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Description	



Synthesis-condition dependence of carbon nanotube growth by alcohol catalytic chemical vapor deposition method

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Abstract

We report the dependence of growth yield of single-walled carbon nanotubes (SWNTs) on heat-treatment time and catalyst film thickness by the alcohol catalytic chemical vapor deposition method. Three types of heat-treatment, synthesis of 30 min, synthesis of 30 min after annealing of 30 min, and synthesis of 60 min, were investigated. Thickness of Co catalyst film was varied from 1 to 10 nm. In the case of thinner Co film less than 3 nm, long synthesis time of 60 min is favorable for the effective SWNT growth, because of the small amount of Co catalyst. In the case of thicker Co film more than 3 nm, an amount of grown SWNTs by 30 min synthesis after 30 min annealing and by 60 min synthesis was much higher than that by 30 min synthesis without annealing, showing that total heat-treatment time of 60 min is important for the SWNT growth. Results suggest that the conversion from the thicker film of Co to nano-particle which act as catalyst takes place during the first 30 min.

Key words: single-walled carbon nanotubes, alcohol catalytic CVD

1. Introduction

Carbon nanotube (CNT) found by S. Iijima [1] is an attractive material because of its unique characteristics originating from the small size and cylindrical structure. Many novel properties such as electron field emission [2], quantum magnetoresistance [3,4], photoconductivity [5], gas adsorption [6–10], and spin coherent transport [11] have been reported. Especially, since single-walled carbon nanotube (SWNT) can be either semiconducting or metallic characteristic depending on the structure [12–15], SWNTs have been much actively studied for application to electronic devices [16,17]. In the case that

CNTs are grown directly on the electronic devices, chemical vapor deposition (CVD) technique is generally used [18,19]. As a feeding gas, methane, carbon monoxide, acetylene and alcohol are used. Temperature and catalysts condition dependence of CNT growth are investigated in each synthesis method.

Morphology of catalyst used for CVD technique is one of important factors for CNT growth. Several catalysts, such as Fe, Co, Ni, and combinations of those metals and catalyst support materials [20] are used in each CVD technique. R. Seidel et al. [21] proposed a model of SWNT growth from the detail experiments of CVD growth under the various conditions. S. Noda et al. [22,23] reported synthesis of SWNTs from catalyst film with gradient thickness deposited by combinatorial masked deposition method.

An alcohol catalytic CVD (ACCVD) method is

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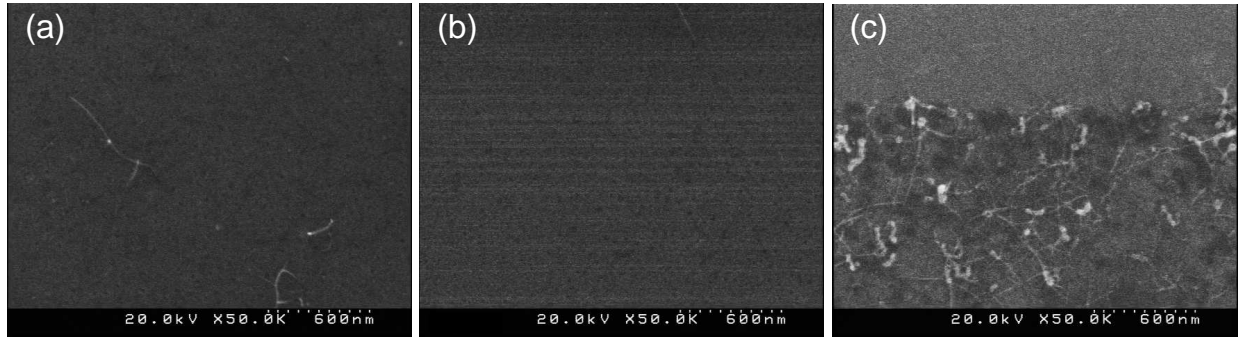


Fig. 1. SEM images of carbon nanotubes synthesized from Co thin films of 1 nm thickness with ethanol gas flow of 3.0 l/min for (a) 30 min (b) 30 min after 30 min annealing and (c) 60 min at 900 °C.

expected to be a potential technique for the fabrication of electronic devices, because of less formation of amorphous carbon [24]. For this purpose, several experimental conditions are studied [25,26]. Relation between synthesis time and yield of SWNTs, however, has not been fully studied yet. In this paper, we report dependence of SWNTs growth on heat-treatment time and thickness of catalyst film by ACCVD method.

2. Experimental details

SWNTs were synthesized by ACCVD method using ethanol as a feeding gas and Co as a catalyst. Each thin film of Co catalysts from 1 to 10 nm thicknesses (t) was deposited on a 100 nm thick SiO₂ film on an n-doped Si substrate by electron beam deposition. The Co-deposited substrate was placed into a quartz tube (27 mm inner diameter, 120 cm long) and the tube was evacuated below 10.0 Pa by a rotary pump. A movable furnace (30 mm tube diameter, 30 cm long) was heated up to synthesis temperature of 900 °C at a different place from where the substrate was placed. Then, H₂/Ar (3% H₂) as a treatment gas was supplied into the quartz tube and the inside tube pressure was kept at 400 Pa. The substrate was fast-heated by quickly moving the heated furnace to the place of the substrate [27]. After the furnace temperature returned to 900 °C, supply of H₂/Ar gas was stopped. The base pressure became around 3.0 Pa after heat treatment with H₂/Ar gas. Ethanol gas flow of about 800 sccm was fed into the quartz tube immediately after stopping supply of H₂/Ar gas for the case of 30 and 60 min synthesis without annealing, whereas ethanol was fed into the quartz tube after keeping at a pressure of 3.0 Pa for 30 min without any gas for the case of 30 min synthe-

sis with 30 min annealing. The pressure inside the quartz tube became 3.0 – 5.0 kPa during ethanol gas flow. After the synthesis process, the furnace was removed from the substrate position and ethanol gas flow was stopped. The sample substrates were characterized by scanning electron microscopy (SEM; Hitachi, S4100) and Raman spectroscopy with laser excitation energy of 632.8 nm (Tokyo Instruments, Nanofinder30).

3. Results and discussion

Figure 1 shows SEM images of CNTs grown from Co thin films of $t = 1$ nm deposited on Si/SiO₂ substrates. The growth conditions of CNTs shown in Figs. 1 (a), (b) and (c) were synthesis time of 30 min, that of 30 min after 30 min annealing, and that of 60 min, respectively. Few CNTs were observed on the substrates of 30 min synthesis with and without annealing, whereas particles and clusters of several tens of nanometers formed and CNTs were observed on that of 60 min synthesis. These results show that CNTs are more grown by synthesizing for 60 min than that for 30 min.

Figures 2(a), (b) and (c) show Raman spectra of SWNTs grown by 30 min synthesis, 30 min synthesis after 30 min annealing, and 60 min synthesis from Co films of $t = 1 - 10$ nm on Si/SiO₂ substrates, respectively. The Raman spectra for each sample were measured at about 20 different positions on the substrate. Raman spectra of $t = 1$ nm in Figs. 2 (a), (b) and (c) were measured on the samples shown in Figs. 1 (a), (b) and (c), respectively. Raman spectra of almost all the samples involve peaks of radial breathing mode (RBM) from 100 to 350 cm⁻¹, which are characteristic of SWNTs [28], and of G-band around 1590 cm⁻¹. In consistent with the results of SEM

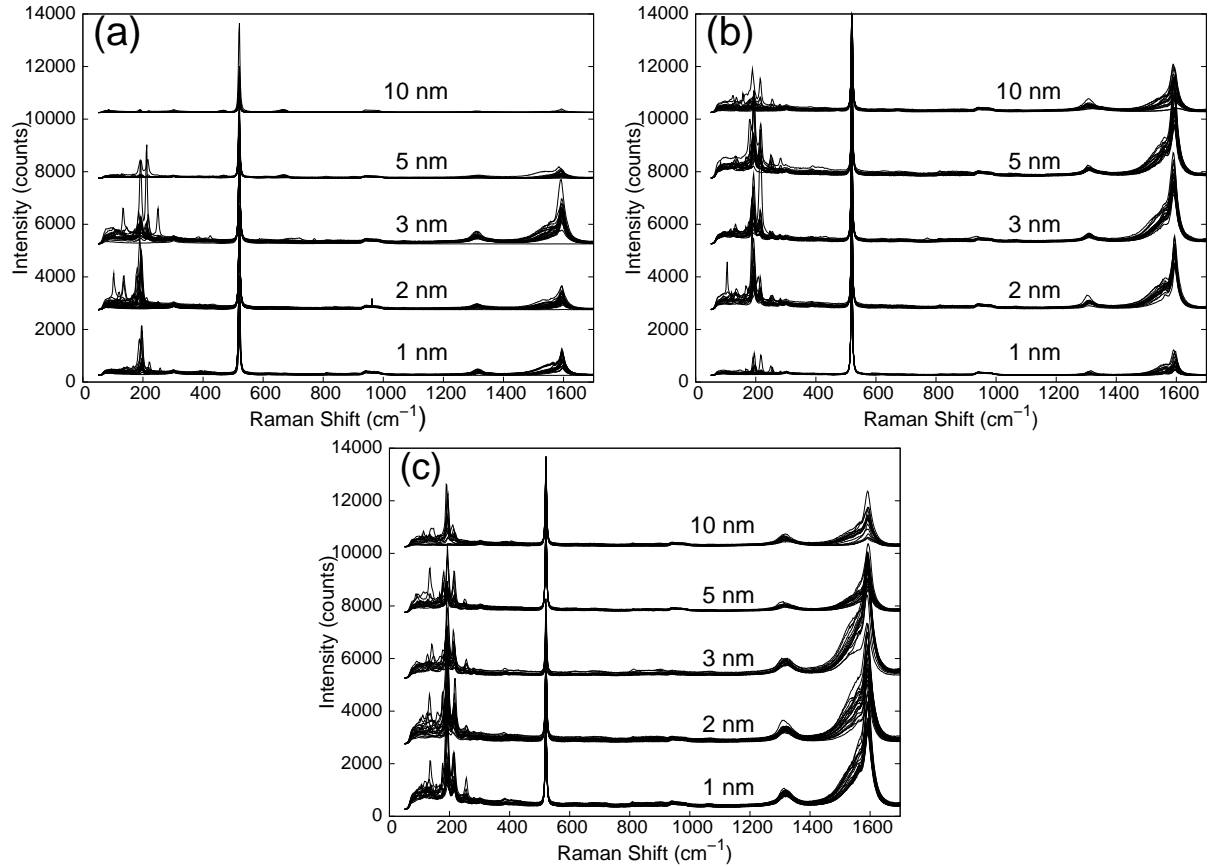


Fig. 2. Raman spectra of carbon nanotubes synthesized from Co thin films of 1 – 10 nm thickness with ethanol gas flow of 3.0 l/min for (a) 30 min, (b) 30 min after 30 min annealing, and (c) 60 min. The spectra in respective thicknesses include about 20 spectra. The spectra were obtained by 632.8 nm laser excitation. The spectrum and respective baseline are shifted for clarity.

observation shown above, Raman peaks originating from SWNTs for the sample grown by 30 min synthesis with and without annealing are weaker than those for the sample grown by 60 min synthesis for $t = 1$ nm. In the case of $t \leq 3$ nm, Raman intensity of RBM and G-band increases with increasing t for the sample grown by 30 min with and without annealing. On the other hand, Raman intensity of sample grown by 60 min synthesis is rather high, and does not depend on the Co film thickness. This result shows that amount of Co catalyst is not enough for 30 min synthesis in the case of $t \leq 3$ nm.

In the case of $t > 3$ nm, the relation between Raman intensity and growth condition is different from that in the case of $t \leq 3$ nm. Raman intensity of samples grown by 30 min synthesis without annealing decreases rapidly with increasing Co film thickness. On the other hand, Raman intensity for samples grown by 30 min synthesis with annealing and by 60 min synthesis are high and does not depend

on the Co thickness. The tendency is very similar each other, although the synthesis time is different. This result shows that total heat-treatment time of 60 min is important for the growth of SWNTs rather than synthesis time.

It is well known that formation of catalyst nano-particle plays an important roll for SWNTs growth. In fact, catalyst nano-particles were formed from a thin film less than 1 nm, and SWNTs were grown from this thin film [29]. In our results, SWNTs were grown from thicker Co films ($t \geq 5$ nm) by long total heat-treatment time of 60 min, as shown in Raman spectra (Figs. 2 (b) and (c)). Assuming that small particle size of catalyst is essential for the growth of SWNTs, our results suggest that it takes about 30 min for the nano-particle formation from the thick Co film ($t \geq 5$ nm). The detailed study on mechanism of conversion from Co film to nano-particles is in progress.

4. Summary

We have investigated the dependence of SWNT growth on heat-treatment time and catalyst thickness by ACCVD method. In the case of thinner Co film, $t \leq 3$ nm, long synthesis time of 60 min is favorable for the effective SWNT growth, because of the small amount of Co catalyst. In the case of thicker Co film, $t > 3$ nm, total heat-treatment time of 60 min is important for the SWNT growth. Results show that the conversion from the film to nanoparticle which act as catalyst takes place during the first 30 min.

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