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Preparation of Catalytic Nanoparticles in Mesoporous Silica Film for Oriented Growth of Single-Walled Carbon Nanotubes

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Vertically oriented single-walled carbon nanotubes (SWNTs) attract considerable attention because it is expected as an ideal field emitter that can realize lower threshold-voltage and higher electric-current than microtips of Si or metals. In this study, we aim that SWNTs are vertically oriented using mesoporous silica film as a guide of the growth for SWNTs. For the orientation, the catalyst for the growth must be attached to the substrate and a catalyst loading method, sputtering method, is investigated in this paper. The mesoporous silica film is coated on the Co thin film deposited by sputtering. From the experimental results, it is concluded that the mesoporous silica film prevents agglomeration of Co catalyst, resulting in the formation of oriented SWNTs from the bottom of the silica mesopores.
Key words: mesoporous silica film, single-walled carbon nanotube, orientation, catalyst loading

1. INTRODUCTION

Since the discovery, single-walled carbon nanotubes (SWNTs) have been an extensive research object in various scientific and industrial fields due to its unique properties and remarkable potentials as an advanced material. In order to utilize SWNTs widely, vertical orientation of SWNTs is accepted as a key technology toward the practical usage as a field emitter [1], a gas sensor [2] and a template for well-ordered nanoporous membrane structure [3].

To achieve vertical orientation of SWNTs, a mesoporous silica film, that has vertical aligned 1-D mesopores, is required. We focused on a mesoporous silica film that was reported by S. P. Naik *et al.*[4] because SWNTs can be vertically grown along the vertical part of mesopores in this film, that has 3-D mesostructure as described in Fig. 1. Judging from the observations using SEM and TEM, one of the mesopores run through the film from the substrate to the surface. Even though SWNTs are too weak to stand alone, it will be realized that some SWNTs are grown along with mesopores. The schematic image of the vertical orientation was described in Fig 1.

In our previous study [5], we have succeeded to synthesize highly pure SWNTs by the catalytic chemical vapor deposition (CCVD) process using ethanol as C source and Fe/Co as a catalyst for SWNTs loaded on the mesoporous silica film.

In this study, we focus on the loading method of catalysts because it is important to control the location of catalysts for vertical orientation of SWNTs. Through controlling the location of catalysts, SWNTs growth is guided by the vertical mesopores of the mesoporous silica film, and vertical orientation of SWNTs is achieved.

2. EXPERIMENTAL

2.1. Catalyst loading by sputtering

A piece of Si substrate (2 cm × 2 cm) with the oxide layer was cleaned by immersing in 1% HF aqueous solution, and then the substrate was washed with distilled/ion-exchanged water. The silicon substrate was set into a chamber, and then Co was sputtered using RST® magnetron sputter at RF 60 W. The sputtering rate was set at 0.33 nm/s. The thickness of Co film was changed from 1 nm to 100 nm by controlling the sputtering period.

2.2. Film preparation

After deposition of Co film, a mesoporous silica film was coated. Adequate amounts of tetraethyl-*ortho*-silicate (TEOS), ethanol (EtOH), H_2O, and HCl were mixed and stirred for 1 h at 65 °C. This solution was then mixed with an ethanol solution of amphiphilic triblock copolymer $(C_2H_4O)_{106}$-$(C_3H_6O)_{70}$-$(C_2H_4O)_{106}$ (BASF, Pluronic F127) and stirred for another 2 h at room temperature. The overall composition of the prepared coating solution was fixed to TEOS:H_2O:HCl:EtOH:F127 = 1:9.2:0.021:40:7.2 × 10^{-3} by molar ratio. The coating solution was mounted on the Co film on Si substrate by a dip-coating method at the dipping rate of 2 cm/min. After the coating, the piece was dried in air at 80 °C overnight, followed by calcination in air at 500 °C for 4 h to remove the copolymer, resulting in the formation of a mesoporous silica film with a typical thickness of 50 nm.

2.3. SWNT synthesis by alcohol CVD

SWNTs were grown by the alcohol catalytic CVD process [6]. The reaction temperature, time, and ethanol vapor pressure employed in this study were 750 °C, 10 min, and 10 Torr, respectively. 3% H_2 in Ar was flown

while heating up and cooling down.

The as-synthesized SWNTs were characterized with FE-SEMs (HITACHI, S-900 and S-5200) and Raman spectroscopy (CHROMEX 501is). Laser wavelength of 488 nm was used for all the Raman measurements. The particle size of the catalysts was observed with the FE-SEM.

3. RESULTS and DISCUSSION

Figure 2 shows typical Raman spectra for the products obtained by the sputtering method. In Fig. 2 (a), the G band, which is originated from graphite, was observed at 1593 cm^{-1}, and the split of the G band revealed the growth of SWNTs. Moreover, the D band, which can be assigned to amorphous carbon having a dangling bond, was faintly observed at around 1350 cm^{-1}. A high relative intensity of the G band to the D band indicates the synthesis of SWNTs with high-purity. On the other hand, both the G band and the D band were apparently observed in Fig. 2 (b). The low G/D ratio represents the formation of mixture of SWNTs and amorphous carbon. In Fig. 2 (c), the peak from carbon nanotubes was hardly observed.

The purity of SWNTs was examined using the G/D ratio in Raman spectra. The results are summarized in Table 1. When the thickness of Co film was below 2 nm without mesoporous silica film, the G/D ratio was high and the SWNTs with high-purity were synthesized. This result was in good agreement with our previous paper [7], in which they claimed that the existence of well-dispersed, nanosized metallic Co particles is required for the highly selective growth of high-quality SWNTs in the CVD process. The results clearly demonstrate that the SWNTs with high-purity were synthesized on the samples with mesoporous silica film, when the thickness of Co film was below 10 nm. On the other hand, when the thickness of the Co film was more than 20 nm, the G/D ratio became remarkably small, suggesting that the purity of SWNTs is reduced, which is denoted as "CNTs" in Table 1. When the thickness of the Co film was 5 or 10 nm, the sample with mesoporous silica film contains SWNTs with high-purity but the sample without mesoporous silica film did not contain any CNTs. In this case, the results in Table 1 are shown as "No CNTs".

In order to confirm the location of Co in the mesoporous silica film, the cross-section was observed by FE-SEM. Figure 3 shows the cross-sectional views of mesoporous silica/Si substrates by FE-SEM, where Co film thickness was (a) 50 nm, (b) 20 nm, (c) 5 nm and (d) 1 nm. In those images, the mesoporous silica film on the Si substrate was partially pealed and the structural information of the catalyst under mesoporous silica film could be obtained.

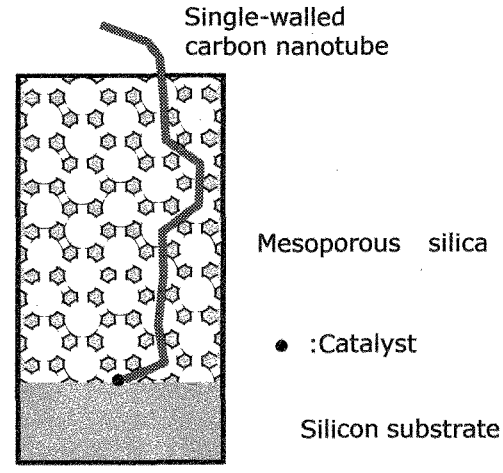

Fig. 1 Guided growth of SWNTs along mesopores

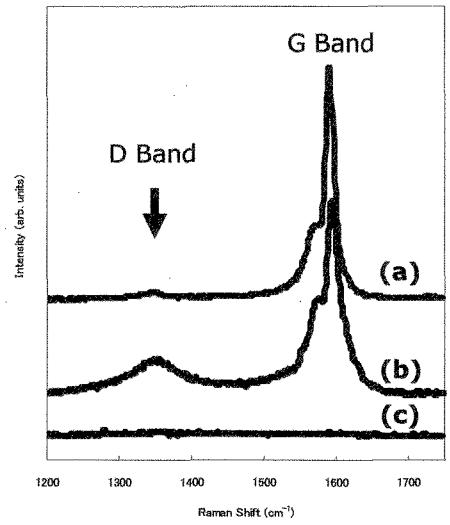

Fig. 2 The Raman spectra of the sample obtained by Co catalyst prepared by sputtering. (a)The thickness of Co layer was 10 nm, with mesoporous silica film (silica layer: 50 nm) (b) 20 nm Co with mesoporous silica layer and (c) 10 nm Co without mesoporous silica layer

Table 1 The influence of Co thickness and mesoporous silica film given on the high-purity synthesis of SWNTs in the sputtering method

Co film thickness	mesoporous silica film	
	With	Without
1 nm	*SWNTs*	*SWNTs*
2 nm	—	*SWNTs*
5 nm	*SWNTs*	No CNTs
10 nm	*SWNTs*	No CNTs
20 nm	CNTs	No CNTs
50 nm	CNTs	No CNTs
100 nm	CNTs	No CNTs

In Fig. 3 (a), the sputtered Co film was found to be agglomerated and the Co particles were transferred to the surface of mesoporous silica film, by the time when the support was heated to the high temperature in the flow of hydrogen. Such reductive atmosphere will lead the Co to agglomerating that result in the decrease in the surface area of catalyst. Also in Fig. 3 (b), the sputtered Co film was found to be agglomerated. But no Co particles were observed on the surface of mesoporous silica film. When Co was sputtered more than 50 nm, the control of the location of catalysts is difficult due to the low melting temperature of Co. In Fig. 3 (c) when the Co film thickness was 5 nm, white particles in mesoporous silica film could be observed. Judging from the image along with others, it seems to be agglomerated Co. Interestingly to note that some particles seem to be located in the border of mesoporous silica film and the silicon substrate. However some Co particles remained inside the mesoporous silica film. In Fig. 3 (d) when the Co film thickness was 1 nm, no agglomerated Co particles were observed in the image. This result

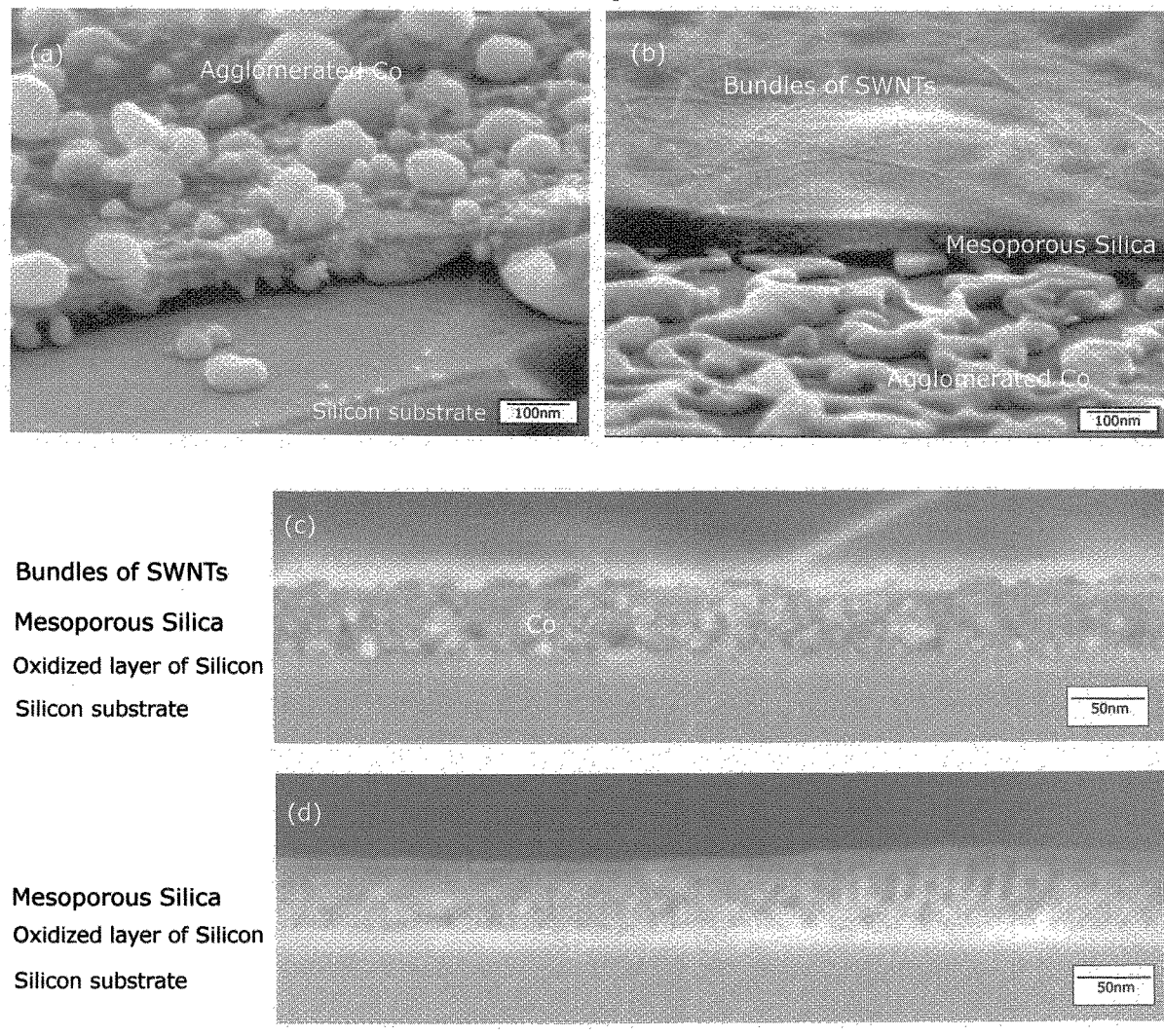

Fig. 3 Cross sectional SEM images of the samples with mesoporous silica film, Co film thickness is (a) 50 nm, (b) 20 nm, (c) 5 nm and (d) 1nm

indicates that Co is not agglomerated and not transferred from the as-sputtered place. It can be deduced that the location of the catalyst is attached to the substrate as expected, by the help of silica mesopores. Up to now, we could not conclude that agglomerating is hindered by mesoporous silica film when the amount of the sputtered Co is small, but the formation of SWNTs with high purity surely supports such a phenomenon. It is shown that a mesoporous silica film contributes the growth of high-quality SWNTs.

4. CONCLUSIONS

A mesoporous silica film, whose mesopores are running through the film, is utilized as a growth guide of SWNT for the first time. By selecting the mesophase, we will be able to achieve the vertical orientation of the SWNTs. In order to realize the orientation, another important factor is the location of the catalyst for SWNTs growth. It must be attached to the substrate. The sputtering method is shown to be promising for the vertical orientation of SWNTs, because of the catalyst location could be controlled on the substrate surface. From this study, it is shown that the mesoporous silica film results in the formation of oriented high-quality SWNTs from the bottom of the silica mesopores.

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