Effects of the electrical conductivity and orientation of silicon substrate on the synthesis of multi-walled carbon nanotubes by thermal chemical vapor deposition

Hyonkwang Choi, Jaeseok Gong, Yeongjin Lim, Ki Hong Im and Minhyon Jeon*

Abstract

We studied the effects of the electrical conductivity and orientation of silicon substrate on both catalytic Fe thin film and the structure and morphology of multi-walled carbon nanotube (MWNT) grown by low-pressure chemical vapor deposition. Both p-type Si(100) and Si(111) substrates with three different doping concentrations (high, low, undoped) were used to evaluate the formation of catalytic nanoparticles and the growth of MWNTs. The morphology of catalytic nanoparticles such as size and density was characterized by field-emission scanning electron microscopy, Cs-corrected energy-filtered transmission electron microscopy, and X-ray photoelectron spectroscopy. Structural characteristics of MWNTs grown on different combinations of silicon substrate orientation and electrical conductivities (σ) were also systematically analyzed. Based on the experimental results, growth modes of MWNTs could be controlled by choosing an appropriate combination of σ and orientation of Si substrates.

Keywords: Multi-walled carbon nanotube, Catalytic nanoparticle, Substrate effect

Methods

The p-type silicon substrates with different orientations and doping concentrations were prepared. The electrical characteristics for both Si(100) and Si(111) substrates at room temperature were measured using Hall measurement equipment (Ecopia HMS-3000, Bridge Technology, Chandler Heights, AZ, USA) and are summarized in Table 1. Silicon oxide layers on the substrate surfaces...
were removed using a conventional process with a buffered oxide etching solution. A 6-nm-thick iron film was deposited on the silicon substrate using an ion sputter. The CVD chamber was on standby and pumped down to a low pressure of less than 20 mTorr [13]. Argon (Ar) gas was flowed into the chamber at a flow rate of 1,000 sccm in this experiment [14]. At the same time, while ammonia (NH₃) gas with a flow rate of 140 sccm was flowed into the reactor, the substrates were heated up to the growth temperature of 900°C for 30 min and then maintained at 900°C for 5 min. Acetylene (C₂H₂) gas was supplied to synthesize MWNTs with a flow rate of 20 sccm for 10 min at 900°C [15,16]. After the growth of MWNTs, the chamber was cooled down to room temperature and purged with Ar ambient. This work has focused on the size contribution and formation of catalyst particles by supporting substrate orientation and conductivity. However, the samples must be taken to the instrument for ex situ analysis. Therefore, we have endeavored that the exposure of samples to air and moisture was minimized. Once the samples were taken out from the chamber and cooled off to room temperature, each sample was divided into small pieces for the characterization by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4300SE, Hitachi, Ltd., Chiyoda-ku, Japan), Cs-corrected energy-filtered transmission electron microscopy (JEM-2200FS, JEOL Ltd., Akishima-shi, Japan), and X-ray photoelectron spectroscopy (XPS; AXIS Nova, Kratos Analytical Ltd., Manchester, UK). The XPS analysis was carried out using an Al K (1,486.6 eV) X-ray (hν = 1,486.6 eV) photoelectron spectrometer. The base pressure of the XPS system was 5.2 × 10⁻⁹ Torr.

### Results and discussion

Figure 1a,b,c,d,e,f illustrates the SEM images of Fe nanoparticles on Si(100) and Si(111) substrates at 900°C by applying the thermal chemical vapor deposition method. In the case of Si(100) substrate, as the σ of the silicon substrate increases, the average size of the Fe particles increases while the average density of the Fe particles decreases, as shown in Figure 1a,b,c. Figure 2 shows a plot of the average size of Fe particles versus the electrical conductivity of the Si(100) substrate. We conducted three different experiments and calculated the average values of the sizes and the densities of the nanoparticles to confirm the reproducibility of our experiment. We found that the average sizes of the Fe particles for substrates U(100), L(100), and H(100) were 55.6, 58.3, and 65.7 nm, respectively. This tendency is coincident with our previous results [9]. However, on the other hand, the average Fe particle size decreased as the electrical conductivity (σ) of Si(111) increased (Figure 1d,e,f). In the case of Si(111) substrate, as the σ of the silicon substrate increases, the average size of the Fe particles decreases while the average density of the Fe particles increases. It was found that the average sizes of

| Table 1 Results of the Hall measurement by van der Pauw method 1 cm × 1 cm size |
|------------------------|------------------------|------------------------|
| Bulk concentration | Conductivity (Ω cm) | Mobility (Vs/cm) |
| Si(100)  | 2.7 × 10¹² | 6.7 × 10⁻⁴ | 15,000 |
| U(100)  | 1.8 × 10¹⁵ | 9.8 × 10⁻² | 350    |
| L(100)  | 6.0 × 10⁹  | 4.3 × 10⁻¹ | 45     |
| H(100)  | 1.0 × 10⁻⁵ | 1.7 × 10⁻² | 59     |
| L(111)  | 1.0 × 10⁻⁵ | 6.1 × 10⁻² | 370    |
| H(111)  | 3.4 × 10⁻⁹ | 8.9 × 10⁻¹ | 1,000  |

U, undoped; L, low; H, high.
the Fe particles for substrates U(111), L(111), and H (111) were 37.9, 30.8, and 28.6 nm, respectively. This result is opposite to that of the Si(100) substrate. Figure 3 shows the histograms of the particle size distribution on both Si(100) and Si(111) substrates.

The contrary tendency of Fe particle size according to substrate orientation could be explained that agglomeration and segregation of Fe particles were affected by atomic density, surface energy, and thermal conductivity of different Si surface orientations at the same thermal condition. The binding energy between Fe film and Si (100) substrate is smaller than that between Fe film and Si(111) substrate. In addition, the surface energy of Si (100), 2.13 J/cm², is almost twice higher than that of Si (111), 1.23 J/cm². Accordingly, it is expected that the catalytic particles could more easily migrate on Si(100) surface by thermal energy. Under these conditions, there exists a high probability of Fe particle agglomeration. Indeed, it was observed that the average diameter of Fe particles on Si(100) substrate was larger than that on Si (111) substrate. When the metal thin film is annealed, particles are formed by film coarsening, and then, they could agglomerate or break down through surface migration, driven by a thermally activated process resulting in a minimization of the surface energy of the metal film-substrate system.

Zero-loss images and electron energy loss spectroscopy (EELS) elemental maps were examined to identify the distribution of Fe, O, and C on substrates U and H after introducing hydrocarbon gas for 5 s, as shown in Figure 4. After heat treatment, Fe particles were formed and oxidized. Oxygen might be provided from oxides on the Fe film after deposition on the silicon substrate or from residual natural oxides on the silicon surface. We found that the Fe particles on substrate U exhibited an oxygen layer, around 3 nm thick, on the surface of small Fe particles. In addition, a few layers of graphite were formed on the oxide layer of the oxidized Fe particle as in Figure 4. On the other hand, a certain amount of oxygen was present throughout the entire image at a very low intensity, and the graphite layers on substrate H were synthesized thicker than those on substrate U.

Figure 5a,b,c shows FE-SEM images of MWNTs grown on silicon substrates U(100), L(100), and H(100). Typical vertical-aligned MWNTs were grown on Si(100) substrates. In the case of Si(100) substrate, substrate U (100) with the lowest electrical conductivity has a dense distribution of thin and long MWNTs with average...
diameters of 30 to 40 nm and a length of around 25 μm. MWNTs with average diameters of 65 to 80 nm and a length of 5 to 6 μm were grown on substrate L(100), and thick and short MWNTs were grown on substrate H (100), which possessed the highest electrical conductivity. In this case, the average diameter and lengths of the MWNTs were found to be around 100 nm and 2 to 3 μm, respectively. For Si(111) substrate, however, the thin and long MWNTs were grown on H(111) substrate, while thick and short MWNTs were grown on substrate U(111), which possessed the lowest electrical conductivity compared with those of H(111) and L(111) substrates. Figure 6 shows cross-sectional and plan-view images of MWNTs grown on silicon substrates U(111), L(111), and H(111). Figure 7 shows a plot of length and diameter of MWNTs versus electrical conductivity of the Si(100) and Si(111) substrates. The average vertical lengths of MWNTs grown on U(111), L(111), and H (111) substrates are 5.3, 6.6, and 8.3 μm, respectively. On the other hand, the average diameter of MWNTs grown on U(111), L(111), and H(111) substrates are 78, 70, and 68 nm, respectively.

Generally, the diameter and length of carbon nanotubes were affected by catalytic metal particle sizes.
in the early stage of growth. Since the average Fe particle size on Si(100) substrate is larger than that on Si(111) substrate, MWNTs grown on Si(100) have larger diameter and shorter length than those grown on Si(111) substrate. As the electrical conductivity of Si(100) substrate increased, Fe particle size is increased, so carbon nanotubes with a short length and large diameter were grown. However, on the other hand, in the case of Si(111) substrate, as the electrical conductivity increased, smaller Fe particles were formed. Accordingly, MWNTs with small-diameter and long carbon nanotubes were synthesized.

Conclusions

In this study, we report the effects of the orientation and electrical conductivity of silicon substrates on the synthesis of MWNTs by thermal CVD. It was found that the size and distribution of Fe particles on silicon substrate could be controlled by varying both orientation and $\sigma$. Accordingly, it is possible that the growth of MWNTs by thermal CVD could be also controlled by using the orientation and $\sigma$. In the case of Si(100) orientation, it was found that as the electrical conductivity of Si(100) substrates increased, the vertical growth of
MWN Ts was restrained while the radial growth was enhanced. On the other hand, in the case of Si(111) orientation, the situation is reversed. In this case, it was found that as the electrical conductivity of Si(111) substrates increased, the vertical growth of MWN Ts was enhanced while the radial growth was restrained. More detailed investigation on this matter is in progress.

As a result, a strong correlation exists between the growth modes of the MWN Ts and the combination of σ and orientation of the silicon substrate. Our results suggest that the combination of σ and orientation of the silicon substrate can be considered as an important parameter for controlling the growth modes of CNTs fabricated by thermal CVD, without the need to alter other growth parameters.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
HC developed the conceptual framework and wrote the paper. JG and YL did the growth and characterization of the CNT. KHI helped in the experimental study and advised on the project. MJ supervised the work. All authors read and approved of the final manuscript.

Acknowledgments
This research was supported by the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (grant no. 20120482). The authors wish to thank Ms. Hyesoo Jeong for plotting the graph. This work was supported by the Ministry of Education, Science and Technology (grant no. 20120482). The authors wish to thank Ms. Hyesoo Jeong for plotting the graph.

Author details
1Department of Nano Systems Engineering, Center for Nano Manufacturing, Inje University, Gimhae, Gyungnam 621-749, Republic of Korea. 2Samsung Electronics Co, Suwon, Gyeonggi 443-742, Republic of Korea.

Received: 21 December 2012 Accepted: 16 February 2013
Published: 27 February 2013

References
1. Takagi D, Kobayashi Y, Horma Y. Carbon nanotube growth from diamond. J Am Chem Soc 2009, 131:6922–6923.
2. Li C, Zhu H, Suenaga K, Wei J, Wang K, Wu E. Diameter dependent growth mode of carbon nanotubes on nanoporous SiO2 substrate. Mater Lett 2009, 63:1366–1369.
3. Lee Y, Park J, Choi J, Ryu H, Lee H. Temperature-dependent growth of vertically aligned carbon nanotubes in the range 800–1100°C. J Phys Chem 2002, 106:7614–7618.
4. Jang JW, Lee OK, Lee CE, Lee TJ, Lee CJ, Noh SJ. Metallic conductivity in bamboo-shaped multiwalled carbon nanotubes. Solid State Commun 2002, 122:619–622.
5. Baker RTK, Barber MA, Harris PS, Feates FS, Waite RJ. Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene. J Catalysis 1972, 26:51–62.
6. Jang JW, Lee CE, Lyu SC, Lee TJ, Lee CJ. Structural study of nitrogen-doping effects in bamboo-shaped multiwall carbon nanotubes. Appl Phys Lett 2004, 84:2877–2879.
7. Ward JW, Wei BQ, Ajayan PM. Substrate effects on the growth of carbon nanotubes by thermal decomposition of methane. Chem Phys Lett 2003, 376:17–22.
8. Handuj S, Srivastava P, Vankar VD. On the growth and microstructure of carbon nanotubes grown by thermal chemical vapor deposition. Nanoscale Res Lett 2010, 5:1211–1216.
9. Yudasaka M, Kikuchi R, Ohki Y, Yoshimura S. Behavior of Ni in carbon nanotube nucleation. Appl Phys Lett 1997, 70:1817–1818.
10. Wei YY, Eres G, Merkulov VI, Lowndes DH. Effect of catalyst film thickness on carbon nanotube growth by selective area chemical vapor deposition. Appl Phys Lett 2001, 78:1394–1396.
11. Kukovitsky EF, L’vov SG, Sainov NA, Shustov VA, Chernozatonskii LA. Correlation between metal catalyst particle size and carbon nanotube growth. Chem Phys Lett 2002, 355:497–503.
12. Hwang S, Choi H, Kim Y, Kang M, Jeon M. Influence of the electrical conductivity of the silicon substrate on the growth of multi-walled carbon nanotubes. J Korea Phys Soc 2011, 58:248–251.
13. Lee CJ, Kim DW, Lee TJ, Choi YC, Park YS. Synthesis of uniformly distributed carbon nanotubes on a large area of Si substrates by thermal chemical vapor deposition. Appl Phys Lett 1999, 75:1721–1723.
14. Choi YC, Bae DJ, Lee YH, Lee BS, Han JY, Choi WB, Lee NS, Kim JM. Low temperature synthesis of carbon nanotubes by microwave plasma-enhanced chemical vapor deposition. Synth Met 2000, 108:159–163.
15. Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, Provencio PN. Synthesis of large arrays of well-aligned carbon nanotubes on glass. Science 1998, 282:1105–1107.
16. Yao Y, Falk US, Morjian RE, Nerushev OA, Campbell EEB. Synthesis of carbon nanotube films by thermal CVD in the presence of supported catalyst particle. Part I: the silicon substrate/nanotube film interface. J Mater Sci: Mater In Electro 2004, 15:533–543.

Cite this article as: Choi et al.: Effects of the electrical conductivity and orientation of silicon substrate on the synthesis of multi-walled carbon nanotubes by thermal chemical vapor deposition. Nanoscale Research Letters 2013 8:110.

doi:10.1186/1556-276X-8-110