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AN STM OBSERVATION OF THE INITIAL PROCESS OF GRAPHITIZATION AT THE 6H-SiC(000$\bar{1}$) SURFACE

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We applied scanning tunneling microscopy (STM) as well as low-energy electron diffraction (LEED) to an analysis of the initial process of graphitization at 6H-SiC(000$\bar{1}$) surfaces. After annealing a 6H-SiC(000$\bar{1}$) surface at 1200°C, there appeared many domains with a single graphite layer in the STM image. Each graphite domain was azimuthally disordered to each other. Many large and small domains with various periodicities were observed in the STM image taken after annealing the surface at temperatures higher than 1300°C. This STM image can be explained as Moiré patterns due to different combinations of two graphite layers. In a LEED pattern azimuthally-rotated graphite 1×1 spots are observed together with the fundamental SiC(0001)1×1 spots, in consistent with the STM result.

1. Introduction

Silicon carbide (SiC) is a very promising material for applications to high-power and high-frequency devices because of its large breakdown field and high electron mobility. In addition, it is interesting that the energy band-gap of SiC is rather wide and shows different values depending on its own crystallographic structures: hexagonal, rhombohedral or cubic. A multilayer structure of the SiC polytypes could become a new material with controllable band-gaps. Moreover, it is expected to be a substrate for heteroepitaxial growth of group III nitrides. Although much works have been carried out to investigate surface structures of the 6H- or 3C-polytype SiC crystals, most of those are concerned with samples terminated with Si. There have been only a few studies for the other polar face of the SiC surface.

Kusunoki *et al.* have recently reported that carbon nanotubes (CNT's) are formed on a SiC(000$\bar{1}$) surface after annealing the substrate at 1700°C in a vacuum furnace.[1] It is interesting to note that on a SiC(0001) surface they could not obtain CNT's but only several graphite layers. The initial process of CNT growth on the SiC(000$\bar{1}$) surface has not been elucidated yet. Forbeaux *et al.* have investigated the gradual graphitization of the 6H-SiC(000$\bar{1}$) surface by angle-resolved inverse photoemission spectroscopy and low-energy electron diffraction (LEED).[2] However, real-space microscopic observations such as a scanning tunneling microscopy (STM) observation have not been carried out yet for the graphitization of the 6H-SiC(000$\bar{1}$) surface too.

In the present study using STM and LEED, we

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investigated the initial process of graphitization at the 6H-SiC(000$\bar{1}$) surface and found that graphite layers without grobal coincidence of their crystallographic orientations grew on the 6H-SiC(000$\bar{1}$) surface when annealed at temperatures higher than 1300°C. We will discuss a possible mechanism of CNT formation on the SiC(000$\bar{1}$) surface.

2. Experimental

The experiment was carried out in an ultrahigh vacuum (UHV) chamber under a base pressure of 1×10^{-8} Pa. The chamber was equipped with a commercial 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.

6H-SiC(000$\bar{1}$) samples of $1\times7\times0.33$ mm^3 were cut from a nitrogen-doped n-type wafer made by CREE Research Inc. The samples were cleaned in acetone, etched in hydrofluoric acid (5%), and rinsed in deionized water before being introduced into the chamber. They were degassed in the UHV for 12 h by resistive heating at a temperature of about 500°C. Since Si atoms tend to desorb from the SiC surface during the degassing process, we deposited Si atoms on the surface after the process. Si was deposited on the SiC(000$\bar{1}$) surface at room temperature, simply by heating a Si wafer (As-doped, 0.005Ωcm) set at 1 cm away from the sample. The Si deposition rate was estimated to be roughly 0.5 monolayer (ML)/s, where ML is defined to be the ideal Si (or C) atomic density in the (000$\bar{1}$) plane. The sample temperatures were measured with an optical pyrometer.

3. Results and Discussion

A distinct 3×3 LEED pattern and a well-developed STM image of the SiC(000$\bar{1}$) surface were obtained when the surface was treated by Si deposition for 10 s at room temperature followed by annealing at 950°C. Figs. 1a and 1b show a filled-state STM image and an empty-state one, respectively. We can observe, in the 3×3 domain, a clear honeycomb arrangement in the filled-state image (Fig. 1a), and one bright protrusion per unit cell in the empty-state image (Fig. 1b).

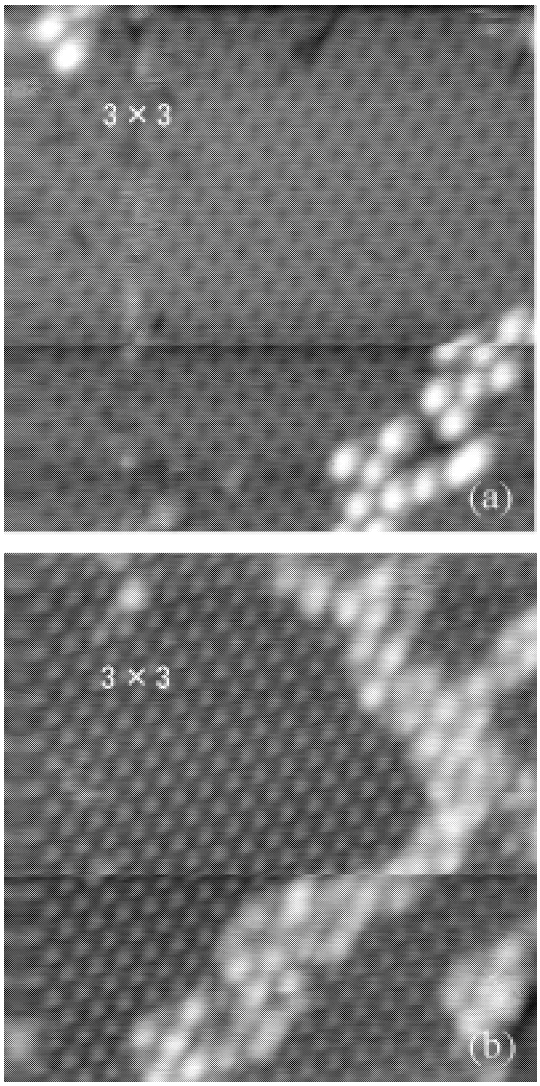

Fig. 1. STM image taken after annealing a 6H-SiC(000$\bar{1}$) surface at 950°C. This image was taken at sample bias (a) $V_s = -2.5$ V and (b) $V_s = 2.5$ V, at tunneling current $I = 0.3$ nA and imaged area $S = 20.0 \times 20.0$ nm^2.

Hoster *et al.* reported 3×3 STM images that resemble our STM images shown in Fig. 1 and proposed a 3×3 structural model on the SiC(000$\bar{1}$) surface.[3] Their model is characterized by 10 additional atoms per 3×3 unit cell on the substrate. They considered the dangling bonds of three adatoms in the unit cell of the outermost layer are responsible for the protrusions observed in the 3×3

STM images. On the other hand, Sasaki *et al.* observed a 3×3 LEED pattern after annealing the 6H-SiC(000$\bar{1}$) surface without Si flux.[4] It is difficult to identify atoms that compose the 3×3 structure only by STM. Therefore, further works are requested both theoretically and experimentally to elucidate the SiC(000$\bar{1}$) surface reconstruction.

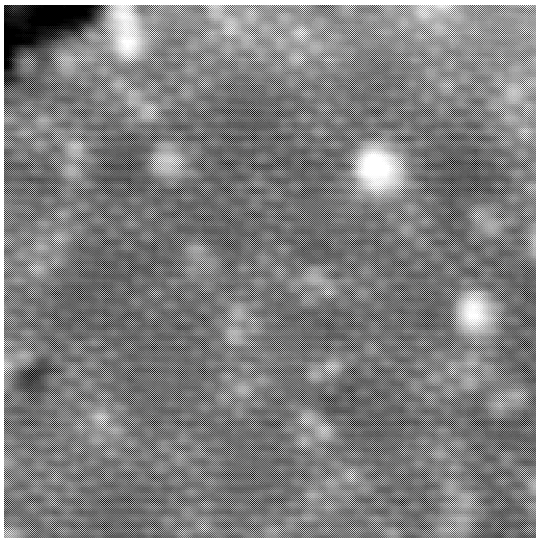

Fig. 2. STM current image taken after annealing a 6H-SiC(000$\bar{1}$) surface at 1000°C. Most area in the figure corresponds to a region with 2×2 periodicity. $V_s = -0.2$ V, $I = 0.3$ nA, $S = 18.5 \times 18.5$ nm^2.

In our previous works,[5,6] we observed the "3×3" structure even for the SiC(0001) surface when the surface was deposited with Si for 10 s at room temperature and was annealed at 750°C. That "3×3" structure showed one bright protrusion per unit cell in both the filled-state and the empty-state STM images. Those results show that the 3×3 structure of the SiC(000$\bar{1}$) surface is different from the "3×3" structure of the SiC(0001) surface.

We obtained an STM image, shown in Fig. 2, after annealing the above 3×3 surface at 1000°C. We can observe some kinds of protrusions on a terrace in the STM image shown in Fig. 2. The average separation of two adjacent protrusions is 0.62 nm. Most of the areas in the figure correspond to a region with 2×2 periodicity. Although Seubert *et al.* presented a model for the 2×2 structure, which has one silicon adatom per unit cell in three-fold hollow coordination,[7] we could not find protrusions in the STM corresponding to their 2×2 structural model. Forbeaux *et al.* reported that the initial growth of graphite occurred on a 2×2 reconstructed surface.[2] However, we could not observe the formation of graphite on the SiC(000$\bar{1}$)2×2 surface.

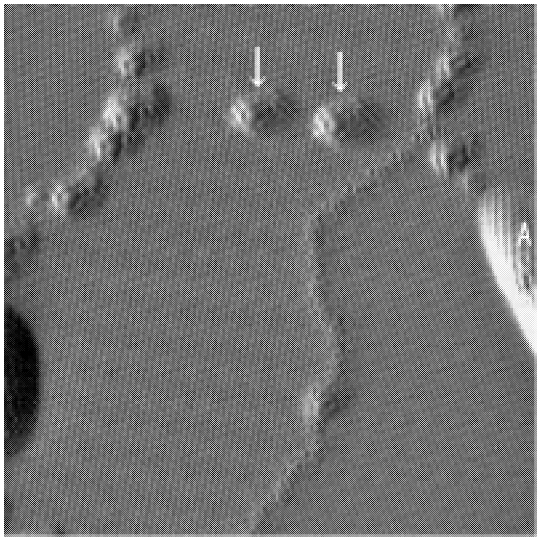

Fig. 3. STM current image taken after annealing a 6H-SiC(000$\bar{1}$) surface at 1200°C for 20 min. $V_s = -2.5$ V, $I = 0.3$ nA, $S = 18.5 \times 18.5$ nm^2.

Fig. 3 shows an STM current image taken after annealing the 3×3 SiC(000$\bar{1}$) surfaces at 1200°C for 20 min. The surface consisted of some domains showing various orientations of rows. The average separation of the two adjacent rows is 0.21 nm. This value means the formation of graphite layers on the surface. The reason the graphite layers were observed in the present STM image not as a honeycomb network but as rows would be a distortion due to asymmetry in the shape of the STM-tip.

In the LEED observation of this surface, we found that elongated spots join to form a closed diffraction ring whose brightest parts define a hexagonal lattice corresponding to the graphite. This result is consistent with the STM image.

We can observe broad protrusions indicated by white arrows in Fig. 3. The diameter of this cap-type structures is about 2 nm. Hisada *et al.* have already reported the formation of cap-type structures on the Si-terminated SiC(0001) surface.[8] It resembles our STM image in Fig. 3, but is different in size (diameter of about 5 nm). They estimated

that these structures were some parts of CNT's. It is reported, on the other hand, that CNT's grow on C-terminated 6H-SiC(000$\bar{1}$) surfaces in the direction perpendicular to the surfaces.[1] We propose the carbon nanocap that works as a precursor of CNT formation is rather the structure labelled "A" than the protrusions indicated by white arrows in Fig. 3. When the graphite or graphene layer grows across boundaries of two adjascent domains with different crystallographic orientations, the growing layer may be lifted up at domain boundaries on the surface, so that the CNT's could be formed.

Forbeaux *et al.* reported that the first graphite layer is strongly bound to the C atom in the top layer of the SiC(000$\bar{1}$) substrate since the π^* state are lacking at low carbon coverage.[2] This strong interaction between the graphite layer and the substrate may cause the formation of azimuthally-disordered graphite layers.

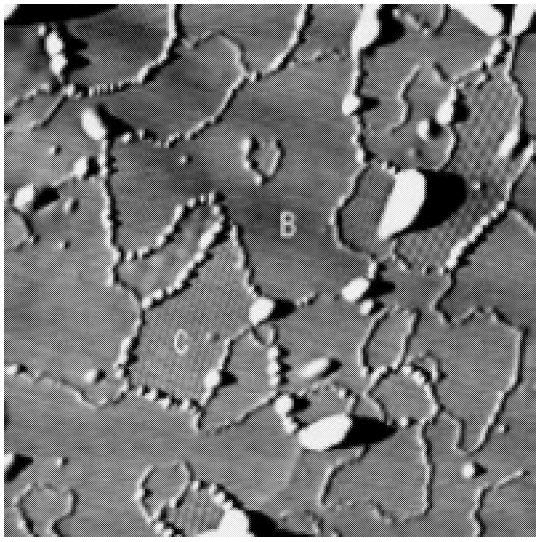

Fig. 4. STM current image taken after annealing a 6H-SiC(000$\bar{1}$) surface at 1800°C for 60 s. $V_s = -2.0$ V, $I = 0.3$ nA, $S = 95 \times 95$ nm^2.

Fig. 4 shows an STM current image taken after annealing a SiC(000$\bar{1}$) surface at 1800°C for 60 s. Many large and small domains showing various periodicities therein have grown, being separated from each other by domain boundaries. For example, the domains labelled "B" and "C" have periodicities of "3.1×3.1" and "5.7×5.7" with respect to the graphite 1×1 structure, respectively. This STM image can be explained as Moiré patterns due to different combinations of two graphite layers. In a LEED pattern shown in Fig. 5, azimuthally-disordered graphite 1×1 spots were observed together with the fundamental SiC(000$\bar{1}$)1×1 spots, although brightest parts in the diffraction ring define a hexagonal lattice, where the lattice basis vectors of graphite are rotated by 30° with respect to that of SiC(000$\bar{1}$) surface. From both STM and LEED observations, we conclude that the surface consists of a mosaic of small crystalline domains with azimuthal disorder, but that domains which are rotated by 30° compared with the lattice basis vectors of the substrate are dominant.

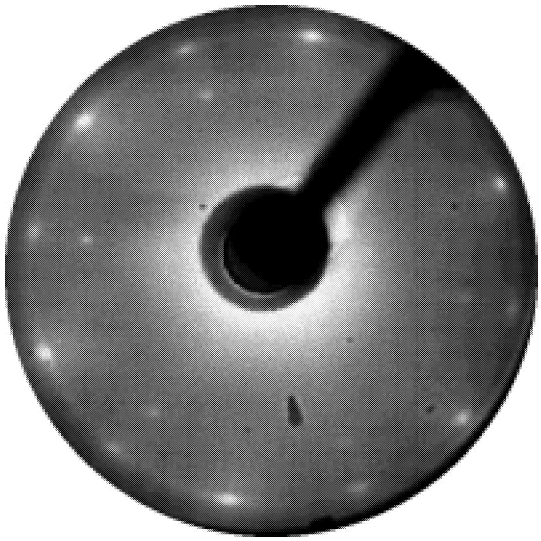

Fig. 5. LEED pattern taken after annealing a 6H-SiC(000$\bar{1}$) surface at 1800°C for 60 s. The electron energy is 61.4 eV.

4. Conclusions

We have visualized by STM the initial process of graphitization at the 6H-SiC(000$\bar{1}$) surface. After annealing the 6H-SiC(000$\bar{1}$) surface at 1200°C, there appear many domains with periodicity corresponding to single graphite layer. Each graphite domain is azimuthally disordered to each other. Many large and small domains with various periodicities are grown after annealing the surface at higher temperatures than 1300°C. When the graphite layer grows across boundaries of two adjascent domains, the growing layer may be lifted up

at domain boundaries on the surface. As a result, the CNT's would begin to be formed from there.

Acknowledgments

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