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Sequential control of step-bunching during graphene growth on SiC (0001)

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We have investigated the relation between the step-bunching and graphene growth phenomena on an SiC substrate. We found that only a minimum amount of step-bunching occurred during the graphene growth process with a high heating rate. On the other hand, a large amount of step-bunching occurred using a slow heating process. These results indicated that we can control the degree of step-bunching during graphene growth by controlling the heating rate. We also found that graphene coverage suppressed step bunching, which is an effective methodology not only in the graphene technology but also in the SiC-based power electronics. *Published by AIP Publishing.*
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Graphene has been attracting a great deal of attention both in basic research and various application fields.[1–6] For future applications, development of a highly reproducible production method of homogenous large-area graphene on insulating substrates is desirable. Among several techniques, the thermal decomposition of SiC is one of the most promising techniques.[7–9] In this technique, wafer-scale single-crystalline graphene can be grown directly on an insulating SiC substrate. As for the growth mechanism, the initial decomposition of the SiC surface leads to the formation of a $6\sqrt{3} \times 6\sqrt{3}R30$ reconstructed structure, which is called a buffer layer.[8,9] In the buffer layer, the in-plane atomic arrangement is almost the same as that of graphene, but some of the carbon atoms have covalent bonds with the silicon atoms beneath them.[10] Further decomposition leads to the conversion of the buffer layer into graphene and a next buffer layer is formed simultaneously underneath graphene.

In recent years, homogeneous monolayer graphene which entirely covers the wafer has been grown by heating the SiC substrate in an atmospheric pressure of Ar.[11,12] Graphene grown by this technique is formed on a relatively bumpy surface with surface steps that have a height of several nanometers, although the surface before graphene growth is atomically flat. This is due to the step-bunching phenomenon, which is defined as the movement of the surface atoms at high temperature and the formation of the high steps and wide terraces.[13] The step-bunching phenomena can be divided into two types. One is minimum step-bunching (MSB) with a limited step height of one or one-half of the unit-cell height. The other is large step-bunching (LSB) to form high steps with a height of more than the unit-cell height. The driving force of step-bunching is the high thermodynamic stability of the (0001) surface and the difference in the step movement speed between different Si-C bilayers, which induce MSB, and the extrinsic kinetic effects which affect the step moving rate, which induce LSB.[13–15] In the above reports about homogeneous graphene growth, LSB occurred with a step-height of more than 10 nm.[12] On the other hand, graphene growth with MSB is actually possible.[9] In other words, the relation between graphene growth and step-bunching is not yet fully understood.

In general, the electronic properties of graphene on SiC depend sensitively on the underlying SiC surface morphology. For example, a graphene device covering the surface step has a much higher resistance than the one on the terrace.[16] In addition, the resistance increases with increasing step heights.[17,18] Thus, the ideal material is graphene on a step-free SiC substrate. In fact, several groups have succeeded to grow graphene on step-free SiC.[19,20] However, a millimeter-scale step-free SiC substrate is hard to obtain. Hence, for realistic applications, when we want high-yield and high-mobility devices over the entire wafer, we need to grow graphene on the low-step surface using the on-axis (low miscut-angle) SiC wafer.[21,22] In other words, we should control the degree of step-bunching. In addition, it is widely known that graphene nucleates at steps on the SiC surface, which strongly affects graphene growth and its homogeneity.[23,24]

There is one systematic study about the relation between graphene growth and step-bunching. Oliveira and coworkers reported that no matter what the initial surface morphology, both LSB and graphene growth occurred.[25] Although their report is very convincing, it is not consistent with some reports where graphene growth only with MSB was possible.[9,26] In order to understand these facts, we should know which occurs first, step-bunching or graphene growth, or whether both occur simultaneously.

The substrates used in this study were nitrogen-doped nominally-on-axis 6H-SiC (0001) wafers purchased from TANKEBLUE Co. Ltd. Details of the pretreatment of the substrate were the same as that of our previous reports.[8–10,23,26] We first checked the temperature range where the step-bunching phenomenon occurred in a hydrogen etching treatment. The substrates were heated in an atmospheric pressure of Ar/H_2 gas flow (4% H_2, 0.5 slm) at 1200–1700 °C for 10 min. For graphene growth, the substrates were heated at 1600 or 1650 °C in an atmospheric pressure of pure Ar gas flow (more than 99.9999%, 0.5 slm). In order to clarify the

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[b)] Author to whom correspondence should be addressed. Electronic mail: w_norimatsu@imass.nagoya-u.ac.jp relation between graphene growth and the step-bunching, we paid attention to various heating rates. For this purpose, we used an infrared-light focusing heater, by which we can heat the sample with the highest heating rate of 1800 °C/min. The heating rates in ramping the temperature from 800 to 1600 °C applied in this experiment were actually 40, 80, 160, and 270 °C/min. The samples thus obtained were investigated by atomic force microscopy (AFM) and Raman spectroscopy.

In order to understand the temperature dependence of just the step-bunching phenomenon, the substrates after hydrogen etching treatment were investigated by AFM. Figure 1 shows the AFM images after hydrogen etching, together with an image of the initial SiC substrate. All surfaces were atomically flat and exhibited a step-terrace structure. The step-height in the initial substrate and the sample heated at 1200 °C (b) was about 0.25 nm, which is the smallest height consisting of one Si-C bilayer. The step-height in the samples heated at (c) 1300 and (d) 1500 °C was about 0.75 and 1.5 nm. We performed the hydrogen etching treatment also at 1400, 1600, and 1700 °C, and found that the step-height was about 1.5 nm. These results indicated that MSB occurred at 1300 °C and the higher temperatures. On the other hand, graphene growth in an atmospheric pressure of Ar starts at more than around 1600 °C.[11,12] These results suggest that the step-bunching occurs at temperatures lower than that of graphene growth.

We then heated the SiC substrates at 1600 and 1650 °C in Ar. Figure 2 shows the temperature profile of the heating process and the AFM topography and phase images of the samples. The samples were annealed at ((b)–(e)) 1600 and ((f)–(i)) 1650 °C for 10 min with the different heating rates of ((b) and (f)) 270, ((c) and (g)) 160, ((d) and (h)) 80, and ((e) and (i)) 40 °C/min. All the surfaces heated at 1600 °C exhibited a flat surface with the very straight step-terrace structure. The step-heights in ((b) and (c)) and ((d) and (e)) were about 0.75 and 4–6 nm, corresponding to the occurrence of MSB and LSB, respectively. This result tells us that the step heights and widths both increased with decreasing heating rates. We have tried other heating rates which are faster or slower than the above rates, and we found that their surface morphologies were similar to ((b) and (c)) or ((d) and (e)), respectively. In the phase images, a uniform contrast was observed. The contrast in the phase image indicates a difference in the material properties on the surface.[26] Hence, the surface was composed of one material. The Raman spectra of these samples are overlaid on the phase image, and no peaks were observed. This indicates that the substrates annealed at 1600 °C in the Ar atmosphere at all heating rates produced no graphene. It should be emphasized here that even a buffer layer was absent. The presence of the buffer layer can be detected by the Raman spectrum; the buffer layer has broad peaks around 1300–1600 cm^{-1} and no 2D band around 2700 cm^{-1}.[27–30] There were actually no broad peaks around 1300–1600 cm^{-1}, indicating the absence of the buffer layer.

The differences between the samples heated at different rates were only in the degree of step-bunching. The faster heating rates effectively suppressed the step-bunching. The use of different heating rates means that there are different holding times in the temperature range where the step-bunching occurs. Also, the boundary between the MSB and LSB was between the heating rates of 160 and 80 °C/min. It suggests that the MSB is the metastable state and the longer annealing time drastically leads to the LSB.

We then raised the temperature to 1650 °C to grow graphene. Figures 2(f)–2(i) show AFM images of samples with different heating rates. There are a few contrasts in the phase image, indicating graphene growth. In the Raman spectra, there are sharp peaks at about 1600 and 2720 cm^{-1}. These peaks are known as the G and 2D bands, which are indicators

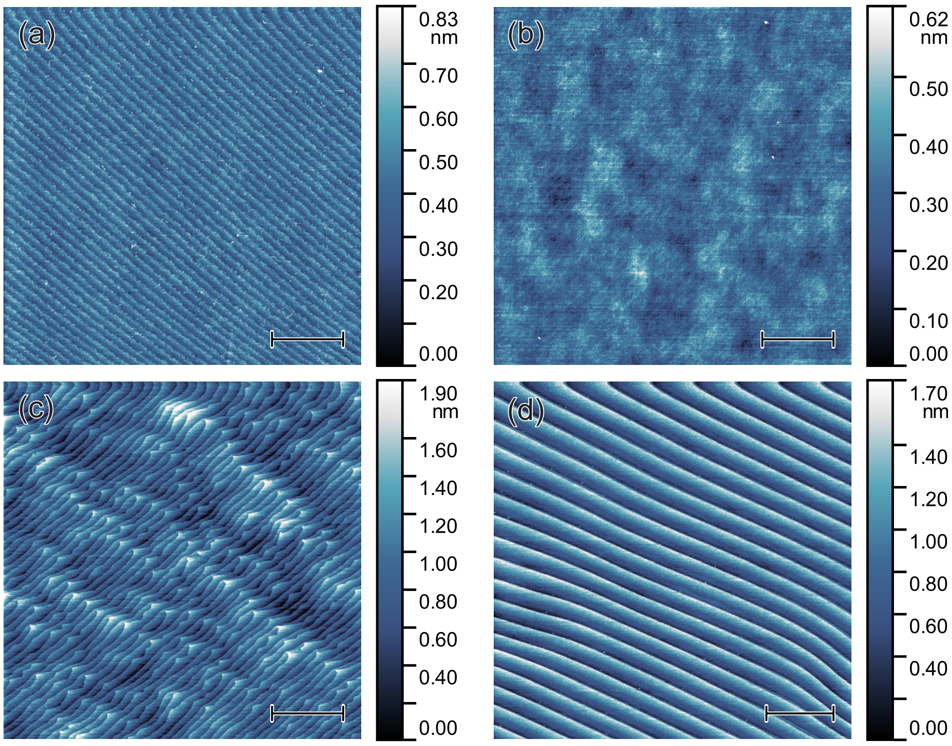

FIG. 1. AFM images of (a) the initial SiC surface after chemical mechanical polishing (CMP) and the surface after hydrogen etching at (b) 1200, (c) 1300, and (d) 1500 °C. The scale bar is 2 μm.

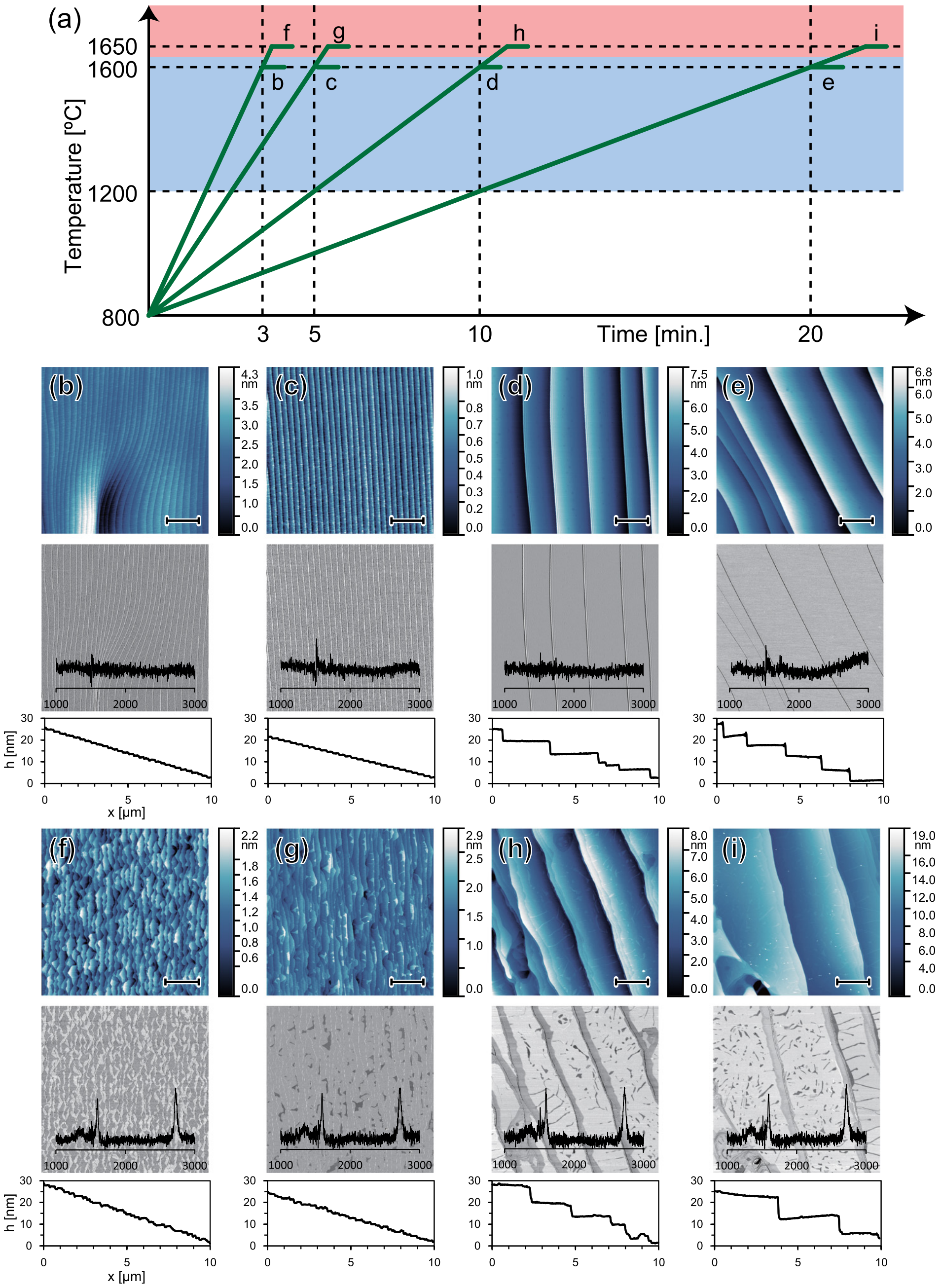

FIG. 2. (a) Temperature profile of the heat treatment at 1600 and 1650 °C. The holding time at these temperatures for all samples was 10 min. The blue and red regions correspond to the step-bunching and graphene growth regions, respectively. ((b)–(e)) and ((f)–(i)) AFM topography and phase images together with the height profile of samples heated at 1600 and 1650 °C, respectively. The scale bar is 2 μm. ((b) and (f)), ((c) and (g)), ((d) and (h)), and ((e) and (i)) are results of the heating rates of 270, 160, 80, and 40 °C/min, respectively. Raman spectra are overlaid in the AFM phase images. In the spectra, the unit of the horizontal axis is cm^{-1}, and the SiC substrate component was subtracted.

of graphene growth. In addition, the 2D peak with a full width at half maximum (FWHM) around or smaller than 40 cm^{-1} and the I_{2D}/I_G ratio of more than 1 indicate that monolayer graphene was formed.[9] The FWHMs and the I_{2D}/I_G were actually (f) 40.6 and 1.20, (g) 46.6 and 1.05, (h) 40.0 and 1.00, and (i) 46.1 cm^{-1} and 1.02, indicating a high coverage of monolayer graphene. However, it is clear from the line-profile that the step heights and terrace widths of ((f), (g), (h), and (i)) were similar to those of the samples ((b), (c), (d), and (e)), respectively, i.e., MSB and LSB occurred in the samples ((f) and (g)) and ((h) and (i)), respectively. These results suggest that the step-bunching did not proceed during the graphene growth process. It should be noted here that the surface miscut angle of all samples in this study was quite similar (0.19 ± 0.02°). Then, differences in the miscut angle can be neglected in understanding the present phenomena.

Based on the above results, we have developed an understanding of four points; (1) the step-bunching occurred between 1200 and 1600 °C (the blue step-bunching region in Fig. 2(a)), (2) the duration of the step-bunching region determined the degree of step-bunching, (3) graphene started to grow at more than 1600 °C in the present atmosphere (the red graphene growth region in Fig. 2(a)), and (4) graphene growth proceeded without any more step-bunching. Now, we have a question to consider. Can step-bunching occur after graphene growth? In order to answer this question, we performed another experiment. We compared the two routes to grow graphene, shown in Fig. 3(a). The route b involves heating the substrate at a heating rate of 270 °C /min from 800 to 1650 °C and keeping at 1650 °C for 30 min. The state just after ramping the temperature to 1650 °C should be similar to that in Fig. 2(f). In other words, we can see the phenomenon occurring after the MSB and the following graphene growth. On the other hand, in the route c, we raised the temperature at a heating rate of 40 °C/min and kept it at 1650 °C for 10 min. This is actually equal to Fig. 2(i). The

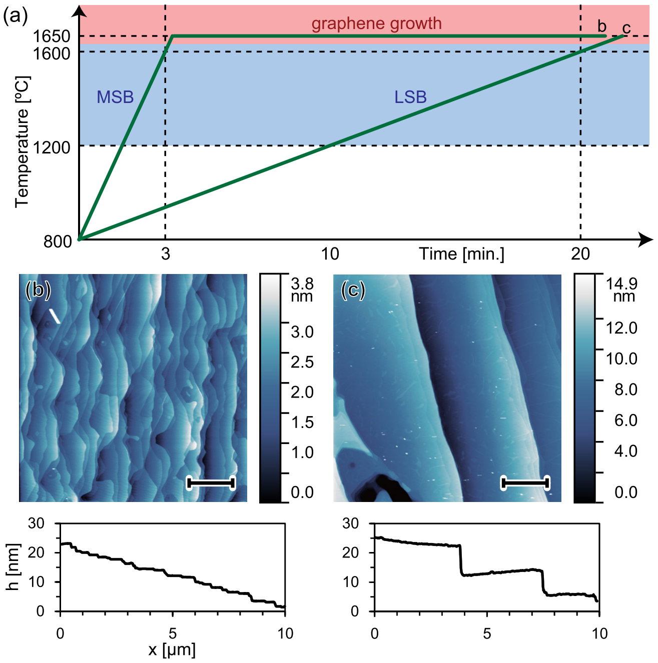

FIG. 3. (a) Temperature profile of two samples; one (b) uses fast heating and a long holding time, and the other (c) employs slow heating and a short holding time. (b) and (c) AFM images and the line profiles of the two samples. The scale bar is 2 μm.

total duration in both the step-bunching and graphene growth temperature regions in route b is longer than that in route c. However, we found that the surface in route b had a low step height of about 0.75–1.50 nm as shown in Fig. 3(b). On the contrary, in Fig. 3(c), the sample annealed by the route c had a large step height and a wide terrace. We also measured the Raman spectra and found that mono- or bi-layer graphene was formed in samples (b) and (c). These results indicate that once graphene grew, step-bunching does not occur.

We summarize the relation between step-bunching and graphene growth in Fig. 4. When the substrates are annealed with a fast or slow heating rate, MSB or LSB occurs, respectively. During and after graphene growth, step-bunching never occurs. In other words, the step-bunching occurs first, and then graphene grows. It suggests that the graphene coverage on the SiC surface strongly suppressed the surface atom motions and so the step-bunching phenomenon was suppressed. This is probably due to the presence of the buffer layer between graphene and SiC. Some of the carbon atoms in the buffer layer have a strong covalent bond with the silicon atoms just beneath.[10] Then, the surface atom motion requires breaking the bonds and re-bonding, which clearly needs a significantly high energy. Thus, the step-bunching phenomenon can be suppressed by graphene growth. It is now important to understand whether only the buffer layer with no graphene can suppress LSB or not, which should be investigated in near future.

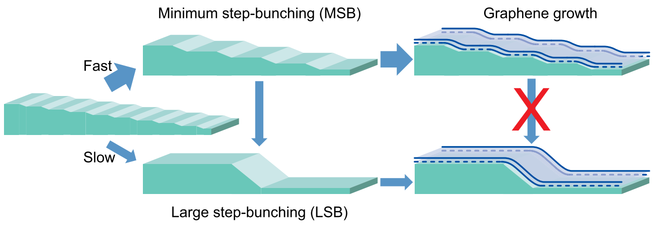

FIG. 4. Schematic diagram of the heating rate effects for the step-bunching and graphene formation phenomena on SiC (0001).

We here discuss the discrepancy between the results in Oliveira's paper[25] and our results. They showed that LSB occurred regardless of the initial SiC surface morphology. On the other hand, we showed that MSB and LSB occurred using fast and slow heating rates. The heating rate in Oliveira's work was about 50 °C/min, which was between the values of 40 and 80 °C/min used in our study, where LSB occurred. Thus, their results are completely consistent with ours. These results clearly show that by controlling the heating rate, we can thoroughly control the degree of step-bunching. In order to obtain the record best electrical properties, a graphene device on a wide terrace without steps is suitable, which can be achieved by graphene growth with a slow heating rate. On the other hand, to obtain high-yield devices over an entire wafer, graphene grown on a surface with low steps is better, which is possible by heating SiC at a fast heating rate. It should be noted here that graphene growth was found to be a possible technique to control the step-bunching phenomenon of the SiC surface. This is very important in the field of the SiC-based power electronics, because the thickness of the insulating oxide surface layer strongly depends on the SiC surface morphology.

In summary, we have investigated the effects of heating rates on graphene formation on SiC (0001), and we found that step-bunching can be controlled by varying the heating rate. Large amounts of step-bunching resulted from slow heating rates. On the other hand, step-bunching was strongly suppressed at fast heating rates. We also found that graphene grown on the SiC surface strongly suppressed the occurrence of further step-bunching.

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