Growth of Graphene on SiC(111) Surfaces via Ion-Beam Irradiation

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We used scanning tunneling microscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy to investigate the influence of ion-beam irradiation on the growth of graphene on 3C-SiC(111) surfaces via the SiC surface decomposition method. When the SiC(111) surface was irradiated with Ar\textsuperscript{+} ions, the surface bonds of the SiC(111) surfaces were broken. After annealing the SiC surface with an Ar\textsuperscript{+} ion beam at an accelerating voltage of 1 keV and an incident angle of 70°, we obtained graphene with few defects. However, in the case of Ar\textsuperscript{2+}-ion-beam irradiation at 60°, the resulting graphene layers exhibited high defect concentrations. We observed that the Si defect and breakage of bonds in the surface region promotes the formation of graphene layers and that the destruction of the deep layers of SiC substrate prevents the growth of graphene. [DOI: 10.1380/ejssnt.2016.121]

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I. INTRODUCTION

Graphene comprises a two-dimensional hexagonal network of carbon atoms, and it is expected to find applications in next-generation electronic devices. Graphene exhibits excellent electronic properties; in particular, electron mobility in graphene is several hundred times greater than that in Si [1, 2]. Graphene can be prepared using various techniques, including the mechanical exfoliation of graphite [3], chemical vapor deposition (CVD) [4, 5], and the thermal decomposition of SiC substrates [6–9]. The SiC surface decomposition method is expected to enable the large-scale production of graphene and is a convenient method for preparing single- or multi-layered graphene samples.

In previous studies, we deposited graphene onto SiC-on-insulator (SiC-OI) substrates. When the thickness of the SiC layer on a SiC-OI substrate was greater than 5 nm, a graphene layer could be grown on the SiC-OI as well as SiC substrate [10]. Thermal decomposition of the SiC(0001) or the SiC(111) surface at high temperatures resulted in the formation of graphene layers on the SiC surface [11]. By contrast, carbon nanotubes (CNTs) could be deposited onto the SiC(0001) or SiC(111) surface [12]. In both cases, the results revealed that ion-beam irradiation of the SiC substrates promote graphene or CNT growth in the SiC surface-decomposition method. However, the relation between the effect of ion-beam irradiation and quality of the formed graphene has not been clarified.

In the present study, we investigated a SiC(111) surface irradiated with an Ar\textsuperscript{+}-ion beam under several sets of conditions. The surface structure after ion-beam irradiation and graphene formation on the SiC(111) surface was observed by scanning tunneling microscopy (STM). Furthermore, to evaluate the quality of the graphene on the SiC-OI, we analyzed this surface using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Herein, we discuss the relation between the conditions of ion-beam irradiation and the formation of graphene.

II. EXPERIMENTAL AND CALCULATIONS

A wafer with a 3C-SiC(111)/SiO\textsubscript{2}/Si(111) structure was fabricated using a silicon-on-insulator (SOI) wafer [13]. The uppermost Si layer of the SOI wafer was thinned to approximately 5 nm by sacrificial oxidation, and the resulting ultrathin top Si layer was converted into a 3C-SiC seed layer via a carbonization process. An epitaxial SiC layer approximately 3000 nm thick was then grown on the SiC seed layer by ultra-high-vacuum (UHV) CVD. Samples measuring 1 × 7 × 0.5 mm\textsuperscript{2} were cut from the wafer. The sample was ultrasonically cleaned in acetone for 5 min before being introduced into a UHV chamber. The samples were degassed in a UHV chamber for 12 h by resistive heating to approximately 500°C. The sample
temperatures were measured using an optical pyrometer. A surface of the sample was irradiated with Ar\(^{+}\) ions at 1–5 keV for 1 h. The incident angle with respect to the surface normal was 60–70\(^{\circ}\), and the current density of the Ar\(^{+}\)-ion beam was 200 nA/cm\(^2\).

The samples were annealed at 1150\(^{\circ}\)C for 2 min in a UHV chamber at a base pressure of 1\(\times\)10\(^{-8}\) Pa. The STM experiments were performed in the chamber without exposing the sample to air. Tips for the STM observations were fabricated from 0.3-mm-diameter tungsten wire etched with 2 M aqueous NaOH in a Pt-loop electrode operated in direct-current mode. The tips were baked out before being used for scanning. Furthermore, the samples were measured by XPS and Raman spectroscopy after transferring them through atmosphere. The X-ray source was an Al K\(\alpha\) anode maintained at 15 kV. The analyzer pass energy was 20 eV, and the take-off angle with respect to the sample surface was 35\(^{\circ}\). Raman spectra were recorded at a fixed laser wavelength of 514.5 nm.

To analyze the surface composition of the SiC(111) surface after Ar\(^{+}\)-ion irradiation, we conducted XPS measurements. Figure 2 shows the deconvoluted Si 2p XPS spectra of 3C-SiC(111) surfaces (a) without and (b) with Ar\(^{+}\)-ion-beam irradiation at 70\(^{\circ}\) and 1 keV for 1 h.

To investigate the SiC surface irradiated with the Ar\(^{+}\)-ion beam, we performed calculations related to the collision of Ar\(^{+}\) ions with a SiC surface using the stopping and range of ions in matter (SRIM) program [14], which is a Monte Carlo simulation method. The calculations related to the conditions of Ar\(^{+}\)-ion irradiation of a SiC layer with a thickness of 10 nm were repeated 1,000 times.

### III. RESULTS AND DISCUSSION

Figure 1 shows the calculation results in the distribution of Si and C vacancies of the SiC surface irradiated with an Ar\(^{+}\)-ion beam. In Fig. 1, the irradiation angle and energy are (a) 70\(^{\circ}\), 1 keV, (b) 60\(^{\circ}\), 1 keV, (c) 45\(^{\circ}\), 1 keV, and (d) 45\(^{\circ}\), 3 keV. As evident in Figs. 1(a–c), Si and C defects concentrated on less than 1 nm from the surface, and its peak position was 0.3 nm. A depth of 1.0 nm corresponds to approximately 6-7 SiC bilayers given that the lattice constant of 3C-SiC is 0.436 nm. When the irradiation angle is large, as shown in Fig. 1(a), numerous Si and C defects are formed near the surface region. In Fig. 1(b), the peak of Si and C defects was wider and lower than that of in Fig. 1(a). In the case of Ar\(^{+}\) ions accelerated at 3 keV (Fig. 1(d)), the effects of the ion beam reached a depth of 10 nm.

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To analyze the surface composition of the SiC(111) surface after Ar\(^{+}\)-ion irradiation, we conducted XPS measurements. Figure 2 shows the deconvoluted Si 2p XPS spectra of the SiC(111) surfaces without and with Ar\(^{+}\)-ion-beam irradiation at 70\(^{\circ}\) and 1 keV for 1 h. The spectrum in Fig. 2(a) contains a single peak corresponding to Si-C bonding at 101 eV. However, we observed that the spectrum shown in Fig. 2(b) could be deconvoluted into two peak structures. The peak at higher binding energy originates from SiO\(_2\). Ar\(^{+}\)-ion-beam irradiation induces cleavage of Si-C bonds; therefore, the surface with dangling bonds was oxidized to form SiO\(_2\). These observations indicate that Ar\(^{+}\)-ion irradiation of the SiC(111) surface breaks surface bonds, thereby changing the surface structures. Consequently, Ar\(^{+}\)-ion irradiation might help the sublimation of Si from the surface during SiC surface was annealing. We expected the formation of graphene layers to be promoted.

Figure 3 shows STM images taken after the irradiated 3C-SiC(111) surfaces were annealed at 1150\(^{\circ}\)C for 2 min at a base pressure of 1\(\times\)10\(^{-8}\) Pa. The white hexagons in Figs. 3(a) and 3(b) correspond to graphene mesh. The white diamonds in Figs. 3(c) and 3(d) correspond to (6\(\times\)6) periodicity in the buffer layers, which led us to conclude that few-layer graphene formed on the
buffer layers [15]. We were not able to infer the difference in the quality of the graphene shown in Fig. 3(a) and that shown in Fig. 3(b). Therefore, to evaluate the quality of the graphene on this surface, we used XPS and Raman spectroscopy.

Figure 4 shows the deconvoluted C 1s XPS spectra obtained after the irradiated 3C-SiC(111) surfaces were annealed at 1150°C for 2 min. The SiC(111) surfaces in Figs. 4(a) and 4(b) were irradiated with Ar⁺-ion beams at incident angles of 70° and 60°, respectively, at 1 keV for 1 h. The peak at 283.5 eV corresponds to Si-C bonding [16]. In Fig. 4(b), a graphene peak at 284.5–284.7 eV, which corresponds to sp²-bonded carbon atoms, decreased in intensity and was wider than that in Fig. 4(a). The peak P at 285.5–286 eV was a remaining component after subtracting SiC and graphene components. The intensity of the peak P increased in the case of irradiation with the Ar⁺-ion beam at 60° compared with 70°. A part of the peak was attributed to sp²-bonded carbon in the buffer layer between graphene and the SiC substrate [16]. Further, we considered that the increase in the intensity of peak P in Fig. 4(b) might be caused by the surface oxidation influences as seen in Fig. 2(b). Therefore, we confirmed that the formation of graphene on the surface depends on the conditions of Ar⁺-ion-beam irradiation.

Figure 5 shows the Raman spectrum of the 3C-SiC(111) surface after Ar⁺-ion-beam irradiation at 1 keV for 1 h, followed by annealing at 1150°C for 2 min. The surfaces in Figs. 5(a) and 5(b) correspond to those in Figs. 3(a) and 3(b), respectively. The D, G, 2D, and D + G peaks are observed in Fig. 5(a) [17]. As shown in Fig. 5(b), the intensities of the D, G, and 2D peaks decreased compared with those in Fig. 5(a). In general, the ratios G/D and G/2D relate to the quality of the graphene and to the number of graphene sheets, respectively. When we irradiated a 3C-SiC(111) surface with the Ar⁺-ion beam at an incident angle of 70°, we obtained two or three layers of graphene. Also, these graphene might have some defects, because D band peak was observed in Fig. 5(a). In the case of Ar⁺-ion-beam irradiation at 60°, we obtained a graphene film with defects. These results are consistent

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
with the XPS observations in Figs. 3 and 4. We observed that the graphene obtained after Ar$^+$-ion-beam irradiation at 70° on the SiC(111) surface possesses few defects. When the damage caused by Ar$^+$-ion beam irradiation concentrates near the SiC surface region, the resulting graphene layer was formed with a few defects. By contrast, when ion-beam damage reached the deep layers of the substrate, we could not obtain high quality graphene.

IV. CONCLUSION

The effect of ion-beam irradiation of SiC(111) surfaces with respect to the growth of graphene via the SiC surface-decomposition method was investigated using STM, XPS, and Raman spectroscopy. When a SiC(111) surface was irradiated with Ar$^+$ ions, the irradiation was induced breakage of SiC(111) surface bonds. After the SiC surface was annealed with Ar$^+$-ion-beam irradiation under several sets of conditions, we observed that the incident angle of the Ar$^+$-ion beam affects the formation of graphene layers. Si defect and breakage of bonds in the surface region by the Ar$^+$-ion beam promotes the formation of graphene. However, destruction of the deep layers of SiC substrate prevents the formation of graphene. We need to clarify the relations between ion-beam irradiation and mechanism of graphene formation in the future.

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