Influence of surface structure modifications on the growth of carbon-nanotubes on the SiC($000\bar{1}$) surfaces

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We report experimental results of carbon nanotubes (CNTs) formation on SiC($000\bar{1}$) surfaces by scanning tunneling microscopy (STM) and transmission electron microscopy (TEM). The CNTs were formed densely and uniformly after annealing a SiC($000\bar{1}$) surface at 1700^{o}C in a low vacuum. However, the CNTs were not formed after annealing the SiC($000\bar{1}$) surface at 1050^{o}C in an ultra-high vacuum followed by annealing the surface at 1700^{o}C in the low vacuum. From the STM and TEM observations, we found that the graphite layers without defects obstruct the formation of the precursor of CNTs on the SiC($000\bar{1}$) surface.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], many studies have been carried out for their electronic and mechanical properties. The promising properties of CNTs have excited considerable interest in their application to electronic devices, scanning probes, field-emission sources, super-capacitors and so forth. The CNTs are produced by various methods such as arc discharge [2], laser vaporization [3], pyrolysis [4,5], plasma-enhanced or thermal chemical vapor deposition (CVD) [6-8]. However, the dynamic processes of CNT growth in those methods have not been elucidated yet.

Kusunoki et al. have reported that CNTs are densely formed in vertical alignment by annealing a SiC($000\bar{1}$) surface at 1700^{o}C in a certain vacuum condition [9-13]. In this process called surface decomposition method, Si atoms are selectively evaporated from the SiC surface and instead residual carbon atoms are concentrated to form aligned CNTs. In this method, the CNTs have grown without any catalytic help of metals or gases. On the counter face, SiC(0001) surface, they could not obtain CNTs but did only several graphite layers parallel to the surface. The surface and interface properties of such graphite layers formed on the SiC substrates have been investigated by various researchers [14-20]. In our previous STM study in the ultra-high vacuum [21], many domains of graphite appeared after annealing the 6H-SiC($000\bar{1}$) surface at temperatures higher than 1300^{o}C. The fact that CNTs are not formed on the SiC($000\bar{1}$) surface in the condition of ultra-high vacuum has not been explained yet.

In the present study using transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and low energy electron diffraction (LEED), we investigated the initial process of CNT growth on the SiC($000\bar{1}$) surface and found that the graphite layer formed on the SiC($000\bar{1}$) surface at 1050^{o}C in an ultra-high vacuum obstructs the formation of CNTs on the surface in the annealing process at 1700^{o}C in a low vacuum. We show that the morphology of the graphite layers on the SiC($000\bar{1}$) surface influences the CNT growth.

2. Experimental

The 6H-SiC samples (nitrogen-doped, *n*-type) with $(000\bar{1})$ surface of the 1.0×7.0×0.33 mm^3 were supplied by CREE Research. They were ultrasonically cleaned in acetone and ethanol, each for 5 min, etched in hydrofluoric acid (5 %), and rinsed in deionised water before being introduced into an ultra-high vacuum (UHV) chamber under a base pressure of 1.0×10^{-8} Pa. The UHV chamber was equipped with an STM (JEOL JSTM-4500XT), a rear-view LEED and sample-preparation facility for direct current heating. The STM observations were performed at room temperature. Tips for STM were made from tungsten wires (0.3 mm in diameter), and were baked out before being used for scanning. The samples were degassed in the UHV for 12 h by resistive heating at a temperature of about 500^oC. After the degassing process, the samples were heated to 1050-1200^oC and held at this temperature for 30 min. The temperature of the sample was measured with an optical pyrometer.

The formation of CNTs on the SiC$(000\bar{1})$ surfaces was performed ex-situ in another chamber. This chamber was maintained at a pressure of 1.0×10^{-2} Pa during the CNT formation. The chamber was equipped with a carbon-boat (thickness: 1 mm, size: 5.0×35 mm^2), on which the samples were set. The samples were heated to 1700^oC at a rate of 20^oC/min, and held at the temperature for 1 h. Formed interfaces on the SiC$(000\bar{1})$ substrates were observed by a cross-sectional TEM (H-9000NAR), using 300-kV electron beams.

3. Results and Discussion

Fig. 1 shows a LEED pattern taken after annealing a SiC$(000\bar{1})$ surface at 1200^oC for 30 min in the UHV condition. In Fig. 1, azimuthally-disordered graphite (1×1) spots were observed together with the fundamental SiC$(000\bar{1})$-(1×1) spots. The brightest parts in the

diffraction ring define a hexagonal lattice, where the unit cell vectors of graphite are rotated by 30^o with respect to those of the SiC($000\bar{1}$) surface. The weak spots in the diffraction ring are attributed to the hexagonal lattice where the unit cell vectors of graphite coincide with those of the SiC($000\bar{1}$) surface. When the surface was annealed at 1050^{o}C in the UHV condition, we found in the LEED pattern that the intensity of the fundamental SiC($000\bar{1}$)-(1×1) spots increased moderately compared with that in Fig. 1. The graphite layer was formed on the SiC($000\bar{1}$) surface after annealing it at higher than 1050^{o}C.

We tried to form the CNTs on the SiC($000\bar{1}$) surface in a low vacuum after the above-mentioned preprocessing of the surface. Figs. 2(a)-2(c) show cross-sectional TEM images of the interfaces formed by annealing the SiC($000\bar{1}$) surfaces at 1050^{o}C, 1200^{o}C and 1350^{o}C for 30 min in the UHV condition followed by annealing the surface at 1700^{o}C for 1 h in the low vacuum, respectively. In Figs. 2(b) and 2(c), we can observe CNTs in both high-density and excellent-alignment with a mean length of about 500 nm. Although the resolution of the used TEM is not enough to measure the diameter of the CNTs, it looks from the image definitely less than 10 nm, which is consist to the reported values, about 3-5 nm [9-13]. Inner structures of the CNTs are not resolved in the present TEM image, but they are known to be multi-walled structure when formed by the surface decomposition method [9-13]. We found here that the preprocessing at 1200^{o}C or 1350^{o}C does not influence the CNT growth. However, we did not observe CNTs but a thin layer on the surface by the preprocessing at 1050^{o}C in Fig. 2(a). Taking into account the fact that graphite (1×1) spots are observed together with the fundamental SiC($000\bar{1}$)-(1×1) spots after annealing the surface at 1050^{o}C, this thin layer is attributed to the graphite layer.

We observed the surface structure of the graphite layers formed on the SiC($000\bar{1}$) surface by STM. Figs. 3(a) and 3(b) show STM current images taken after annealing the SiC($000\bar{1}$) surface 1050^{o}C and 1200^{o}C for 30 min in the ultra-high vacuum, respectively. In Fig. 3(b), we find several domains consisting of various arrangements of small protrusions labeled “A”. The average separation of two adjacent protrusions was 0.25 nm, which

corresponding to the lattice spacing of graphite 0.246 nm. This value means the formation of graphite layers on the SiC($000\bar{1}$) surface. We can also observe the broad protrusions labeled “B” at the domain boundaries and the upheaved structure labeled “C”. The SiC($000\bar{1}$) surface annealed at 1050^{o}C was covered with a graphite layer without defects such as domain boundaries or upheaved structures, as shown in Fig. 3(a).

We propose that the generation of CNTs on the SiC($000\bar{1}$) surface depends on the roughness of the surface. When the SiC($000\bar{1}$) surface is annealed in the low vacuum, residual oxygen in the chamber may attack the surface and expels the Si atoms of the surface. As a result, the surface becomes rough and produces the precursors of CNTs on the surface. Finally, they grow up to become CNTs. The graphite layers with domain boundaries are formed on the surface after annealing it at 1200^{o}C and 1350^{o}C, though graphite layers without defects are formed on the surface after being annealed at 1050^{o}C in the ultrahigh vacuum. When these samples are annealed at 1700^{o}C in the low vacuum, the CNT growth can be observed at the samples with pre-annealing at 1200^{o}C and 1350^{o}C in the ultrahigh vacuum, though the CNT growth cannot be succeeded at the sample with pre-annealing at 1050^{o}C. The protrusions or the upheaved structures at domain boundaries observed in the samples with pre-annealing at 1200^{o}C and 1350^{o}C in the ultrahigh vacuum become growth nuclei of CNT. However, a precursor or a growth nucleus of CNT is hardly formed on the surface with pre-annealing at 1050^{o}C. While annealing the sample in the low vacuum, the graphite layers without defects on the SiC($000\bar{1}$) surface may block the attacking of the residual oxygen atoms to the interface.

4. Conclusions

We have investigated influence of the surface structure modifications in the growth of CNTs on the SiC($000\bar{1}$) surfaces. After annealing the SiC($000\bar{1}$) surface at 1200^{o}C in the ultra-high vacuum, there appear many protrusions, which might be precursor of CNTs, in the domain boundary of the graphite in the STM image. When this surface is annealed at

1700°C in the low vacuum, the CNTs are formed on the surface. On the other hand, the surface annealed at 1050°C in the ultra-high vacuum is covered by the graphite layer without defects. The CNTs are not generated on the surface after being annealed at 1700°C in the low vacuum. The CNT growth is suppressed by the morphology of the graphite layer on the SiC($000\bar{1}$) surface.

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Figure Captions

Fig. 1. LEED pattern taken after annealing the SiC($000\bar{1}$) surface at 1200^{o}C for 30 min. The electron energy is 61.4 eV.

Fig. 2. Cross-sectional TEM image of interfaces formed by annealing the SiC($000\bar{1}$) surfaces (a) at 1050^{o}C, (b) at 1200^{o}C and (c) at 1350^{o}C for 30 min in an ultra-high vacuum followed by annealing the surfaces at 1700^{o}C for 1 h in a low vacuum.

Fig. 3. (a) STM current image taken after annealing the SiC($000\bar{1}$) surface at 1050^{o}C for 30 min in an ultra-high vacuum. This image was taken at sample bias V_S = +0.013 V and imaged area S = 15x15 nm^2. (b) STM current image taken after annealing the SiC($000\bar{1}$) surface at 1200^{o}C for 30 min in an ultra-high vacuum. V_S = +2.5 V, S = 20x20 nm^2.

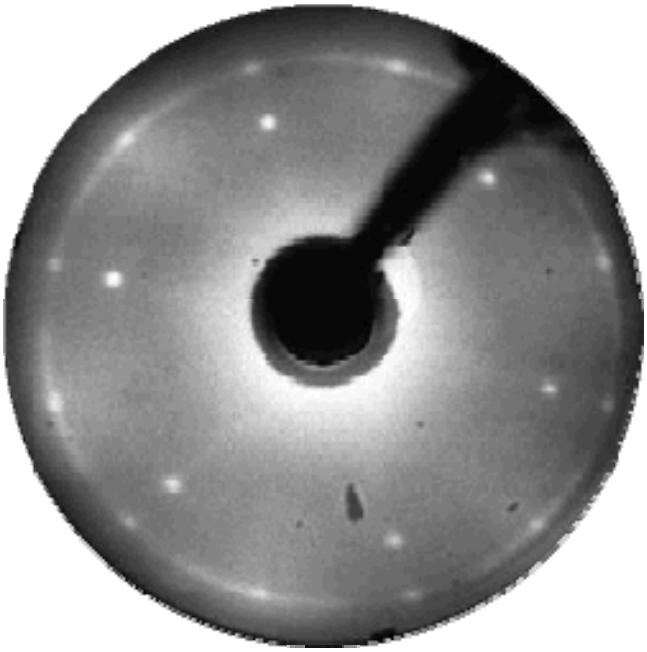

Fig. 1. T. Yamauchi et al.

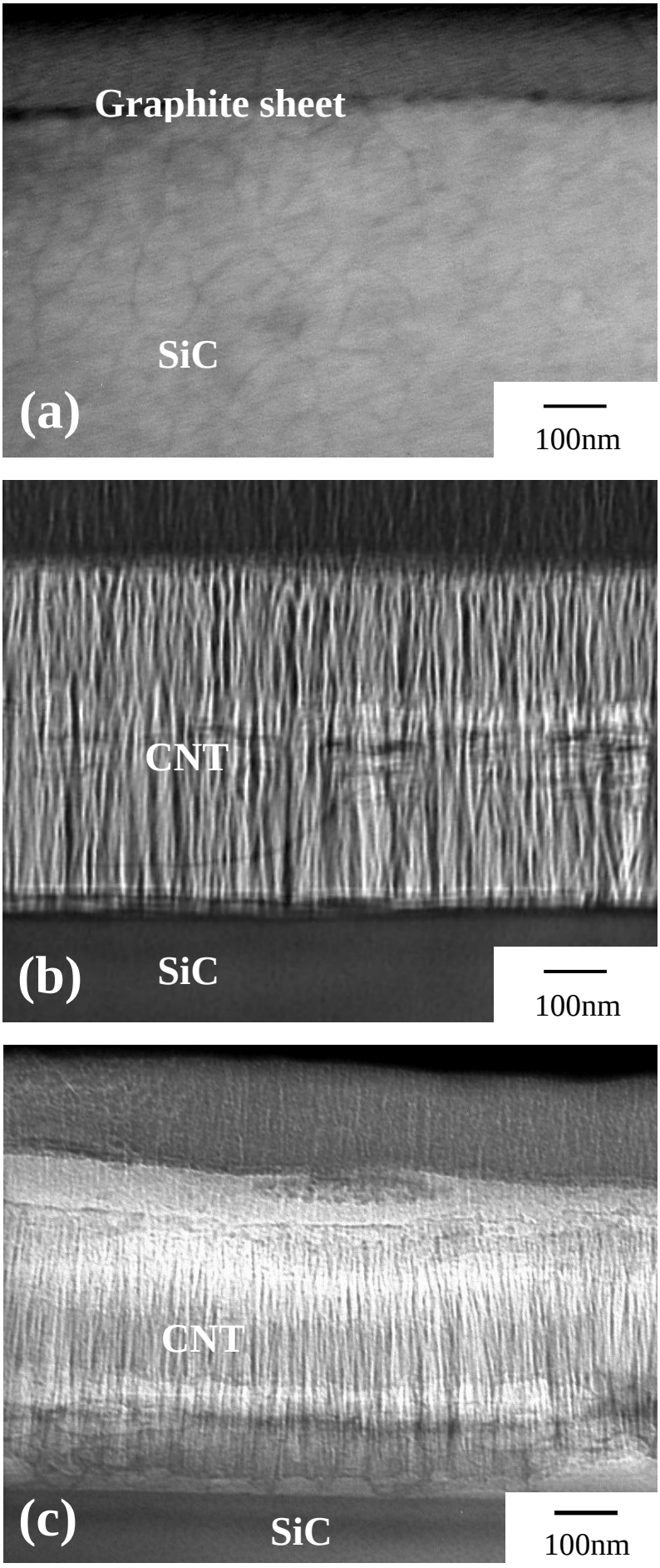

Fig. 2. T. Yamauchi et al.

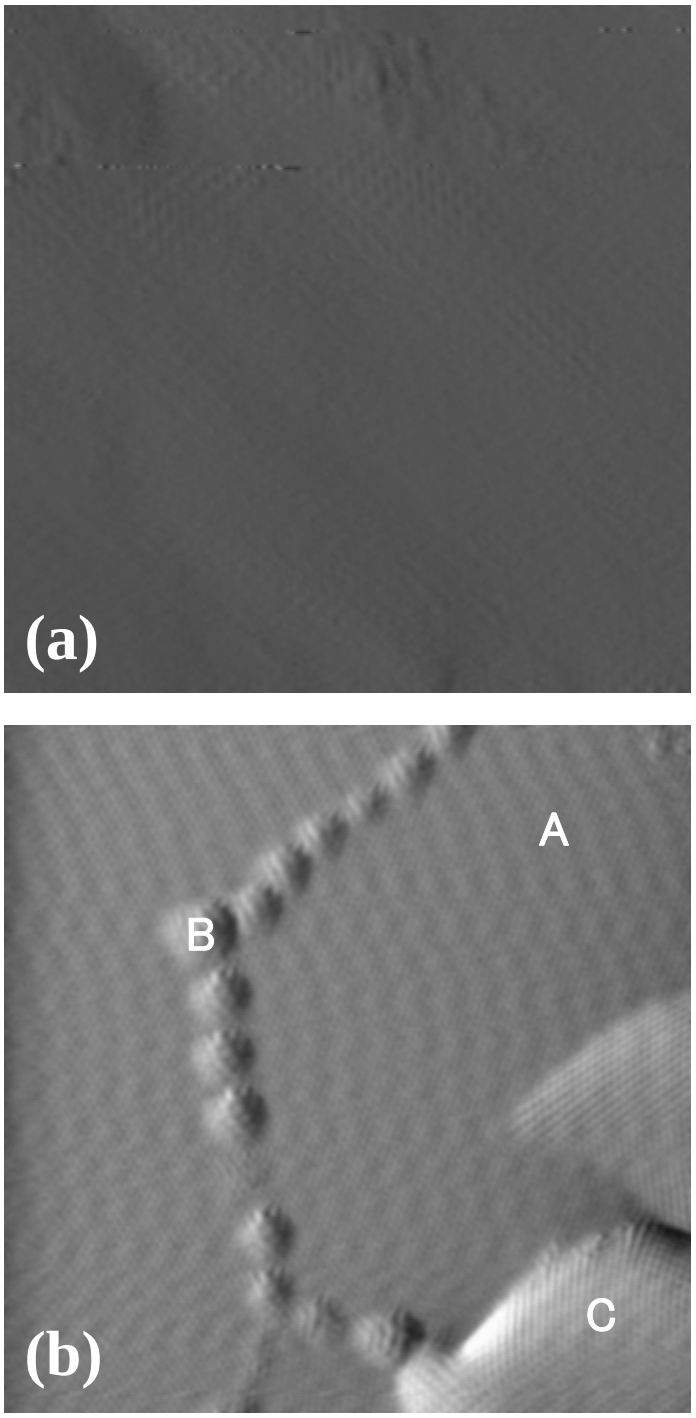

Fig. 3. T. Yamauchi et al.