growth process of carbon nanotubes on 3C-SiC(\overline{1}1\overline{1}) surfaces that carbon nanotubes are formed by the lift of a part of graphite layers along the [11\overline{2}0] direction by a generation of pentagons and heptagons in the graphite layers composed of hexagons [12]. We believe that similar phenomenon, folding of graphite layers, takes place on the Si-terminated surface. In the case of the folding, generation of pentagons and heptagons are not required. The STM image of the surface after annealed up to 1800°C in Fig. 8 suggests that mounds are formed at several areas on terraces by the folding of the surface layer. It is considered that this is the initial stage for the generation of type B structures. The folding of the surface layer would be due to the stress induced by the crystallization from amorphous carbon to graphite. It seems that the stress on the C-terminated surfaces is relaxed by the generation of carbon nanotubes, and that on the Si-terminated surfaces is
FIG. 6: STM images of the 4H-SiC(000\bar{1}) C-terminated surfaces obtained in the series of the annealing process, after the pre-heating (a)(b), after annealed up to 1000°C (c)(d), 1400°C (e)(f), 1700°C (g)(h), 1800°C (i)(j). Sample bias voltages are -7.00 V (a)(b), -6.92 V (c)(d), -6.00 V (e)(f), -8.00 V (g)(h) and -6.00 V (i)(j). Tunneling current is 0.30 nA for all the images.
FIG. 7: RHEED patterns from the Si-terminated surfaces obtained in the series of the annealing process, before the heating (a), after the pre-heating (b), after annealed up to 1000°C (c), 1400°C (d), 1700°C (e), 1800°C (f), taken in the direction of [1010]. The beam energy and the glancing angle are 10 keV and about 4°, respectively. The intense diffraction spot indicated by an arrow α corresponds to the spot of the (10) rod for the graphite lattice rotated by 30° with respect to the SiC lattice. The weak diffraction spots indicated by arrows β correspond to the double diffraction spots between the SiC lattice and the graphite lattice rotated by 30° with respect to the SiC lattice.

relaxed by the generation of string-shaped structures.

In order to confirm the models, cross sections around type A and type B structures were observed by TEM. Figure 9(a) shows the TEM image of the cross section around the type A structure. SiC substrate is covered with graphite layers, and the type A structure is on the graphite layers just above the step edge. On the other hand, in the TEM image of the cross section around the type B structure shown in Fig. 9(b), the type B structure is on the SiC substrate and covered with graphite layers. TEM images shown in Fig. 9 explain the difference of the generation mechanism between type A and type B structures. As the type A structure is on graphite layers in Fig. 9(a), it is generated before the formation of graphite layers. That means that type A structures are generated by the promotion of the graphitization at step edges. On the other hand, as the type B structure is under graphite layers in Fig. 9(b), it is generated after the formation of graphite layers. That means that type B structures are generated by the folding of graphite layers.

On the C-terminated surface, string-shaped structures are not observed after annealed up to 1800°C. However, as shown in Figs. 6(e) and (f), string-shaped structures are transitionally generated on the C-terminated surface in the annealing process. As carbon nanotubes grow preferably on C-terminated surfaces than Si-terminated surfaces [9, 10], the generation of string-shaped structures is considered to be restricted by the growth of carbon nanotubes. Considering the fact that string-shape structures are also generated on the C-terminated surface where step edges are not observed clearly after annealed up to 1000°C, we speculate that type A structures are generated by not only the promotion of the graphitization at step edges but also the relaxation of the surface stress at step edges.

It is important to control the formation of steps on SiC surfaces in order to design the network of string-shaped structures. It has been reported that SiC sur-
faces with periodic steps are obtained by gaseous etching in H₂ or HCl/H₂ at 1300 to 1700°C [13-20]. By using the technique, atomically flat terraces with widths of 200 to 400 nm and a step height of about 1.5 nm, a 6 monolayer-height atomic step, are formed on on-axis (0001) Si-terminated surfaces. It has also been reported that widths of terraces on off-axis surfaces are much narrower, 20 to 80 nm when the offset angle is 3.5°, than those on on-axis surfaces [21]. The results suggest that distances between two strings of type A are possible to be controlled by changing offset angles on the surfaces. However, in use of off-axis surfaces, appearances of thermodynamically stable surfaces have to be taken into consideration. For example, Figs. 1(a) and (c) show that the surface after annealed up to 1000°C consists of two kinds of facets. Existences of the two kinds of facets are also clearly confirmed by the RHEED pattern from the surface annealed up to 1000°C. As shown in Fig. 10, two types of the streaks of the SiC (11) rod, in the directions indicated by the blue and the red lines, are observed in the RHEED pattern. The streak in the direction indicated by the blue line corresponds to the (0001) surface tilted 8° with respect to the normal of the specimen surface, and that in the direction indicated by the red line corresponds to the (112n) surface. The 1̅1̅ and the 00 spots of the SiC are also split into different directions, although they are difficult to be distinguished in the presented RHEED pattern. The geometric analysis of the RHEED pattern reveals that the (112n) surface is tilted about 13° with respect to the (0001) surface. As the streak of the SiC 11 corresponding to the (112n) surface already exists on the surface before the pre-heating as shown in Fig. 7(a), it is considered that the (112n) surface tilted about 13° with respect to the (0001) surface is thermodynamically stable below 1000°C. The streak of the SiC 11 have disappeared in Figs. 7 (e) and (f), which means that the (112n) surface at 1000°C transformed into other surfaces or disordered structures by the successive annealing. The TEM image in Fig. 9 (a) shows that the (112n) surface tilted about 23° with respected to the (0001) surface is formed at 1800°C. Terrace widths of 15 to 20 nm at 1000°C have changed into 50 to 100 nm at 1800°C. Thus, in order to design the network of string-shaped structures on SiC surfaces, further study is required to reveal step bunching mechanisms on SiC surfaces, and also mechanisms that type B structures generated in terraces grow across bunched steps.

V. SUMMARY

We have investigated the development of the network of string-shaped structures on the SiC surfaces with an offset angle of 8° by annealing in UHV. The network of string-shaped structures is developed on the 4H-SiC(0001) Si-terminated surface by annealing at 1800°C, however, not developed on the 4H-SiC(0001) C-terminated surface. The network developed on the Si-terminated surface is composed of string-shaped structures along and perpendicular to step edges. String-shaped structures along step edges are generated at 1400°C, followed by the generation

FIG. 8: STM image of the Si-terminated surface after annealed up to 1800°C. Mounds are formed at several areas on terraces by the folding of the surface layer, which is considered to be the initial stage for the generation of string-shaped structures perpendicular to step edges.

FIG. 9: Cross sectional TEM images of string-shaped structures (a) along and (b) perpendicular to step edges. Note that positions of string-shaped structure are different between (a) and (b).
FIG. 10: RHEED pattern from the Si-terminated surface after annealed up to 1000°C. The solid white line corresponds to the shadow edge, and the dashed white line corresponds to the surface of the specimen. Two types of the streak of the SiC 11 indicated by the blue and the red lines shows existences of two kinds of facets, corresponding to the (0001) and the (11\text{2n}) surfaces, respectively. The (11\text{2n}) surface is tilted by about 13° with respect to the (0001) surface.

Acknowledgments

The authors would like to thank to Mr. H. Watanabe and Mr. T. Matsui of \textit{DENSO CORPORATION} for their technical supports and useful discussion in the TEM observations, and Dr. K. Hara of the Advisor of \textit{DENSO CORPORATION} for his encouragement in the present study.


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