Influence of heating rate upon the growth of carbon nanotubes by the SiC surface decomposition method

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Abstract. The effect of heating rate upon the formation of carbon nanotubes (CNTs) on a SiC(000\bar{1}) surface was investigated. The samples were heated to 1700 °C at a heating rate of 100–400 °C min⁻¹ in the ultrahigh vacuum (<1.0×10⁻⁸ Pa) or low vacuum (1.0×10⁻² Pa) chamber and held at temperature for 1 h. Sample cross sections were observed using transmission electron microscopy (TEM) with a 300 kV electron beam. When using a slow heating rate, CNTs are observed on the SiC(000\bar{1}) surface. However, when the heating rate exceeds 400 °C min⁻¹, an amorphous layer is formed on the interface between the CNT layer and the SiC substrate. It is thought that excess carbon atoms are decomposed and cannot form CNTs, but instead form an amorphous layer at the interface.

1. Introduction

Carbon nanotubes (CNTs) are one of the most interesting materials in nanotechnology and nanodevices, because of their superior structural, mechanical, chemical, thermal, and electrical properties [1–4]. After the discovery of CNTs was reported by Iijima in 1991 [5], much research has been carried out on the electric and mechanical properties of CNTs. As a result, it has been understood that CNTs have different physical properties according to their structure (tube diameter, chirality and type). In particular, the zigzag, armchair, and chiral type structures have been reported [6]. The armchair type exhibits metallic-like electrical characteristics; however, it has been known to have semiconductive characteristics like the chiral type. The zigzag type exhibits metallic or semiconductive characteristics.

Kusunoki et al. reported a surface decomposition method as one method for generating CNTs, where a SiC surface is annealed [7]. This method produces high density, highly aligned zig-zag type CNTs [8]. As this method does not require the use of a catalyst, impurities do not mix with the CNTs during the growth process. It is thought that the surface morphology, density of defects, annealing temperature, atmosphere at the surface and heating rate, etc. influence CNT generation by the surface decomposition method. It is known that CNTs are generated on the C-face of SiC(000\bar{1}) by this method, but are not grown on the Si-face. We reported that CNT growth can be suppressed depending on the morphology of the graphite layer on a SiC(000\bar{1}) surface [9]. In the present study, the heating rates used to achieve the annealing temperature were increased. Cross-sections of the annealed
samples were observed using transmission electron microscope (TEM), and the effect of the heating rate upon the formation of CNTs on a SiC(0001) surface was investigated.

2. Experimental Procedure

6H-SiC(0001) samples (nitrogen-doped, n-type, 1.0×7.0×0.33 mm³) were supplied by CREE Research. The samples were ultrasonically cleaned in acetone and ethanol for 5 min each, etched in hydrofluoric acid (5%), and then 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 a STM (Jeol JSTM-4500XT), a rear-view low energy electron diffraction (LEED) and sample-preparation facility for direct current heating. The samples were degassed in the UHV chamber for 12 h using resistive heating at a temperature of approximately 500 °C. After the degassing process, the samples were pre-annealed at 1250 °C for 30 min. The temperatures of the samples were measured with an optical pyrometer.

The formation of CNTs on the SiC(0001) surfaces was performed in another low vacuum chamber. This chamber was maintained at a pressure of 1.0×10⁻² Pa during the formation of CNTs. The chamber was equipped with a carbon-boat (thickness: 1 mm, size: 5.0×35 mm²), on which the samples were set. The samples were heated to 1700 °C at heating rates of 100 and 400 °C min⁻¹, and held at the temperature for 1 h. The interfaces formed on the SiC(0001) substrates were observed using a cross-sectional TEM (Hitachi, H-9000NAR), with a 300 kV electron beam.

3. Results and Discussion

Figure 1. Cross-sectional TEM image of the interface formed by pre-annealing a SiC(0001) surface at 1250 °C for 30 min in UHV, followed by annealing at 1700 °C (heating rate of 100 °C min⁻¹) for 1 h in a low vacuum.

Figure 1 shows a cross-sectional TEM image of the interface formed by pre-annealing a SiC(0001) surface at 1250 °C for 30 min in UHV, then at 1700 °C for 1 h in a low vacuum, with a heating rate of 100 °C min⁻¹. It was found that the SiC surface is decomposed by the annealing process, and CNTs are generated on the surface; CNTs in high density with excellent alignment and a mean length of approximately 57 nm were observed. Kusunoki et al. have reported that multi-wall CNTs are formed by the decomposition of a SiC(0001) surface [8]. It is thought that the CNTs grown in this study were multi-wall CNTs, because the CNT diameter was larger than ca. 1 nm, which is the usual diameter of single wall CNTs.

Figure 2. (a) Cross-sectional TEM image and (b) ED pattern of the interface formed by pre-annealing a SiC(0001) surface at 1250 °C for 30 min in UHV, followed by annealing at 1700 °C (heating rate of 400 °C min⁻¹) for 1 h in a low vacuum.
The cross-sectional TEM image of a SiC(0001) surface pre-annealed at 1250 °C for 30 min in UHV, followed by annealing at 1700 °C (heating rate of 400 °C min\(^{-1}\)) for 1 h in a low vacuum, is shown in Fig. 2. It was found that CNT growth occurs, even if the heating rate is increased. The mean length of the CNTs is approximately 48 nm. The top surface of the CNTs is flat, as was also observed for a heating rate of 100 °C min\(^{-1}\). However, a new layer appears at the interface between the CNTs and the SiC surface. The pattern of rings observed using electron diffraction (ED) confirms this new layer is an amorphous carbon layer.

Figure 3(a) shows the cross-sectional TEM image of the SiC surface pre-annealed at 1250 °C for 30 min in a low vacuum, with heating rate of 400 °C min\(^{-1}\). The sample was further annealed at 1700 °C for 1 h in a low vacuum at the same heating rate. The cross-sectional TEM image of the interface formed by annealing is shown in Fig. 3(b). The growth of CNTs is not confirmed at the surface of the sample pre-annealed at 1250 °C in a low vacuum. This indicates that at low vacuum and below 1250 °C, the surface does not decompose. However, CNTs were formed on the same surface when annealed at 1700 °C in low vacuum. It was found that annealing temperatures over 1250 °C were necessary for CNT growth on the SiC surface by the surface decomposition method under a low vacuum. When the SiC surface is annealed at 1700 °C (heating rate of 400 °C min\(^{-1}\)) in a low vacuum after pre-annealing at 1250 °C in a UHV, an amorphous carbon layer is formed. However, an amorphous carbon layer was not confirmed at the interface only of the low vacuum annealed sample, although similar annealing temperatures were used. In the surface decomposition method, the surface temperature is an important parameter, and assists in Si-C bond breaking. CNTs are generated when the SiC surface is annealed at 1700 °C, although CNT growth does not occur when pre-annealing at 1250 °C in a low vacuum (Fig. 3). This indicates that annealing the surface at 1250 °C in a low vacuum is not sufficient for decomposition of the SiC surface.

From Figs. 1 and 2, it was observed that an amorphous layer is formed at the interface of the CNTs and SiC substrate with an increase of the heating rate. The existence of the amorphous layer is not confirmed at a heating rate of 100 °C min\(^{-1}\) or less. However, the amorphous layer appears at the interface when the heating rate exceeds 400 °C min\(^{-1}\). It is not thought that this is directly related to the breaking of Si-C bonds, because the heating rate is different from the annealing temperature. For CNT generation by the surface decomposition method, decomposed Si becomes SiO and is desorbed. It is thought that oxygen is a residual gas at low vacuum, and a residual gas at the SiC substrate. We have reported that carbon nano-caps are formed on a SiC(0001) surface, after the surface is annealed in an UHV [9]. The carbon nano-caps are small protrusions seen at the early stage of growth. This means that surface decomposition takes place in an ultrahigh vacuum (a space with little residual gas). We propose the generation of oxygen as a remnant gas at the SiC substrate. When the heating rate is low, the time taken to reach the annealing temperature at which surface decomposition occurs is longer. Oxygen on the surface form SiO and O\(_2\), and these molecules desorb. However, it is thought that the oxygen atmosphere around the surface is fine, because oxygen is slowly got out from the surface if the heating rate is low. The time required to achieve the annealing temperature is shortened when the heating rate becomes high; therefore, oxygen is rapidly got out from the surface within a short time, and a dense oxygen atmosphere is formed. The growth rate of CNTs depends on the decomposition rate on the surface and the formation rate of CNTs. When the heating rate is high, the initial surface
decomposition rate becomes high, due to the presence of excess oxygen on the surface. As a result, the surface decomposition rate exceeds the formation rate of CNTs during the early growth stage. It is thought that the decomposition of excess carbon cannot form CNTs, and instead becomes an amorphous layer at the interface.

The sample annealed only in a low vacuum does not form an amorphous layer, although the heating rate is high (Fig. 3). However, for the sample annealed in UHV, followed by annealing in a low vacuum, an amorphous layer was confirmed at the interface (Fig. 1). A carbon nano-cap forms on the surface when annealing at 1200 °C in an UHV. Therefore, when this sample is annealed, CNTs are formed at once, because it has carbon nano-caps. The sample annealed only in a low vacuum previously forms a nano-cap, followed by CNT growth. In the case of the sample annealed in an ultrahigh vacuum, CNTs growth can occur at once, because the surface has carbon nano-caps. Since the heating rate is the same as that at low vacuum, the oxygen atmosphere is also similar in the growth early stage. The decomposition rate of SiC in the early growth stage of the CNTs is also the same as that at low vacuum.

For the annealing process in a low vacuum, it is supposed that the amorphous layer does not form, because the formation rate of nano-caps is smaller than the formation rate of CNTs. Therefore, an amorphous layer forms at the interface between the CNTs and the SiC substrate where nano-caps have formed on the surface. Interfacial structures in each annealing condition are shown in Table 1.

Table 1. Interfacial structures at each heating rate.(Pre-annealing temp.=1250 °C, annealing temp.=1700 °C)

| Heating rate(°C min⁻¹) | Pre-annealing in UHV +annealing in LV | Pre-annealing in LV +annealing in LV |
|------------------------|--------------------------------------|--------------------------------------|
| 100                    | only CNTs layer                       | only CNTs layer                       |
| 400                    | CNTs layer + amorphous carbon layer   | only CNTs layer                       |

4. Conclusion
The influence of the heating rate upon the growth of CNTs on the SiC(000 1) surfaces was investigated. In the case of a low heating rate, CNTs growth occurs on the SiC(000 1) surface. However, when the heating rate exceeds 400 °C min⁻¹, an amorphous layer is formed at the interface between the CNTs and the SiC substrate. Since the surface has excess oxygen when the heating rate is high, the initial surface decomposition rate becomes high. As a result, the surface decomposition rate exceeds the CNT formation rate of during the early growth stage. It is thought that decomposed excess carbon cannot form CNTs, and instead becomes an amorphous layer at the interface.

CNTs are formed when annealing at 1700 °C or more in a low vacuum. However, an amorphous layer is not formed even if the heating rate is 400 °C min⁻¹ in a low vacuum. It is proposed that the reason for this is that the formation rate of the nano caps is low compared with the formation rate of CNTs.

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