# Influence of oxygen on the growth of carbon nanotubes by the SiC surface decomposition method

T. Yamauchi[a,*], K. Nagamatsu[a], Y. Karayama[a], M. Naitoh[a], S. Nishigaki[a], H. Okado[b]

[a] *Department of Electrical Engineering and Electronics, Kyushu Institute of Technology, Sensui, Tobata, Kitakyushu, Fukuoka 804-8550, Japan*

[b] *Department of Applied Science for Integrated System Engineering, Kyushu Institute of Technology, Sensui, Tobata, Kitakyushu, Fukuoka 804-8550, Japan*

Abstract

The influence of oxygen on the development of carbon nanotubes (CNTs) during the annealing process of the surface decomposition method on SiC(000-1) surfaces was investigated. In the case of annealing a SiC substrate under ultra-high vacuum conditions, carbon nanofibers (CNFs) form between the CNT layer and the substrate. However, CNTs form without CNFs by annealing the substrate in an oxygen atmosphere. The mean length of CNTs is longer than those formed without an oxygen atmosphere. From cross sectional transmission electron microscopy images, it was found that oxygen plays an important role in CNT growth by the surface composition method.

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* Corresponding author. *E-mail address:* yamauchi@ele.kyutech.ac.jp (T. Yamauchi).

## 1. Introduction

The surface decomposition method is a simple growth method by which carbon nanotubes (CNTs) can be developed by annealing a SiC substrate under a low vacuum condition [1]. In this method, CNTs are grown without the catalytic assistance of metals, unlike other methods such as plasma-enhanced and chemical vapor deposition [2-4], arc discharge [5], etc., so that impurities are not mixed with the CNTs during the growth process. Moreover, this method produces high density and highly aligned zig-zag type CNTs [6].

We think that surface morphology, annealing temperature, atmosphere at the surface, and heating rate influence CNT generation by the surface decomposition method. It has been clarified that CNTs will organize only on the C-face of a SiC substrate, and not on the Si-face [7]. However, we have reported that CNT growth is suppressed if graphite layers are formed on the SiC substrate before the growth process [8]. The relation of the heating rate to CNT growth has also been examined. In the case of a low heating rate of 100 °C/min, CNTs grow on the SiC(000-1) surface. However, when the heating rate exceeds 400 °C/min, an amorphous layer is formed at the interface between the CNTs and the SiC substrate [9]. Kusunoki *et al*. reported that oxygen is involved in the mechanism of CNT growth by the surface decomposition method [10]. The purpose of this study is to investigate the influence of oxygen on the development of CNTs during the annealing process of the surface decomposition method.

## 2. Experimental

A 6H-SiC wafer with a (000-1) C-face was supplied by CREE Research. The wafer was cut into $1.0\times7.0\times0.33$ $mm^3$ sections. These samples were ultrasonically cleaned in acetone and ethanol for 5 min each, then rinsed in deionized water before being introduced into an ultra-high vacuum (UHV) chamber under a base pressure of $1.0\times10^{-8}$ Pa. The UHV chamber was equipped with an inlet valve for oxygen gas, a rear-view low energy electron diffractometer (LEED), and a sample preparation facility for direct current heating. The temperatures of the sample were measured with an optical pyrometer.

Samples were heated to 1250 °C at a rate of 100 °C/min, and held at temperature for 15 min to 2 h under several vacuum conditions. Oxygen gas was introduced to the UHV chamber using a variable leak valve. The amount of oxygen was determined from an ion gauge signal. CNT growth was carried out in an oxygen atmosphere at $5\times10^{-6}$ Pa. Samples were cut into three piece and polished to a thickness of 50 μm using diamond seats, and then thinned using a focused ion beam (FIB). Interfaces formed on the SiC(000-1) substrates were observed using a cross-sectional transmission electron microscope (TEM) (Hitachi TEM H-9000NAR) with a 300 keV electron beam.

## 3. Results and discussion

We have previously observed interfaces formed by annealing a SiC substrate at 1250 °C for 30 min in a low vacuum (LV; $1\times10^{-2}$ Pa), and reported that CNTs are not formed below 1250 °C in the LV condition [9]. However, the growth of CNTs under high vacuum conditions has not been clarified. The influence of the vacuum conditions on CNT generation was investigated. Firstly, the generation of CNTs was attempted in a high vacuum (HV; $2\times10^{-5}$ Pa) condition. Figures 1(a) and (b) show cross-sectional TEM images of interfaces formed by annealing SiC(000-1) surfaces at 1250 °C for 1 and 2 h in the HV condition. The SiC surfaces were decomposed by the annealing process, and CNTs were formed on the SiC substrates. CNTs were observed in excellent alignment with a mean length of approximately 150 nm and 210 nm for annealing times of 1 and 2 h, respectively. The mean length of the CNTs increases according to the annealing time. The interface between the CNT layer and the SiC substrate was not disordered for both annealing times examined.

Secondly, we attempted to form CNTs on a SiC substrate under UHV conditions ($6\times10^{-7}$ Pa). Cross-sectional TEM images of the interfaces formed by annealing SiC(000-1) substrates at 1250 °C for 15 min and 1 h in UHV are shown in Figs. 2(a) and (b), respectively. CNTs were grown on the SiC substrate for an annealing time o 15 min, and the interface structure was well ordered. The mean length of the CNTs was approximately 270 nm. This length is longer than that of CNTs formed by annealing for 1 h in a HV. Two carbon phases appeared after annealing for 1 h in the

UHV condition. One phase near the surface is CNT with a mean length of 350 nm and the other phase at the SiC side is carbon nanofibers (CNF) with a mean length of approximately 1.8 μm. They were identified by electron diffraction. The CNF layer is very thick compared to the CNT layer. This layer was not confirmed for the substrate annealed for 15 min in the UHV. That is to say, it is clear that the CNF layer is not generated in the early stage of surface decomposition under UHV conditions.

Electron diffraction (ED) patterns of the CNT layer and the new layer shown in Fig. 2(b) are given in Figs. 3(a) and (b). The ED pattern of the CNT layer consists of six-fold {10-10} streaks due to the diffraction from horizontal graphene net planes, and {0002} spots due to that from vertical planes of the well-ordered CNTs. This pattern is a typical pattern for the zigzag structure of CNTs. On the other hand, the ED pattern of the CNF layer shows {0002}, {0004}, {10-10} and {11-20} rings, which correspond to an ED pattern for carbon fibers [11].

The results for the growth of CNTs under HV and UHV conditions shows that CNTs grown under the UHV condition are longer than those grown under the HV condition. However, a CNF layer forms between the CNT layer and the SiC substrate with the passage of time. If Si atoms can be uniformly desorbed by the surface decomposition of the SiC surface, CNTs are formed while reflecting the substrate structure. It is understood that oxygen participates in the Si desorption reaction from the SiC surface [10]. Many works have been reported to the oxidation behavior of

SiC[12-14]. The oxidation of SiC can be classified into three features. There are an active oxidation, a passive oxidation and bubble formation. In the active oxidation, SiO molecules which oxidized at SiC surface desorbed from the surface. In the passive oxidation, the other words, the formation deposition of a $SiO_2$ on the SiC surface[15]. Maruyama et al. has been shown a phase diagram for the interaction of O2 with the SiC surface, showing the active-passive oxidation [16] At the high temperature, the active oxidation is possible even if the oxygen pressure is high. At the low temperature, on the other hand, the active oxidation is impossible and the oxidation of SiC becomes passive oxidation when the oxygen pressure is high.

The oxygen partial pressure under the HV condition is higher than that under the UHV condition. Therefore, the oxidation of SiC under the HV condition does not actively oxidize easily. The desorption of SiO under the HV condition was slower than that under the UHV condition, and CNTs were shorter. However, oxygen is almost exhausted at the stage where the surface is decomposed to some extent, because there is little oxygen under UHV conditions. The surface decomposition reaction should not advance under conditions with very little oxygen. Therefore, it is thought that CNTs do not develop, but instead CNFs are generated at the interface between the CNT layer and the substrate, because Si atoms at the surface are not uniformly removed.

CNT growth was then attempted in an oxygen atmosphere. Cross-sectional TEM images of the

interface formed by annealing at 1250 °C for 15 min and 2 h in an oxygen atmosphere of $5\times10^{-6}$ Pa are shown in Figs. 4(a) and (b). A CNF layer is not present at the interface of the CNT layer and the SiC substrate. The mean length of the CNTs grown over 15 min is approximately 250 nm. This length is almost the same as that for CNTs annealed for 15 min under UHV conditions. In addition, the length of the CNTs grown by annealing for 2 h is 760 nm. Therefore, it is clear that the growth rate of CNTs increases by annealing in an oxygen atmosphere.

The reaction for surface decomposition of SiC can be written as,

$SiC(s) + 1/2O_2(g) \rightarrow SiO(g) + C(s)$ .

Previously, Kusunoki *et al*. explained the mechanism of this reaction as follows [10]. Si atoms at the SiC surface are oxidized and a graphite sheet is formed by annealing above 1000 °C. Furthermore, the C-C bonds of the graphite sheet begin to break slightly with oxidation near 1300 °C, and oxygen penetrates the surface of the SiC substrate. Si atoms are selectively oxidized, and SiO molecules are formed and desorb from the substrate. At this time, the graphite sheet is deformed to form carbon nanocaps by SiO pressure. The carbon nanocaps formed develop into CNTs from the surface of substrate. This reaction is dominated by oxidation advancing from the surface.

Therefore, CNTs can grow easily during the early stage of CNT generation. However, CNT growth does not easily continue, so that supply of oxygen to the interface between CNTs and the SiC substrate is required for further CNT growth. The mean length of CNTs grown by annealing at

1250 °C for 15 min under UHV conditions is 270 nm, while that for 1 h is 350 nm. It was found that the growth rates decrease as CNT growth increases. In the case of annealing in an oxygen atmosphere, the oxygen supply to the interface increases, because the amount of oxygen around the substrate in the oxygen atmosphere is larger than that under UHV conditions. Therefore, Si atoms in the interface are uniformly removed by oxidation, and CNTs generation occurs.

On the other hand, in case of annealing under UHV conditions, CNFs are generated between the CNT layer and the substrate. When a stable oxygen supply is not available, the Si atoms are not uniformly removed. Oxygen cannot be easily supplied to the interface when the interface between the CNTs layer and the substrate reaches a certain depth. It is thought that the reason for CNF formation is the shortage of oxygen. Hence, CNF layer is not confirmed under the HV condition and the oxygen atmosphere. It is understood that the growth rate of CNFs is several times that of CNTs, because the CNF layer is very thick compared with the CNT layer. However, the mechanism for generation of the CNF layer by annealing the SiC substrate under UHV conditions has yet to be clarified.

## 4. Conclusions

The influence of oxygen on the development of CNTs on SiC(000-1) surfaces during annealing was investigated. In the case of annealing SiC(000-1) at 1250 °C for 15 min under UHV conditions,

CNTs with a mean length of 270 nm were generated. CNFs form between the CNT layer and the substrate with further annealing. However, CNTs are generated without CNF formation by annealing the substrate in an oxygen atmosphere, and the mean length of those CNTs is longer than those formed without an oxygen supply. Therefore, it is clear that oxygen plays an important role in CNT growth by the surface composition method.

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Figure captions

Fig. 1. Cross-sectional TEM image of interfaces formed by annealing SiC(000-1) surfaces at 1250 °C for (a) 1 h and (b) 2 h in a HV.

Fig. 2. Cross-sectional TEM image of interfaces formed by annealing SiC(000-1) surfaces at 1250 °C for (a) 15 min and (b) 1 h in an UHV.

Fig. 3. ED patterns of (a) the CNT layer and (b) the carbon nanofiber layer formed by annealing at 1250 °C for 2 h in UHV.

Fig. 4. Cross-sectional TEM images of interfaces formed by annealing SiC(000-1) surfaces at 1250 °C for (a) 15 min and (b) 2 h in an oxygen atmosphere ($5\times10^{-6}$ Pa).

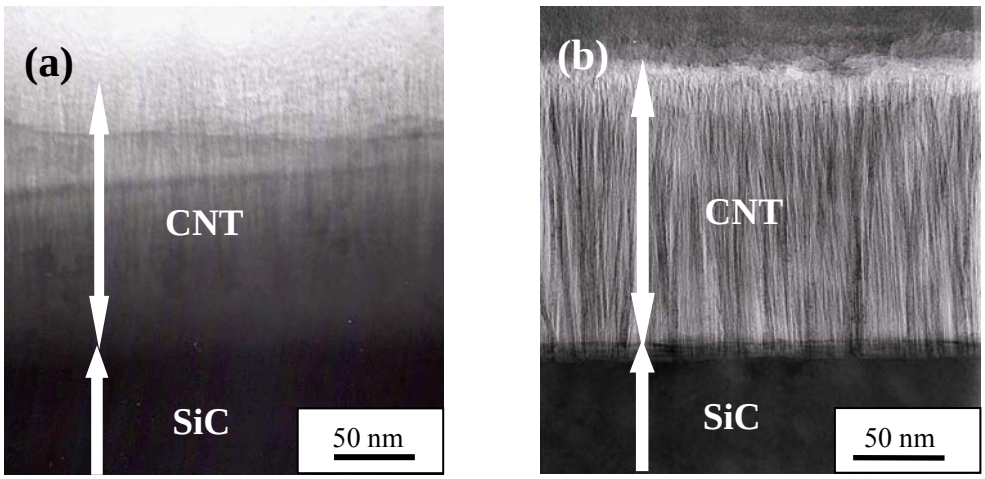


Fig. 1. Yamauchi *et al*.

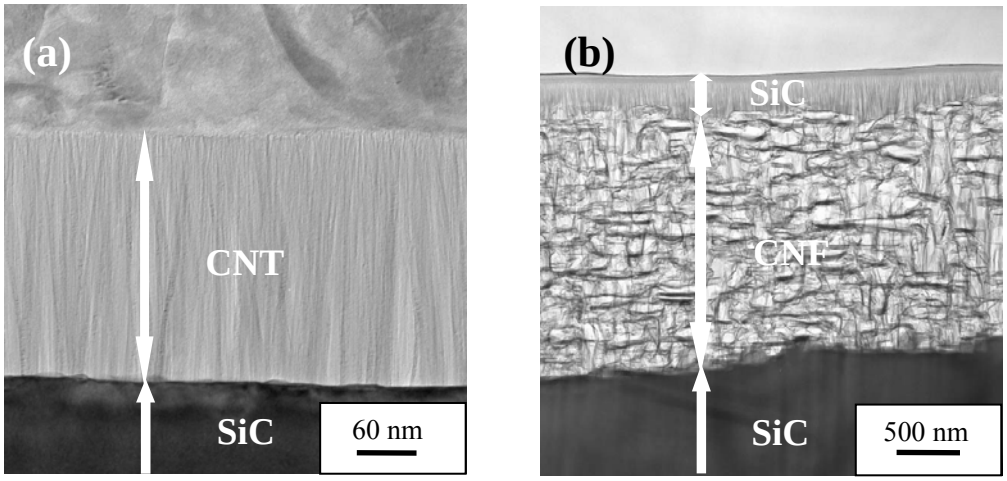


Fig. 2. Yamauchi *et al*.

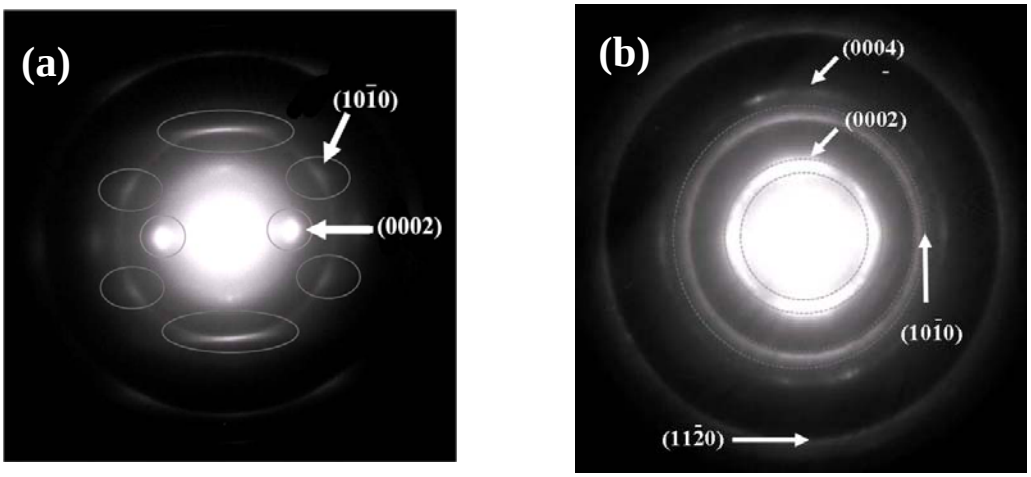


Fig. 3. Yamauchi *et al*.

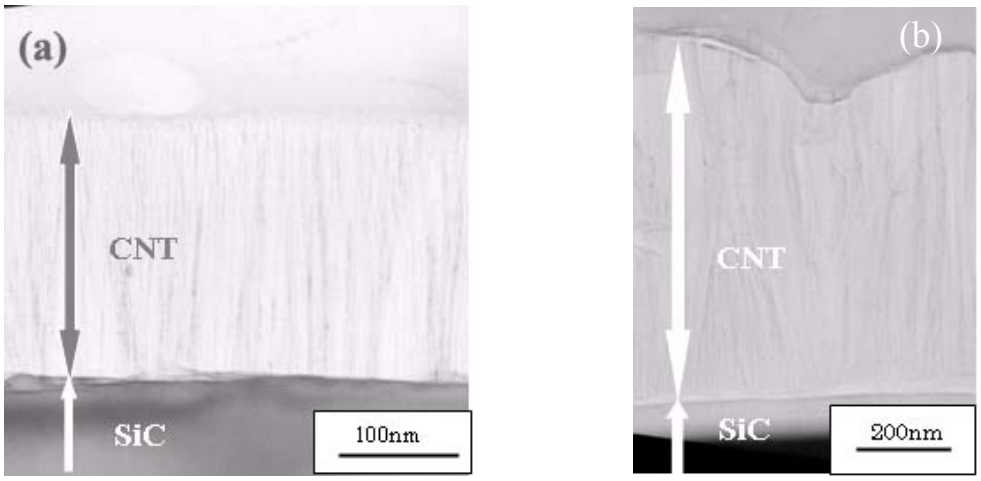


Fig. 4. Yamauchi *et al*.