

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. Three kinds of catalyst loading methods are examined here. The first one is an impregnation method; the calcined mesoporous silica film is immersed in solution of cobalt acetate and iron acetate. The second one is an incorporation method; mesoporous silica film is prepared using Co/Fe-doped silica sol solution. The third one is a sputtering method; the mesoporous silica film is coated on the cobalt thin film deposited by sputtering. From these investigations, 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 practical usage as a field emitter [1], a gas sensor [2] and a template for well-ordered nanoporous membrane structure [3].

In our previous study [4], a mesoporous silica film was applied for the orientation of SWNTs, since SWNTs can be vertically grown along the vertical mesopores of mesoporous silica film pores from the catalyst at the bottom of the pores. We have succeeded to synthesize highly pure SWNTs by catalytic chemical vapor deposition (CCVD) process using ethanol as C source and Fe/Co as a catalyst loaded on mesoporous silica film. The mesoporous silica film should have mesopores which 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.

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

2. EXPERIMENTAL

2.1. Film preparation

A mesoporous silica film was coated on a Si substrate. Adequate amounts of tetraethyl-*ortho*-silicate (TEOS),

ethanol (EtOH), H₂O, 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 (C₂H₄O)₁₀₆ (C₃H₆O)₇₀ (C₂H₄O)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:H₂O:HCl:EtOH:F127 = 1:9.2:0.021:40:7.2 × 10⁻³ by molar ratio. The coating solution was mounted on a piece of Si substrate (2 cm × 2 cm) 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.

2.2. Catalyst loading by impregnation

An impregnation method was carried out in our previous study [4]. The procedure was as follows.

Catalytic materials were loaded on the calcined mesoporous silica film. Cobalt acetate and iron acetate were dissolved in ethanol to form metal acetate solution so that the weight concentration of both metals were kept constant at 0.01wt% in this work. The calcined mesoporous silica film was placed at the bottom of a glass beaker containing the metal acetate solution and then transferred into a desiccator for evacuation by a rotary pump for 1 h. The piece was washed with ethanol immediately after dipping out of the solution with ethanol. The piece was heated up to 400 °C in air.

2.3. Catalyst loading by incorporation

The incorporation was carried out in accordance with the literature by Huang et al. [5] Cobalt acetate and iron

acetate were mixed in a mesoporous silica coating solution; the weight concentration of both metals were kept constant at 0.01wt%. The mesoporous silica film was prepared simultaneously using the Co/Fe-doped coating solution.

2.4. Catalyst loading by sputtering

An Si substrate 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. After deposition of Co film, mesoporous silica film was coated.

The catalyst loading methods investigated here are summarized in Fig. 1, and, the catalyst particles for SWNTs growth are expected to be located as illustrated by each method.

2.5. 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% H₂ in Ar was flown while heating up and cooling down.

The as-synthesized SWNTs were characterized with FE-SEM (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 FE-SEM.

3. RESULTS and DISCUSSION

Figure 2 shows the typical Raman spectra for the products obtained by 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 slightly 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 of the G band and the D band were 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.

Among the samples prepared by three different methods tested in this study, the purity of SWNT was compared using the G/D ratio in Raman spectra. In the procedures of the impregnation and the incorporation, the catalysts would be dispersed throughout the whole pores of mesoporous silica film. In these cases, SWNTs might grow by the catalyst on the surface of mesoporous silica film, and there is little possibility for SWNTs orientation. Therefore, we will discuss here the location of loaded catalysts achieved by the sputtering method. 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

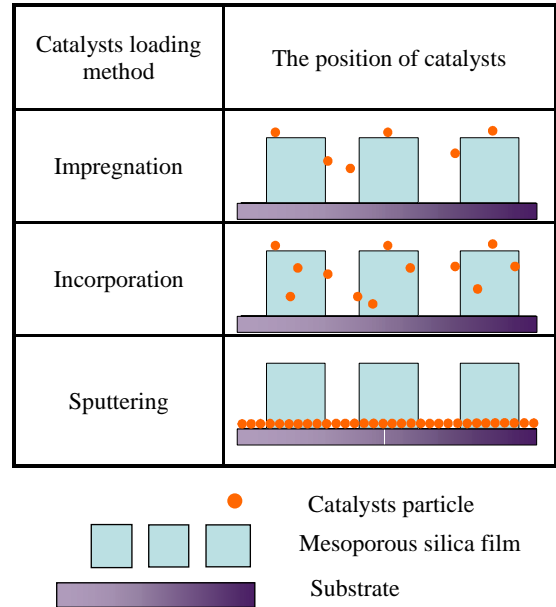


Fig. 1 Catalyst preparation for oriented growth of SWNT

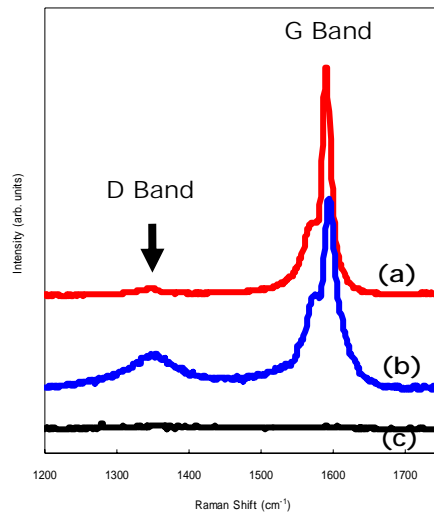


Fig. 2 The Raman spectra of (a) the sample obtained by Co catalyst prepared by sputtering. The thickness of Co layer was 10 nm, with mesoporous silica film (silica layer: 50 nm) (b) 20 nm Co with mesoporous silica layer and (c) 10 nm Co without mesoporous silica layer.

Table 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 | <i>SWNTs</i> | <i>SWNTs</i> |
| 2 nm | - | <i>SWNTs</i> |
| 5 nm | <i>SWNTs</i> | No CNTs |
| 10 nm | <i>SWNTs</i> | No CNTs |
| 20 nm | CNTs | No CNTs |
| 50 nm | CNTs | No CNTs |
| 100 nm | CNTs | No CNTs |

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 mesoporous silica film, the cross-sectional surface 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 peeled and the structural information of the catalyst under mesoporous silica film could be obtained. In Fig. 3 (a), the sputtered Co film was found to be agglomerated and the Co particles were

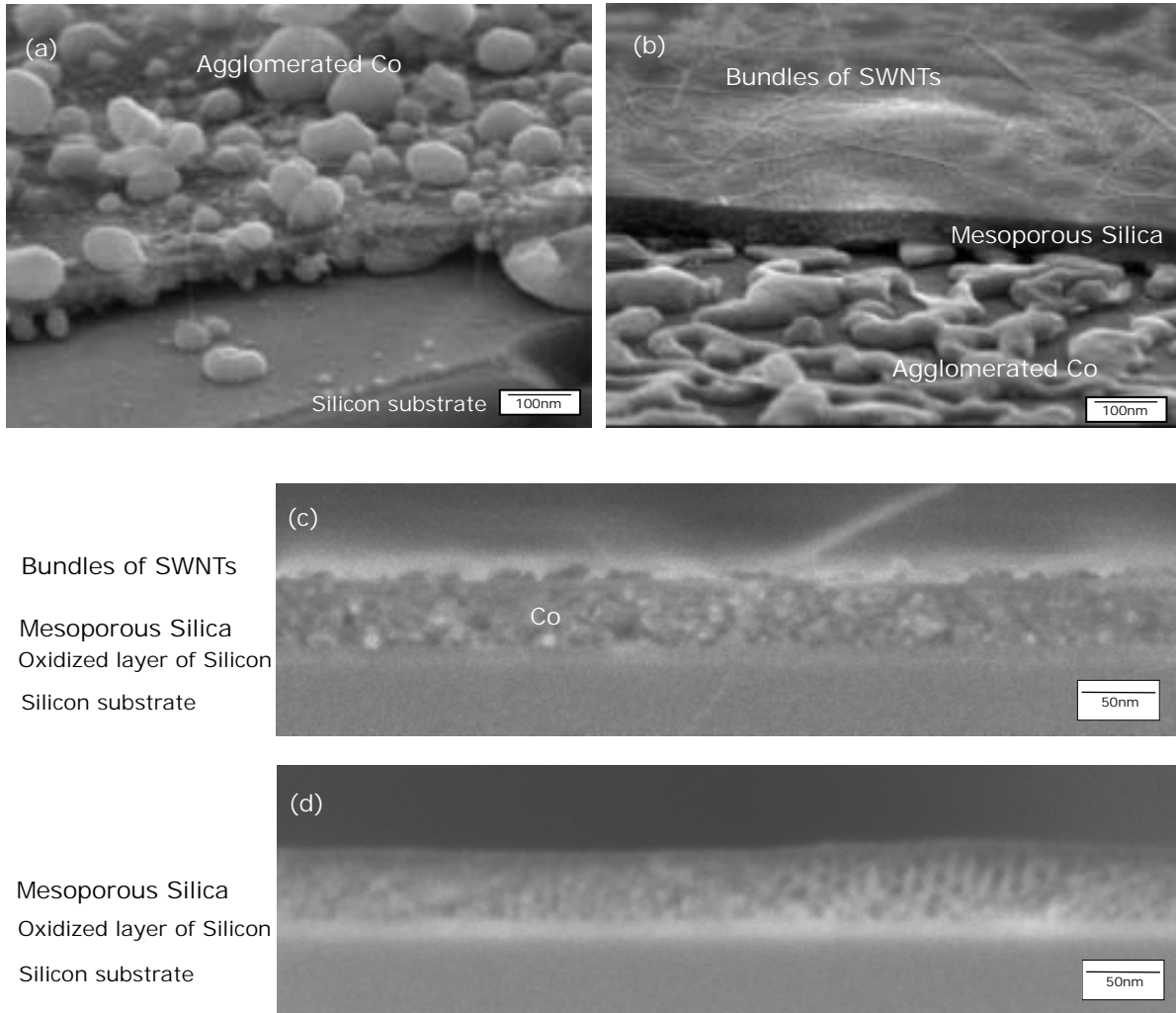


Fig. 3 Cross sectional SEM images of the samples with mesoporous silica film, Co film thickness is (a) 50 nm, (b) 20 nm, (c) 5 nm and (d) 1nm

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 cobalt to agglomerating that is decreasing 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 cobalt, resulting in the agglomerating 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 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 might reveal such 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, for the first time, as a growth guide of SWNT. By selecting the mesophase, we will be able to obtain vertical orientation of the SWNTs. In order to achieve the orientation, another important factor should be controlled, that is the catalyst for SWNTs growth. They must be attached to the substrate. Three kinds of catalyst loading methods are examined here, and the last sputtering method is shown to be promising for the vertical orientation of SWNT, because of the catalyst location could be controlled on the substrate surface. From this study, it is proposed that the mesoporous silica film prevents agglomeration of Co catalyst at a high temperature, resulting in the formation of oriented high-quality SWNTs from the bottom of the silica mesopores.

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