

## **Growth control of carbon nanotubes on silicon carbide surfaces using the laser irradiation effect**

(former title: Formation of carbon nanotubes on silicon carbide surfaces and selective growth control by the laser irradiation)

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We have investigated laser irradiation effects on the growth of carbon nanotubes (CNTs) on 6H-SiC(000 $\bar{1}$ ) surfaces. CNTs were formed densely and uniformly after annealing a 6H-SiC(000 $\bar{1}$ ) surface at 1700°C in a vacuum, without laser-irradiation. However, amorphous carbon layers were formed on the 6H-SiC(000 $\bar{1}$ ) surface and the CNT growth was suppressed when the surface was irradiated by the ArF excimer laser with about 10mJ/cm<sup>2</sup> for 5min in air before being annealed.

*Keywords:* Nanotubes; Laser irradiation; Silicon carbide; Transmission electron microscope

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# 1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], many researchers have studied the synthesis of high-quality CNTs using various methods such as arc discharge [2], laser vaporization [3], pyrolysis [4,5], plasma-enhanced or thermal chemical vapor deposition (CVD) [6-8]. The remarkable structural, electrical and mechanical properties of CNTs have generated considerable interest in their application in many nanoelectronic devices, for example, field emission sources, scanning probes, nanotransistors, supercapacitors or rectifiers [9-11]. The field electron emitter working at relatively low voltages [12,13] would be of great technical importance in the applications of CNTs. In order to make nanoelectronic devices using CNTs, it is important to establish a technology of CNT growth at any locations of the substrate selected by exterior controls.

Kusunoki *et al.* have reported that CNTs with high-density and high-alignment are formed vertically on a  $6\text{H-SiC}(000\bar{1})$  surface by annealing the substrate at  $1700^\circ\text{C}$  in a vacuum furnace [14-17]. In this process, called surface-decomposition method, the CNTs have grown without any catalytic help of metals or gases. The surface on which CNTs have successfully grown is the polar  $(000\bar{1})$  surface, corresponding to the Si-terminated  $(0001)$  face. On the other polar face, the C-terminated  $(000\bar{1})$  surface, however, they could not obtain CNTs but did only several graphite layers parallel to the surface. It is suggested that the atomic structure of several upper most layers of the  $(000\bar{1})$  surface may be a key factor to form CNTs. If we can change the surface structure of selected areas using exterior stimulants such as laser light, it will become possible to make CNTs at desirable positions on the substrate.

In the present study we have investigated the laser-irradiation effects on the growth process of carbon nanotubes (CNTs) on  $6\text{H-SiC}$  surfaces. We report that, when the  $6\text{H-SiC}(000\bar{1})$  surface was irradiated by the ArF excimer laser before being annealed, the CNT growth was strongly suppressed, and, instead, amorphous carbon layers were formed on the surface.

## 2. Experimental

The 6H-SiC samples with  $(000\bar{1})$  or  $(0001)$  surfaces of the size  $1 \times 7 \times 0.33 \text{ mm}^3$  were quarried from nitrogen-doped  $n$ -type wafers supplied by CREE Research Inc. They were cleaned in acetone and rinsed in deionized water before being introduced into a vacuum chamber.

The base pressure of the chamber was maintained at  $1 \times 10^{-4}$  Pa during the sample annealing. The chamber was equipped with a carbon-boat (thickness:1mm, size: $5 \times 35 \text{ mm}^2$ ), on which the samples were set. The samples were annealed at  $1700^\circ\text{C}$  for 1 hour through the ohmic heating of the carbon-boat. The annealing temperature was measured with an optical pyrometer.

The samples were stimulated by the light of 193nm wavelength from an ArF excimer laser (in air before being annealed). The irradiated power was  $0.01 \text{ J/cm}^2$  times 5min. Also used was the light with a wavelength of 248nm from the KrF excimer laser with a power  $0.01 \text{ J/cm}^2$  times 7min. Formed interfaces on the 6H-SiC( $000\bar{1}$ ) and  $(0001)$  substrates were observed by a cross-sectional transmission electron microscope (TEM: H-9000NAR), using 300 kV electron beams.

## 3. Results and Discussion

Fig. 1a shows a cross-sectional TEM image of an interface formed by annealing the 6H-SiC( $000\bar{1}$ ) surface at  $1700^\circ\text{C}$  for 1 hour. We can observe high-density and excellent-alignment CNTs with a mean length of about 50nm. Kusunoki *et al.* reported that CNTs with a length of 170nm were formed by an annealing at  $1700^\circ\text{C}$  for half an hour [17]. There is a slight difference in the rate of the CNT formation between the two experiments. Although the two nominal rates of CNT formation cannot be directly compared with each other, because of differences in the base pressure or the quenching temperature of the substrates, it may safely be said that the present experiment reproduced well the result of

Kusunoki *et al.* and confirmed the growth condition for the CNTs.

Fig. 1b shows a cross-sectional TEM image of a 6H-SiC(0001) surface region obtained by the treatment of ArF laser-irradiation followed by the annealing at 1700°C for 1 hour. We notice an amorphous layer on the 6H-SiC(0001) surface. Its thickness reaches 35nm. We performed a chemical analysis for this amorphous layer by Auger electron spectroscopy, and detected only a signal corresponding to C species (not shown here). Therefore, we speculate that Si atoms are removed from the surface by the annealing and the carbon amorphous layer is formed there. Figs. 2a and 2b show cross-sectional TEM images obtained by annealing a non-irradiated, and an irradiated 6H-SiC(0001) surfaces, respectively. We can observe in Fig. 2a a thin layer whose thickness is 4nm. Taking into account the reported fact that graphite layers are formed on the 6H-SiC(0001) surface by annealing the surface at temperatures higher than 1250°C [17], this thin layer likely corresponds to the graphite layer.

When the laser-irradiated 6H-SiC(0001) surface was annealed, we found a formation of an amorphous carbon layer on the surface. Its thickness was 33nm. This value nearly coincides with that on the 6H-SiC(0001) surface. For the non-irradiated 6H-SiC(0001) surface, we found that the surface structure is hardly decomposed. This result indicates that graphite layers, formed on the 6H-SiC(0001) surface, suppress either the formation of the amorphous carbon layer or the elimination of the Si atoms from the surface.

Fig. 3 shows a cross-sectional TEM image of an interface region formed by annealing the 6H-SiC(0001) at 1700°C for 1 hour after KrF excimer laser irradiation. CNTs were formed on the 6H-SiC(0001) in spite of carrying out the laser irradiation.

From these experimental results we consider possible effects of the laser irradiation onto the 6H-SiC(0001) surface along the proposed growth mechanism in the surface decomposition method. In this method, Si atoms that compose the 6H-SiC(0001) substrate lattice are removed from the surface region in the initial stage of annealing and C atoms that are left behind form a graphite layer parallel to the surface. Moreover, the graphite layer

changes its shape to a cap of nanometer-scale by prolonged annealing, and then, the cap would become a precursor for the CNT formation. From their scanning tunneling microscopy (STM) observation Naitoh *et al.* reported that many domains, each of which is a single graphite sheet, appeared after annealing the  $6\text{H-SiC}(000\bar{1})$  surface at  $1200^\circ\text{C}$  [18]. Crystallographic directions of those graphite domains were azimuthally disordered. By annealing the surface at higher temperatures than  $1300^\circ\text{C}$ , they obtained multi-sheet graphite domains. We speculate that caps were formed owing to the decomposition of graphite layers in the domains by the additional annealing.

On the  $6\text{H-SiC}(0001)$  surface, graphite layers are also formed but their crystallographic directions are azimuthally ordered well. These graphite layers on the  $6\text{H-SiC}(0001)$  surface do not change to caps in the annealing process. They tend to play a role of suppressing the desorption of Si atoms. The interaction between the graphite layers on the  $6\text{H-SiC}(0001)$  surface would be stronger than those on the  $6\text{H-SiC}(000\bar{1})$  surface. Such a difference may cause the suppression of CNT precursor formation on the  $6\text{H-SiC}(0001)$  surface.

The laser irradiation induces breaking of surface bonds. The surface structure is changed from the original one of the non-irradiated  $6\text{H-SiC}(000\bar{1})$  surface, which was suitable for the CNT growth, to a modified structure. As a result, CNTs do not grow but amorphous carbon layers are formed after annealing the modified surface. The wavelengths of the lights from the ArF excimer laser and the KrF excimer laser used in this experiment are 193nm and 248nm, respectively. Their photon energies are 6.4eV and 5.0eV. The dosed power was approximately the same for the two cases. The extent of surface restructuring induced by the laser irradiation would depend on the photon energy. Further experiment is needed in this respect. For the  $6\text{H-SiC}(0001)$  surface, amorphous carbon layers are formed, instead of graphite layers, after annealing the surface with laser irradiation. The amorphous carbon layer grown on the  $6\text{H-SiC}(0001)$  surface is as thick as that on the  $6\text{H-SiC}(000\bar{1})$  surface. The effect of laser irradiation on the surface restructuring is substantially the same for the (0001) and the (000 $\bar{1}$ )

surfaces.

## 4. Conclusions

We have shown that the CNT growth can be controlled by using the ArF excimer laser. CNTs with high-density and high-alignment were formed by annealing the non-irradiated 6H-SiC(0001) surface, at 1700°C in a vacuum. However, amorphous carbon layers, instead of CNTs, were formed on the 6H-SiC(0001) surface when the surface was irradiated by the ArF excimer laser with about 10mJ/cm<sup>2</sup> for 5min in air before being annealed. There may be high potentialities in a technique of surface modification by ArF excimer laser irradiation for the CNT growth control in order to use CNTs in the development of new-type electronic devices.

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Fig. 1. Cross-sectional TEM images of interfaces formed by annealing the  $\text{SiC}(000\bar{1})$  surfaces at  $1700^\circ\text{C}$  for 1 hour, (a) without and (b) with the ArF excimer laser irradiation.

Fig. 2. Cross-sectional TEM images of interfaces formed by annealing the  $\text{SiC}(000\bar{1})$  surfaces at  $1700^\circ\text{C}$  for 1 hour, (a) without and (b) with the ArF excimer laser irradiation.

Fig. 3. A cross-sectional TEM image of an interface formed on the  $\text{SiC}(000\bar{1})$  surface by the treatment of KrF excimer laser irradiation followed by annealing at  $1700^\circ\text{C}$  for 1 hour.

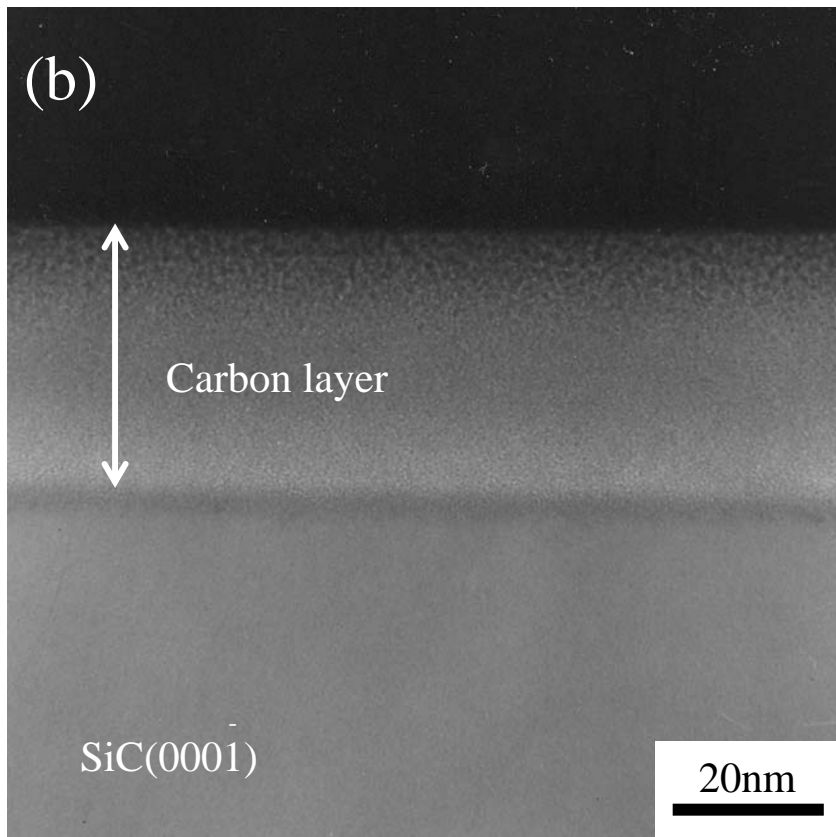
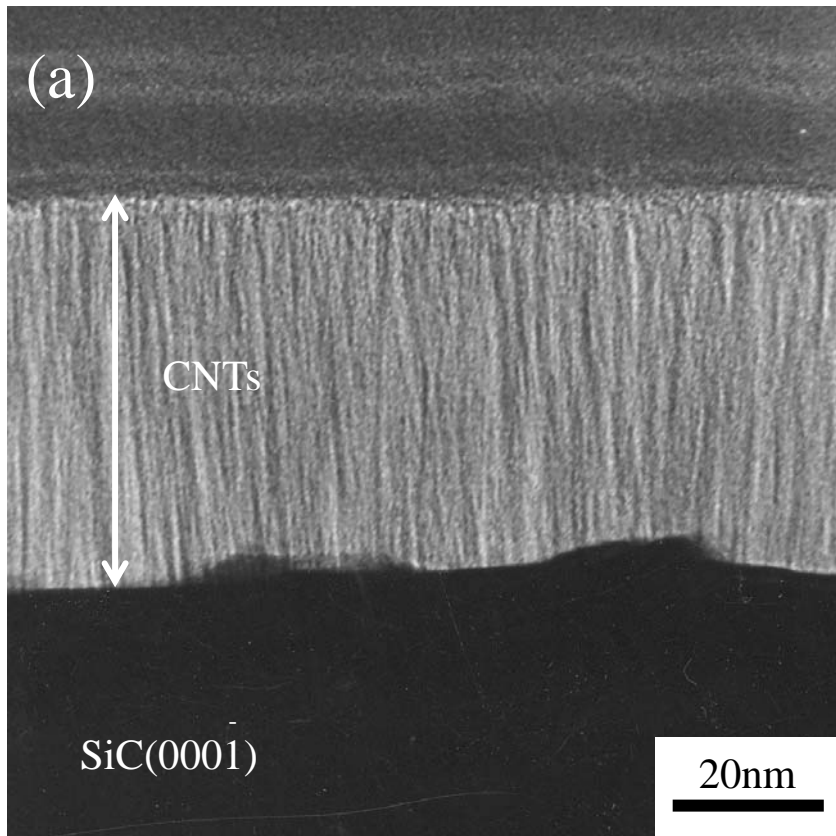


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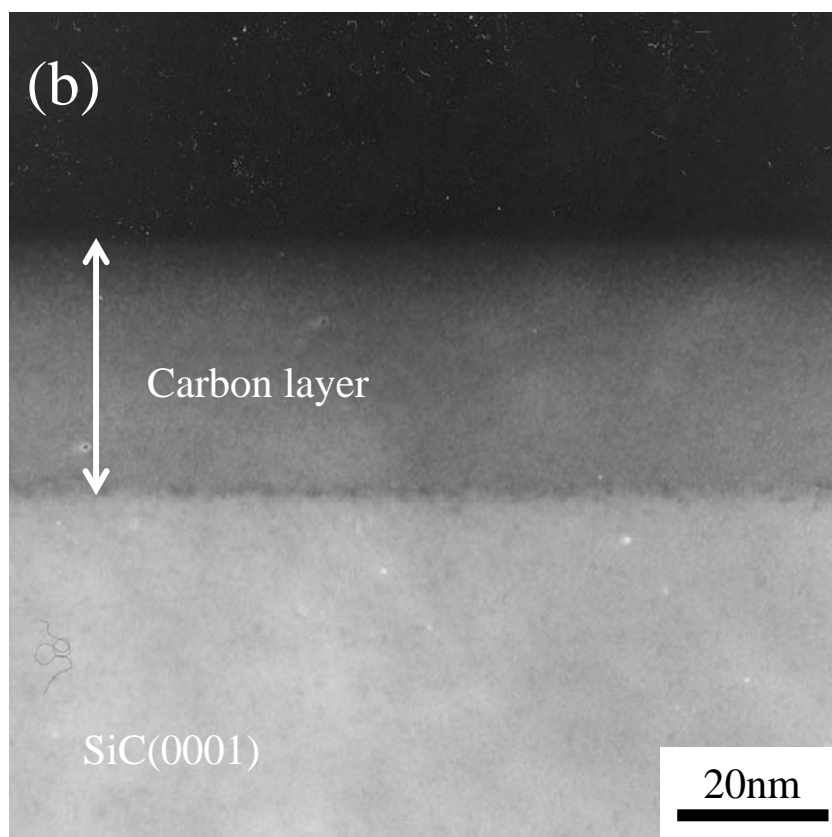
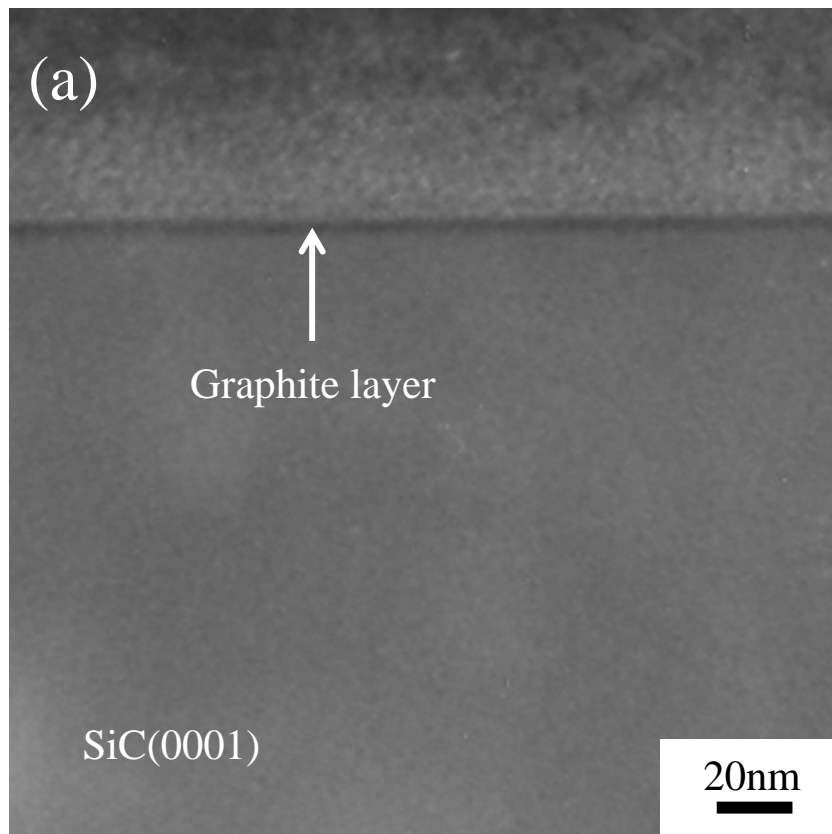


Fig.2. H. Konishi *et al.*

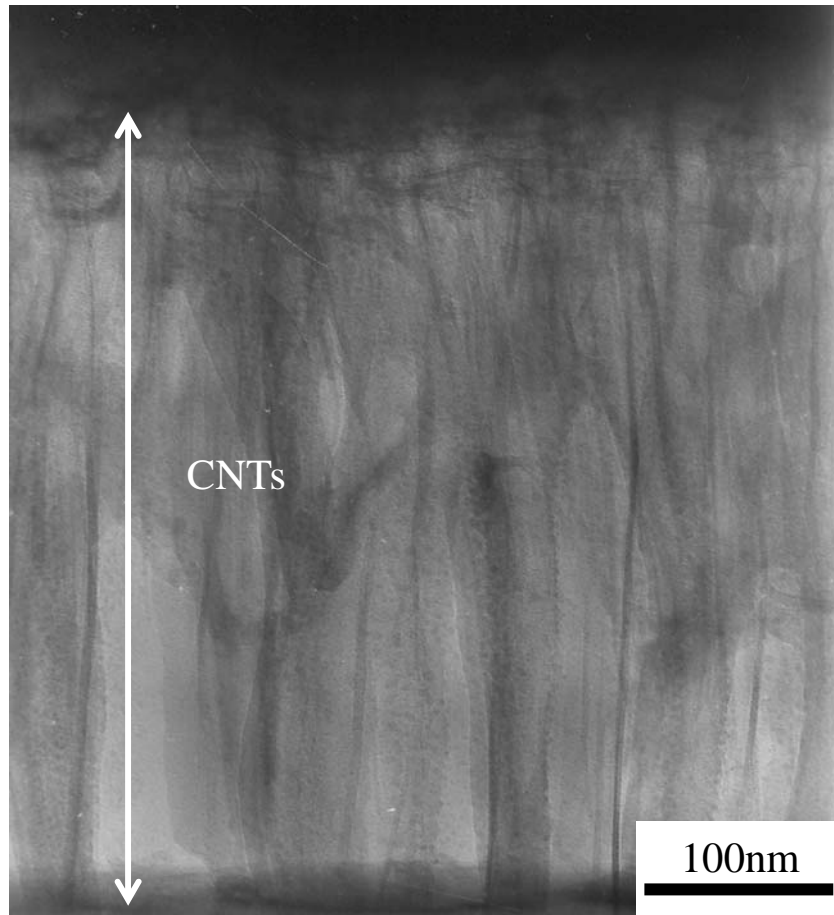


Fig.3. H. Konishi *et al.*