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# Infrared reflection absorption spectroscopy investigation of carbon nanotube growth on cobalt catalyst surfaces

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To clarify the effect the oxygen has on the carbon nanotube (CNT) growth mechanisms, the authors use infrared absorption spectroscopy for the monitoring of CNT growth on cobalt catalyst surfaces. CNT grew when methanol was used as a reaction gas, while they did not grow when methane was used. The authors observed spectral changes due to the formation of cobalt oxides and methoxides on the cobalt catalyst surfaces only during the growth of CNT. The results indicate that partial oxidation of the cobalt catalyst surface increases the adsorption probability of the reaction gas and ultimately induces growth of CNT. © 2007 American Institute of Physics.

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Carbon nanotubes (CNTs) are easily fabricated from carbon hydride gases using a metal catalyst.<sup>1</sup> Furthermore, CNTs have many interesting and useful properties, for example, they (1) are lightweight and have high elasticity and strength as well,<sup>2-4</sup> (2) have high chemical resistance and a high melting point,<sup>2-4</sup> and (3) have alternative conduction characteristics (a conductor or a semiconductor).<sup>5-7</sup> Therefore, CNTs have been widely studied as one of the most fundamental materials for nanoelectronics and bioelectronics. For example, the use of CNTs as a via interconnect in LSI technology is studied, focusing on their metallic characteristics.<sup>8</sup> However, it is difficult to control the properties of CNT and to produce highly dense CNT. Especially, for applications of CNTs to electronic devices, control of the electric properties is required. Therefore, it is necessary to elucidate the growth mechanism of CNT, and it is especially quite important to reveal the chemical reaction of carbon hydride gases on metal catalysts, nevertheless the detail of the reaction process on the metal surface under the condition of CNT growth has not been reported. Recently, it was reported that highly dense CNTs are grown by introducing a carbon hydride gas containing a small percentage of water molecules and that oxygen atoms or water molecules would enhance CNT growth, i.e., oxygen atoms are key to CNT growth on metal catalyst.<sup>9,10</sup>

Here, we report on the observation of the infrared (IR) absorption of CNT on cobalt nanodot catalyst surfaces using infrared reflection absorption spectroscopy (IR-RAS). CNTs

are grown by thermal chemical vapor deposition (CVD) with either methanol ( $\text{CH}_3\text{OH}$ ) or methane ( $\text{CH}_4$ ).

Cobalt catalyst substrates were prepared by radio frequency sputtering a 6 nm film of titanium followed by a 2.5 nm film of cobalt on *p*-type Si (001). CNTs were grown in vacuum on the as-prepared substrates at a growth temperature of 600 °C by introducing  $\text{CH}_4$  or  $\text{CH}_3\text{OH}$  in the vacuum chamber. Growth times were from 1 to 120 min under a gas pressure of 1 kPa and substrate temperatures were quenched during the collection of IR spectra. Figure 1 shows a schematic of the vacuum chamber and IR detection setup. Briefly, an IR light beam from an interferometer (ABB, workir) was focused through a potassium bromide (KBr) window with the vacuum chamber onto the substrate surface at an incident angle of 80° off normal, and then the reflected IR beam was detected with a deuterium triglycine sulfate detector with a resolution of 4  $\text{cm}^{-1}$ .

Figure 2 shows IR-RAS spectra for the cobalt catalyst surfaces collected after introducing (a)  $\text{CH}_3\text{OH}$ , (b) water,

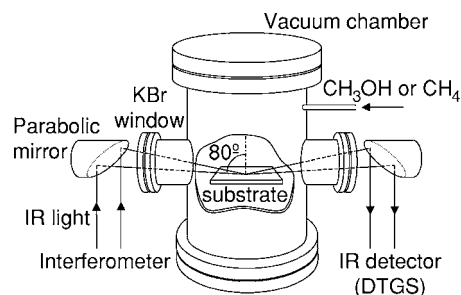


FIG. 1. Schematic of the vacuum chamber and IR detection setup.

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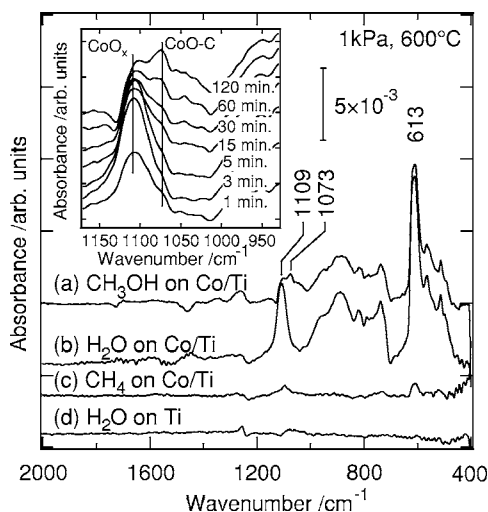


FIG. 2. IR-RAS spectra for the cobalt catalyst surfaces collected after introducing (a)  $\text{CH}_3\text{OH}$ , (b) water, and (c)  $\text{CH}_4$  of 1 kPa at a substrate temperature of  $600^\circ\text{C}$  for 2 h, and (d) for the titanium surfaces exposed to water in the same condition. The insertion shows the time evolution of IR-RAS spectra in the region of the C–O stretching vibration mode during CNT growth using  $\text{CH}_3\text{OH}$ .

and (c)  $\text{CH}_4$  of 1 kPa at a substrate temperature of  $600^\circ\text{C}$  for 2 h, and (d) for the titanium surfaces exposed to water in the same condition. An IR spectrum before gas introduction was used as reference.

Absorption peaks and bands appear in the case of introducing  $\text{CH}_3\text{OH}$ , while IR spectral changes are negligible in the case of introducing  $\text{CH}_4$ . The lack of spectral changes for  $\text{CH}_4$  indicates that chemical reactions did not take place on the cobalt catalyst surfaces. Figure 3 shows Raman spectra and field emission scanning electron microscope (FE-SEM) images for the substrate surfaces after introducing (a)  $\text{CH}_3\text{OH}$  and (b)  $\text{CH}_4$ . The Raman spectra and the FE-SEM images confirmed that CNT did not grow when using  $\text{CH}_4$ . On the other hand, the *G* and *D* bands of multiwalled CNT were observed in Raman spectra and CNT growth was also confirmed in the FE-SEM image for growths using  $\text{CH}_3\text{OH}$ , indicating that the presence of oxygen is critical to the growth of CNT on cobalt catalyst surfaces.

To investigate the effect the oxygen has on chemical reactions on cobalt catalyst surfaces, we exposed the surface to water at 1 kPa at  $600^\circ\text{C}$ . As shown in Fig. 2(b), in the

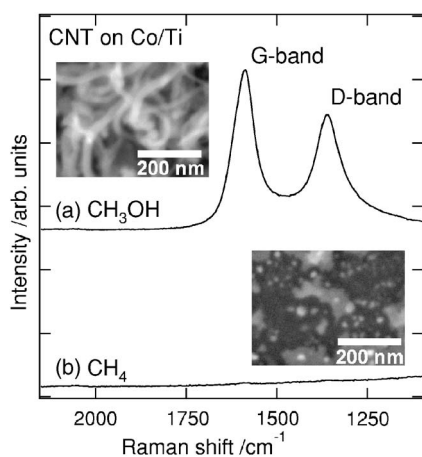


FIG. 3. Raman spectra and FE-SEM images for the substrate surfaces after introducing (a)  $\text{CH}_3\text{OH}$  and (b)  $\text{CH}_4$ .

case of introducing water, two peaks appear at 613 and  $1109\text{ cm}^{-1}$  and a band is observed between  $700$  and  $1000\text{ cm}^{-1}$ . On the other hand, as shown in Fig. 2(d), they are not observed in an IR spectrum for the titanium film surface exposed to water in the same condition. Therefore, the appearance of these peaks and band in Fig. 2(b) indicates that water molecules oxidize the cobalt catalyst surfaces. The peaks at 613 and  $1109\text{ cm}^{-1}$  are due to the LO phonon mode of Co–O (Refs. 11 and 12) and the vibration mode of the topmost layer of cobalt oxides such as  $\text{CoOCo}$ ,<sup>13</sup> respectively. The absence of the LO phonon mode around  $690\text{ cm}^{-1}$  indicates formation of cobalt oxides with a low symmetry,<sup>14</sup> that is, the cobalt oxides are very thin and have a complicated structure. Interestingly, the peaks and the band due to cobalt oxides are also observed in the case of CNT growth using  $\text{CH}_3\text{OH}$  [Fig. 2(a)], although their intensity is small compared to the case of introducing water. That is, cobalt catalyst surfaces are partially oxidized during CNT growth. On the other hand, in the case of introducing  $\text{CH}_4$ , cobalt catalyst surfaces are hardly oxidized as seen by the lack of IR spectral changes [Fig. 2(c)]. These results indicate that partial oxidation of the cobalt catalyst surfaces likely induces CNT growth.

The insertion in Fig. 2 shows the time evolution of IR-RAS spectra in the region of the C–O stretching vibration mode during CNT growth using  $\text{CH}_3\text{OH}$ . A peak at  $1073\text{ cm}^{-1}$  can clearly be seen, which was not present in the IR spectrum for cobalt surfaces oxidized by water [Fig. 2(b)]. The peak intensity increased with time, indicating that the cobalt catalyst surface was active after quenching the substrate temperature. It is therefore likely that this peak is due to  $\text{CH}_3\text{OH}$  molecules adsorbed on cobalt catalyst surfaces. It was reported that  $\text{CH}_3\text{OH}$  molecules adsorbed via an oxygen atom on cobalt surfaces to generate methoxide<sup>15</sup> and that the C–O stretching vibration mode of methoxide on the partially oxidized cobalt surface appears at  $1063\text{ cm}^{-1}$ , which was observed by high-resolution electron energy loss spectroscopy.<sup>16</sup> Therefore, appearance of the peak at  $1073\text{ cm}^{-1}$  [Fig. 2(a) and the insertion in Fig. 2] indicates the formation of methoxide on cobalt catalysts. In the insertion in Fig. 2, the C–O stretching vibration mode of methoxide hardly appeared at the initial stage of CNT growth and its intensity drastically increased after growth of the surface cobalt oxide peak at  $1109\text{ cm}^{-1}$ . Chen and Friend reported that partial oxidation of the cobalt surface can change the reactivity of it.<sup>16</sup> Therefore, the time evolution of IR spectra in the insertion in Fig. 2 indicates that the cobalt oxide or the interface between the cobalt oxide and the metal cobalt increases the adsorption probability of the reaction gas, and ultimately induces the growth of CNT. The mechanism of CNT growth on cobalt catalyst is as follows. The methoxide formed on the cobalt oxide or at the interface decomposes and carbon is dissolved in the cobalt catalyst. Oxygen oxidizes the cobalt catalyst surfaces. The dissociation of methoxides also produces hydrogen. Some volatilizes and some reduces oxides on the cobalt catalyst. Finally, CNTs grow using carbon dissolved in the cobalt catalyst.<sup>17</sup>

In summary, in this study, we investigated the CNT growth process using IR-RAS. CNTs were grown on cobalt catalyst surfaces by thermal CVD process and monitored by IR-RAS. CNT grew in the presence of  $\text{CH}_3\text{OH}$  only and was confirmed with Raman spectroscopy and scanning electron microscopy. Absorption peaks and a band due to cobalt ox-

ides were observed by IR-RAS. We observed the growth of a peak at  $1073\text{ cm}^{-1}$ , which is due to methoxide adsorbed on the cobalt catalyst surfaces. These results indicate that oxygen plays an important role in the CNT growth mechanism and that partial oxidation of the cobalt catalyst surfaces might increase the adsorption probability of the reaction gas as well as induce the CNT growth.

<sup>1</sup>S. Iijima, *Nature (London)* **354**, 56 (1991).

<sup>2</sup>Hsu-Chiang Kuan, Chen-Chi M. Ma, Wei-Ping Chang, Siu-Ming Yuen, Hsin-Ho Wu, and Tzong-Ming Lee, *Compos. Sci. Technol.* **65**, 1703 (2005).

<sup>3</sup>T. Natsuki and M. Endo, *Appl. Phys. A: Mater. Sci. Process.* **A80**, 1463 (2005).

<sup>4</sup>M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, *Nature (London)* **381**, 678 (1996).

<sup>5</sup>Kazuyoshi Tanaka, Kenji Okahara, Mayumi Okada, and Tokio Yamabe, *Chem. Phys. Lett.* **191**, 469 (1992).

<sup>6</sup>Kenji Okahara, Kazuyoshi Tanaka, Hiroo Aoki, Tohru Sato, and Tokio

Yamabe, *Chem. Phys. Lett.* **219**, 462 (1992).

<sup>7</sup>Noriaki Hamada, Shin-ichi Sawada, and Atsushi Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).

<sup>8</sup>Mizuhisa Nihei, Masahiro Horibe, Akio Kawabata, and Yuji Awano, *Jpn. J. Appl. Phys., Part 1* **43**, 1856 (2004).

<sup>9</sup>Kenji Hata, Don N. Futaba, Kohei Mizuno, Tatsunori Namai, Motoo Yumura, and Sumio Iijima, *Science* **306**, 1362 (2004).

<sup>10</sup>Don N. Futaba, Kenji Hata, Takeo Yamada, Kohei Mizuno, Motoo Yumura, and Sumio Iijima, *Phys. Rev. Lett.* **95**, 056104 (2005).

<sup>11</sup>M. Lenglet, J. Lopitiaux, L. Terrier, P. Chartier, J. F. Koenig, P. Nkeng, and G. Poillerat, *J. Phys. IV* **3**, 447 (1993).

<sup>12</sup>P. Nkeng, J.-F. Koenig, J. L. Gautier, P. Chartier, and G. Poillerat, *J. Electroanal. Chem.* **402**, 81 (1996).

<sup>13</sup>Federico Grillo, Marta Maria Natile, and Antonella Glisenti, *Appl. Catal., B* **48**, 267 (2004).

<sup>14</sup>Tao Sun, Michel L. Trudeau, and Jackie Y. Ying, *J. Phys. Chem.* **100**, 13662 (1996).

<sup>15</sup>D. A. Chen and C. M. Friend, *J. Phys. Chem. B* **101**, 5712 (1997).

<sup>16</sup>D. A. Chen and C. M. Friend, *J. Phys. Chem. B* **102**, 106 (1998).

<sup>17</sup>R. T. K. Baker, *Carbon* **27**, 315 (1989).