

In situ NEXAFS Analysis of the Formation of Carbon Nanotubes by Thermal Decomposition of SiC(000 $\bar{1}$) Surface

We performed *in situ* carbon K-edge NEXAFS (near-edge X-ray absorption fine structure) measurements at high temperatures to clarify the process of formation of carbon nanotubes (CNTs) by thermal decomposition of the SiC(000 $\bar{1}$) surface. Above 1000°C, Si atoms desorbed, and subsequent graphitization of the remaining carbon atoms occurred. Upon heating above 1300°C, the graphene flakes were initially oriented parallel to the surface, but their orientations changed toward the surface normal during the progression of CNT formation. In addition, at the initial stage, aromatic fragments composed of a few carbon hexagons were present parallel to the surface. These results suggest that the graphitization to CNTs occurred above 1000°C with the desorption of Si atoms utilizing the dangling bonds of carbon atoms on the SiC surface.

Synthesis of aligned carbon nanotube (CNT) films on an SiC(000 $\bar{1}$) surface by thermal decomposition is a unique technique because high-density zigzag-type multi-walled CNTs can be selectively produced by simply heating the SiC(000 $\bar{1}$) surface in vacuum [1]. At the beginning of the CNT growth, cap-like structures comprising hemispherical graphene layers, i. e., “carbon nanocaps,” are formed on the SiC surface [2, 3]. Although these carbon nanocaps determine the CNT diameters, their formation mechanism has been poorly understood. In this study, we performed *in situ* carbon K-edge near-edge X-ray absorption fine structure (NEXAFS) measurements and clarified the true process of formation of CNTs.

The carbon K-edge NEXAFS measurements were performed at BL-7A. After HF etching, 6H-SiC(000 $\bar{1}$) C-face substrates were introduced into the NEXAFS analysis chamber and heated to the target temperature in H₂

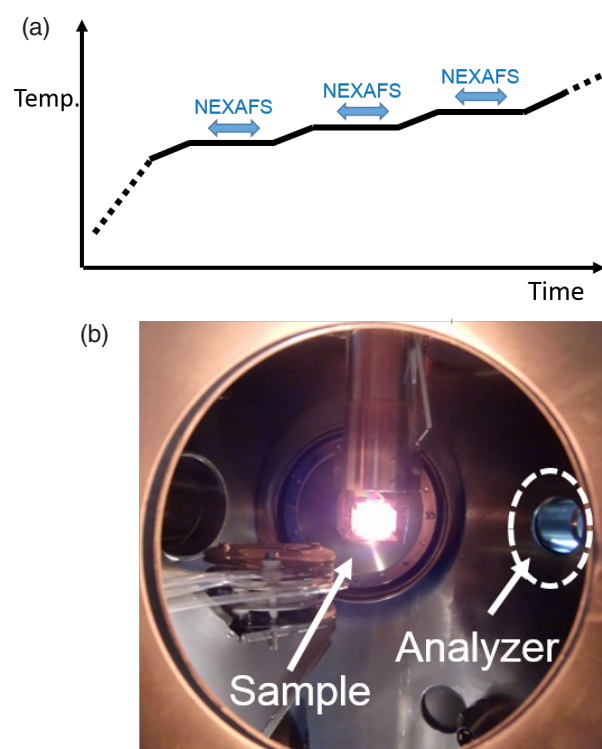


Figure 1: (a) Schematic diagram of the temperature rise process for the NEXAFS measurements. (b) Photograph of the sample in the analysis chamber. (c) Schematic diagram of the geometry of the sample and analyzer in the NEXAFS chamber.

at a pressure of 1×10^{-2} Pa, and then NEXAFS measurements were performed in ultra-high vacuum (UHV). A schematic temperature rise diagram for the NEXAFS measurements is shown in Fig. 1a. The samples were heated using a PBN heater, and the temperature of the sample surface was monitored with an infrared pyrometer. A photograph of the sample heated at 1300°C in the analysis chamber is shown in Fig. 1b.

The NEXAFS spectra were obtained in the Auger electron yield detection mode by monitoring the KLL carbon Auger peak by a hemispherical electron energy analyzer (Gammadata Scienta SES-200) because it is highly surface sensitive and suitable for the detection of thin carbon layers on the SiC surface. A schematic diagram of the location of the sample relative to the synchrotron radiation beam is shown in Fig. 1c.

To investigate the orientation of the C–C bonds utilizing the photon linear polarization, we performed the NEXAFS measurements at two incident angles (θ), 30° and 90°. In addition, X-ray photoelectron spectroscopy (XPS) measurements were performed just before and soon after each NEXAFS measurement with a photon energy of 430 eV for investigating the surface composition and estimating the thickness of the CNT layers on the SiC surface.

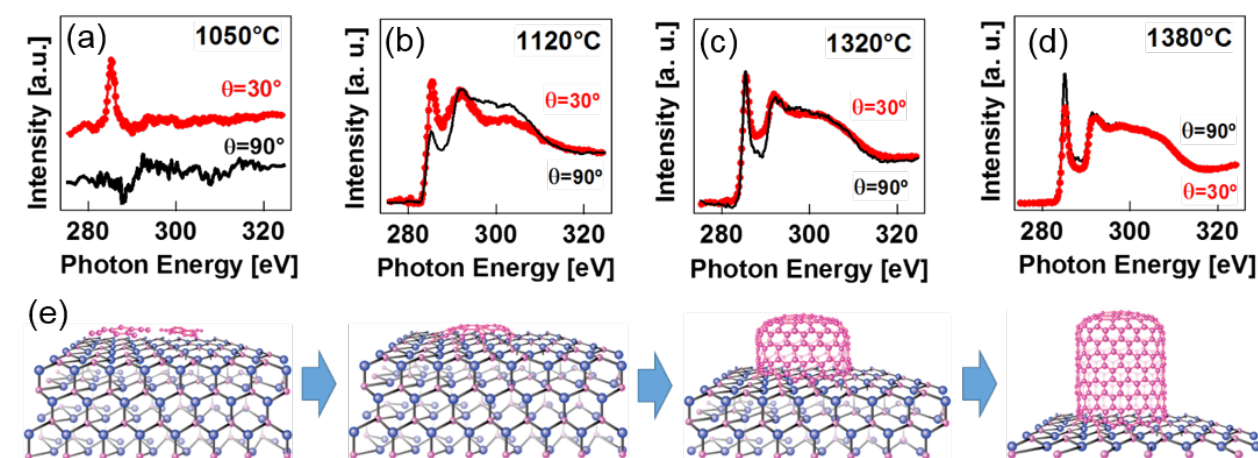


Figure 2: C K-edge NEXAFS spectra of SiC C-face during heating at (a) 1050°C, (b) 1120°C, (c) 1320°C, and (d) 1380°C. For heating at 1050°C, the difference spectra after subtraction of the pristine SiC C-face spectra, are shown. All spectra were measured at two incident angles, $\theta = 30^\circ$ and 90° . (e) The growth process images of CNTs on the SiC C-face by thermal decomposition.

The *in situ* carbon K-edge NEXAFS spectra for the SiC C-face are shown in Fig. 2 [4]. Figure 2a shows the difference spectra, in which the NEXAFS spectra for the pristine SiC C-face were subtracted from those at 1050°C. A sharp π^* resonance peak with a negligible weak σ^* resonance feature appeared at $\theta = 30^\circ$, and the former disappeared at $\theta = 90^\circ$. Taking into account the NEXAFS spectra of molecules with conjugated bonds on solid surfaces [5], this spectral shape suggests the formation of aromatic fragments composed of a few carbon hexagons parallel to the SiC surface soon after desorption of Si atoms by heating. Figure 2b–d show the *in situ* NEXAFS spectra for the SiC C-face at 1120, 1320, and 1380°C. At 1120°C, the π^* resonance peaks appeared for both incidence angles, indicating that carbon materials composed of sp^2 orbitals accumulated on the SiC surface. The π^* resonance peak for $\theta = 30^\circ$ was higher than that for $\theta = 90^\circ$, which was similar to that for graphite [6], indicating that crystallization occurred to form graphene-like layers, which were mostly parallel to the surface. At 1320°C, the spectral shapes became approximately the same for the two incidence angles, and when the sample temperature rose to 1380°C, the intensity of the π^* resonance peak at $\theta = 90^\circ$ was stronger than that at $\theta = 30^\circ$. These spectra show that the orientation of the C–C bonds changed with the increase in temperature, and that a majority of the graphene-like carbon is oriented perpendicular to the surface at 1380°C.

Taking into account the NEXAFS results and the CNT length estimated from the XPS measurements, simplified images of the proposed growth process of CNTs on the SiC C-face are shown in Fig. 2e. At the beginning of desorption of Si atoms, the graphene layers parallel to the surface corresponding to the top layers of carbon nanocaps are formed. Then, carbon

nanocaps are formed with a further progression of desorption of Si atoms. As the CNT formation proceeds, the cylindrical parts of the CNTs become longer, and the ratio of graphene sheets perpendicular to the surface increases. This formation process was consistent with a recent density-functional tight-binding molecular dynamics (DFTB/MD) simulation [7], and the orientation change toward the surface normal is considered to be caused by the dangling bonds of residual carbon atoms on the SiC surface. Our result shows the possibility of controlling the diameter and the number of walls of CNTs through the decomposition process, which might lead to fabrication of CNT devices.

REFERENCES

- [1] M. Kusunoki, C. Honjo, T. Suzuki and T. Hirayama, *Chem. Phys. Lett.* **366**, 458 (2002).
- [2] M. Kusunoki, T. Suzuki, T. Hirayama, N. Shibata and K. Kaneko, *Appl. Phys. Lett.* **77**, 531 (2000).
- [3] T. Maruyama, T. Shiraiwa, N. Fujita, Y. Kawamura, S. Naritsuka and M. Kusunoki, *Jpn. J. Appl. Phys.* **45**, 7231 (2006).
- [4] T. Maruyama, S. Naritsuka and K. Amemiya, *J. Phys. Chem. C* **119**, 26698 (2015).
- [5] N. Witkowski, F. Hennies, A. Pietzsch, S. Mattsson, A. Föhlisch, W. Wurth, M. Nagasono and M. N. Piancastelli, *Phys. Rev. B* **68**, 115408 (2003).
- [6] S. Banerjee, T. H.-Benny, S. Sambasivan, D. A. Fischer, J. A. Misewich and S. S. Wong, *J. Phys. Chem. B* **109**, 8489 (2005).
- [7] N. Ogasawara, W. Norimatsu, S. Irie and M. Kusunoki, *Chem. Phys. Lett.* **595–596**, 266 (2014).

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