Diameter Selective Growth of Vertically Aligned Single Walled Carbon Nanotubes by Ethanol Flow Control

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ABSTRACT

Nanotechnologies based on single walled carbon nanotubes (SWNTs) are developing very rapidly because of their outstanding mechanical, electrical, and optical properties. However, large scale synthesis of SWNT with desired structures still have many difficulties. In particular, controlling the diameter and chirality of SWNT is one of the biggest challenges that need to be solved. In this presentation, we introduce the study on role of ethanol flow rate in a chemical vapor deposition (CVD) for the selective diameter distribution on vertically aligned single walled carbon nanotubes (VA-SWNTs) and selective synthesis of desired structure (single walled, double walled and multi walled carbon nanotube) by systematically deposited catalyst particles.

Keywords: carbon nanotube, diameter control, raman, ethanol flow rate

1 ITRODUCTION

Carbon nanotubes (CNTs) are unique nanostructures with remarkable electronic and mechanical properties, some stemming from the close relation between CNTs and graphite, and from their one-dimensional aspects. As other intriguing properties have been discovered, such as their remarkable electronic transport properties[1], their unique Raman spectra[2], and their unusual mechanical properties[3], interest has grown in their potential use in nanometer sized electronics and in a variety of other applications. The full technological potential of CNTs has been hindered somewhat by the difficulty associated with the control of their properties such as structure, diameter, and chirality. In recent years, significant research efforts have concentrated on overcoming these barriers[4-7]. Chemical vapor deposition (CVD), which offers versatile control and the possibility of scaling-up, is the most attractive method of producing CNTs because of the critical role played by catalyst nanoparticles. Although the growth mechanism of CNTs in CVD is still unclear, the size of the metal catalyst nanoparticles approximately determines the eventual structure and diameter of the CNTs. We have shown that the structures of CNTs can be controlled by controlling the metal catalyst nanoparticles. Additionally, we introduce the study on role of ethanol flow rate in a CVD for the selective diameter distribution of VA-SWNTs.

2 EXPERIMENTAL

For synthesis of structure selective VA-CNTs growth, we first prepared new catalyst system using cobalt (Co) as a catalyst. For catalyst system, Al/SiO_2 multilayered substrate was used. And Co was deposited on Al/SiO_2 multilayer using sputter. In order to grow CNTs selectively desired structure, Co catalyst film was deposited by different sputter current at the same sputter time (3 sec/5mA and 3 sec/25mA). The growth of CNTs was performed in a 1.25-in. quartz tube and a furnace. $Co/Al/SiO_2$ substrate was loaded in a quartz tube. A loaded wafer was baked at 400 °C for 10 min and inside of the quartz tube was evacuated by a rotary pump, heated at 850 °C for growth CNTs. During the heat-up the furnace, argon-hydrogen mixture gas was supplied so that the pressure was 700 torr. And ethanol vapor was supplied as a carbon source for 30 min with determined flow rate. In order to investigate the role of ethanol flow rate in CVD for the selective diameter distribution on VA-SWNTs, the ethanol flow rate is controlled by systematically varying while keeping all other CVD parameters, such as growth pressure, growth temperature, and growth time.

3 RESULT AND DISCUSSION

Figure 1a, 1b, 1c, and 1d show low magnification and high magnification SEM images of vertically aligned carbon nanotubes. Ethanol CVD results in the growth of dense and vertically aligned CNTs with several hundred height in a 30-min growth time. The best result to date is 1 mm in 30-min. First sample (Figure 1a, 1c, and 1e) was synthesized using Co catalyst system was deposited by 3sec/5mA. VA-SWNTs were up to 98% on substrate as

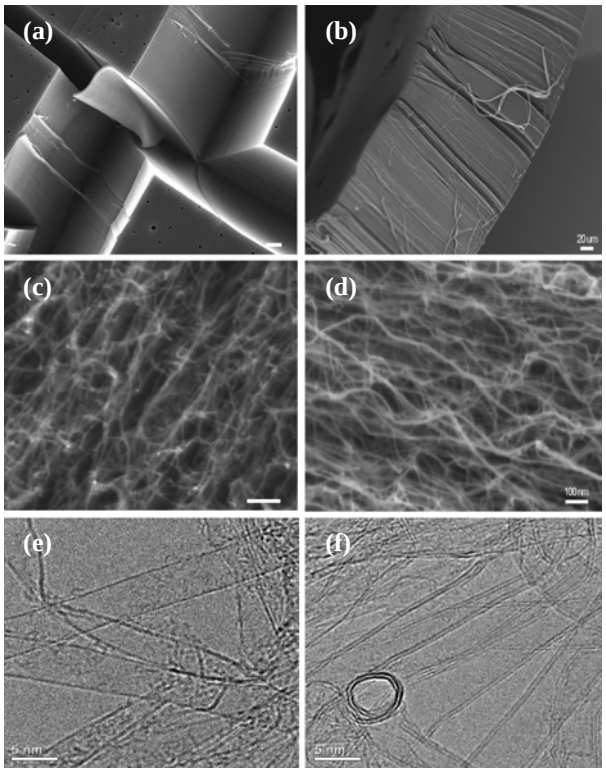

Figure 1: SEM and TEM images of vertically aligned CNTs synthesized with different sputter conditions. (a) low magnification SEM image of VA-SWNTs, (b) low magnification SEM image of VA-DWNTs, (c) high magnification SEM image of VA-SWNTs, (d) high magnification SEM image of VA-SWNTs, (e) HR-TEM image of VA-SWNTs, and (f) HR-TEM image of VA-DWNTs. Scale bars of a, b are 20 μm, scale bars of c, d are 100 nm.

shown Figure 1e. In case of second sample (Figure 1b, 1d, and 1f), CNTs were synthesized using Co catalyst system was deposited by 3sec/25mA. On second sample, VA-DWNTs were up to 97% as shown Figure 1f. Using different catalyst deposition condition, we obtained the structure selective growth of VA-SWNTs and VA-DWNTs.

The diameter selective growth of highly dense and VA-SWNTs were synthesized by three different flow rate of ethanol vapor (50, 100 and 200 sccm), the carbon source, in a CVD as shown Figure 2. It is clearly seen that SWNTs are vertically aligned for all ethanol flow rate such as 50, 100 and 200 sccm indicating that our ethanol CVD process is effective for SWNTs growth. In this experiment, one interesting feature was found in Raman studies, especially in Radial Breathing Mode (RBM) mapping process. Raman map and image score gives us spatial distribution of SWNTs diameter. Therefore, statistical treatment of Raman images can quantify the diameter distribution on substrates. RBM of SWNTs gives information on the diameter and chirality of SWNTs. The diameter of SWNTs can be calculated from the equation; $d(\text{nm}) = A/[\omega_R(\text{cm}^{-1})]$, where d is the diameter of SWNT, A is a proportionality constant (248), and ω is the RBM frequency[8]. In order to investigate the large scale diameter distribution of three different VA-SWNTs, Raman maps were recorded using Raman microscope and mapping stage. The excitation laser was 785 nm, the Raman mapping area was 10 μm by 10 μm at 0.3 μm laser steps, the exposure time was 5 second/spectrum, and the number of accumulations is 14. The 600 gr/mm grating was used, and the confocal hole diameter was set to 200 μm. Rman maps were processed using Modeling function in LabSPEC 5 (HORIBA Jobin Yvon).

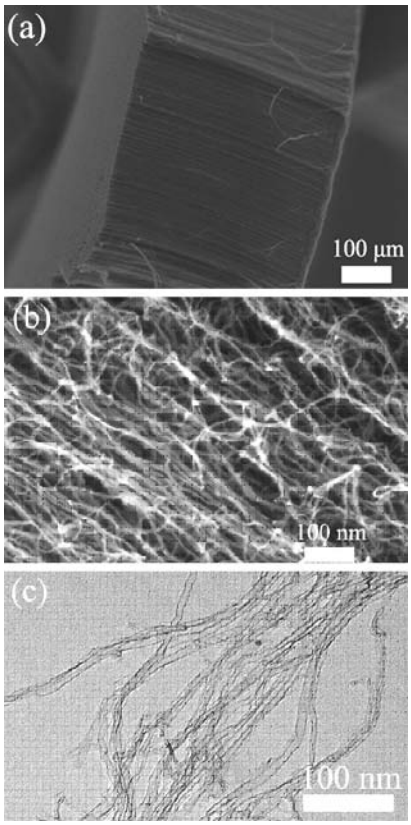

Figure 2: SEM and TEM images of vertically aligned SWNTs. (a) low magnification SEM image of VA-SWNTs synthesized with 50 sccm flow rate of ethanol, (b) high magnification SEM image, (C) TEM image shows that VA-CNTs are single walled carbon nanotubes

Raman spectra models and score images of SWNTs grown with three different flow rate of ethanol vapor are shown Figure 3. A multivariate analysis algorithm (direct classical least square, DCLS) was applied in an unsupervised mode to extract significantly different Raman spectra (models) and to calculate scores of individual

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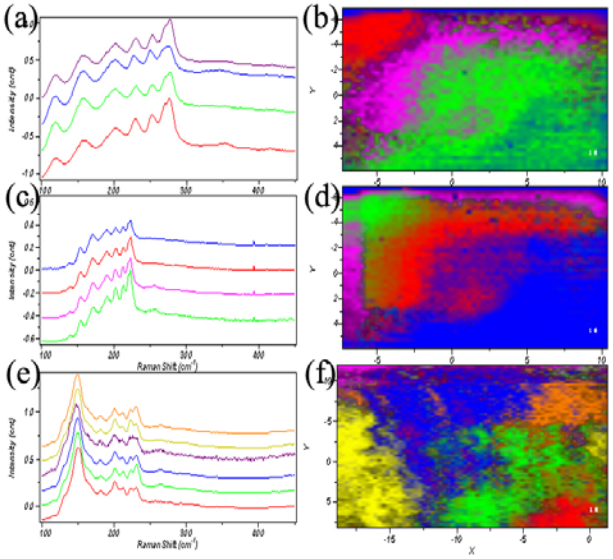

Figure 3: (a), (c) and (e) show models produced from Raman maps over 10 × 10 μm^2 area (b), (d) and (f) show corresponding score images. (a) and (b) are results from VA-SWNTs grown with 50 sccm ethanol flow rate, (c) and (d) 100 sccm, (e) and (f) 200 sccm.

spectra with respect to these models. The RBM models recorded from VA-SWNTs synthesized with 50 sccm ethanol flow rate (Figure 3 a) produced four model spectra with the RBM peak positions ranging between 159 cm^{-1} and 291 cm^{-1}. These RBM frequencies correspond to VA-SWNTs diameter in the range of 0.89 nm – 1.55 nm. The corresponding Raman image shows the diameter distribution of the VA-SWNTs with the four factors represented with corresponding colors. For example, green areas in the Raman image represent the spatial diameter distribution of VA-SWNTs corresponding to the green factor (spectrum). Vertically grown SWNTs with 100 sccm ethanol flow rate also yielded 4 different RBM models whose frequencies range from 143 cm^{-1} to 231 cm^{-1} (Figure 3 c). The diameter distribution of VA-SWNTs grown with 100 sccm ethanol flow rate is 1.07 nm to 1.73 nm. In the case of the 200 sccm ethanol flow rate, VA-SWNTs produced 6 different RBM models in the range of 119 cm^{-1} to 243 cm^{-1} (Figure 3 e). The observed RBM frequencies correspond to VA-SWNTs diameters from 1.02 nm to 2.08 nm. From images (Figure 3 b, d and f), we can determine RBM spectrum among the several RBM spectra on 10 by 10 μm^2 region of each sample. From above results, as the ethanol vapor flow rate increased from 50 sccm to 200 sccm, the diameter distributions of VA-SWNTs were enlarged. The diameter distribution of VA-SWNTs changed from 0.85 nm – 1.55 nm with 50 sccm ethanol flow rate to 1.02 nm – 2.08 nm with 200 sccm ethanol flow rate.

In summary, using different catalyst deposition condition, CNTs were synthesized selectively single walled, double walled and multi walled carbon nanotubes. Additionally, our results show that the diameter distribution selective synthesis of SWNTs was closely correlated with flow rate of ethanol vapor.

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