Synthesis of Single-Walled Carbon Nanotubes in Mesoporous Silica Film and Their Field Emission Property

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ABSTRACT. We have succeeded in direct synthesis of single-walled carbon nanotubes (SWNTs) on a conductive substrate coated with a 3D mesoporous silica film, and observed the field emission. Co catalysts for the growth of SWNTs are deposited on the substrate by electroplating. The particle size of the catalyst is well controlled inside defined space of the mesoporous silica film. Furthermore, the location of Co particles can be controlled in the mesopores by the electroplating method. Mono-dispersed SWNTs are grown along with the mesopores that are normal to the substrate, because Co particles are deposited at the bottom of the mesopores. It is also found that the mesoporous silica film prevents the aggregation of Co catalysts and the distortion of Au layer as the conductive substrate. The field emission measurement shows that the turn-on field is 4.2 V/μm at 10 μA/cm^2. The field enhancement factor is about 1500. This approach provides an efficient methodology for fabricating SWNTs-based field emitters.

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1. INTRODUCTION

Carbon nanotubes (CNTs) have been expected as a field emitter providing a stable current at very low electric fields compared with those using silicon or molybdenum, because CNTs are conductive materials with high aspect ratio as well as high chemical stability and high mechanical strength [1].

Since de Heer et al. first reported the field emission properties from multi-walled carbon nanotubes (MWNTs) [2], many researches have been devoted to fabricate a field emitter using MWNTs. However, some unsolved problems, such as current density, threshold voltage and fabrication processes of CNTs, still remain. The threshold voltage can be reduced with SWNTs because a field enhancement factor of SWNTs is larger than that of MWNTs [3]. Direct synthesis of SWNTs on a conductive substrate is the most simple fabrication process of such a field emitter. Moreover, if the density of SWNTs on the substrate can be controlled, the density of the current from the field emitter would be tunable.

To date, the field emission from SWNTs mounted on an electrode has been reported; a macroscopic fragment of raw SWNTs is picked up with tweezers and is fixed on top of tungsten tip [4]. A field emitter using a SWNTs array prepared on a conductive substrate has been reported [5]. The array is, however, prepared using pre-synthesized SWNTs. To the best of our knowledge, no field emitter using a SWNTs array directly synthesized on a conductive substrate has been reported. The position and the particle size of catalysts can be controlled for the fabrication of a field emitter by our strategy as shown below.

We have investigated direct synthesis of SWNTs on a substrate. Murakami et al. have reported that high-purity SWNTs are synthesized from metal catalysts embedded in a mesoporous silica film using alcohol catalytic CVD (ACCVD) process [6]. Hu et al. have examined morphology and a chemical state of Co-Mo catalysts for the growth of SWNTs, and they concluded that well-dispersed nano-sized Co metal particles play an important role in the synthesis of high-purity SWNTs [7]. Ciuparu et al. have also reported that the size of Co catalysts can be controlled by the pore size of mesoporous silica [8]. These researches indicate that high-purity SWNTs can be synthesized by the control of the size of catalyst particles using a mesoporous silica film.

Kemmochi et al. have reported that Co layer between the substrate and a mesoporous silica film can catalyze the synthesis of high-purity SWNTs and also work as the conductive layer for field emitter devices [9]. However, it is difficult to fabricate a field emitter by that method, because Co layer is distorted and its conductivity is lost during the reduction process for the activation of the catalyst at 750 °C. Alternative approach must be developed to achieve for the electrical contact.

In this article, we report on the fabrication of a field emitter using a SWNTs array grown from a mesoporous silica film formed on the surface of the conductive substrate. Co particles are selectively deposited at the bottoms of the mesopores on the conductive Au layer by electroplating after the calcination process. Co is not transferred and aggregated on the surface of the mesoporous silica film without complete oxidation. Electrical contact between SWNTs and the surface of the conductive substrate is successfully achieved through this novel electroplating deposition of catalysts.

2. EXPERIMENTAL

2. 1. Preparation of mesoporous silica film on conductive substrate

Figure 1 shows the schematic diagram of preparation of mesoporous silica film and synthesis of SWNTs.

The Au-sputtered Si substrate was chosen as a conductive substrate. A piece of Si wafer with oxidized layer was cleaned by immersing in 1% HF aqueous solution, and then washed with distilled/ion-exchanged water. Ti was sputtered on the Si wafer as a stress relaxation layer to prevent Au layer from peeling off. Then Au was sputtered on Ti layer as an electrode layer. Each sputtering was carried out by a magnetron sputter coater.

Mesoporous silica films with uniform mesopore-diameter of 2.5 nm were prepared according to the literature [10]. Two grams of tetraetthyl-*ortho*-silicate (TEOS), 0.5 g Brij 30 [$C_{12}H_{25}(OCH_2CH_2)_4OH$], 2 g ethanol and 0.5 g HCl (0.1 M) were mixed at 45 °C for 15 min, resulting in the formation of clear sol. To this clear sol, 0.5 g water was added and the mixture was stored at room temperature for 90 min before coating the film. The molar composition of the sol was 1 TEOS: 0.006 HCl: 2 EtOH: 0.14 Brij

30: 3 H_2O. The film was fabricated on the Au-sputtered substrate by dip-coating at 4 cm/min using a dip coater. The as-coated mesoporous silica film was dried at room temperature for 24 hours, followed by calcination in an electric furnace at 400 °C in air for 4 hours to remove surfactants. According to XRD, this film has 3D *Ia3d* cubic structure. Nitrogen adsorption shows that pore size is 2.5 nm.

2. 2. Synthesis of SWNTs

Co, as the catalyst for synthesis of SWNTs, was deposited by electroplating method. The amount of Co was optimized by changing the plating time. Samples with the plating times of 60, 120, 180, and 240 s are denoted as sample 60, sample 120, sample 180, and sample 240, respectively. The mesoporous silica-coated substrate was immersed into distilled water for 30 minutes under vacuum. Then, a part of the substrate (1 cm^2) was immersed into the plating solution ($CoSO_4 \cdot 7H_2O$ 0.05 mol/L, H_3BO_3 0.4 mol/L, NH_4Cl 0.4 mol/L and Na lauryl sulfate 0.01 g/L) [11]. Co was electrodeposited on the conductive Au layer as a cathode using Pt wire as an anode. Voltage was applied to keep the current constant. The actual current was 100 μA and the plating periods were set for 60, 120, 180, or 240 s. After that, the substrate was immediately picked out from the plating solution and washed with distilled water. The substrate was dried at room temperature overnight.

SWNTs were synthesized by the alcohol catalytic CVD (ACCVD) process [12] [13]. The reaction temperature, time, and ethanol vapor pressure employed in this study were 750 °C, 5 min, and 10 Torr, respectively. Synthesized SWNTs were characterized with Raman spectroscopy (CHROMEX 501is) and FE-SEM (HITACHI, S-900). The laser wavelength of 488 nm was used for the Raman measurements.

2. 3. Field emission measurement

The field emission property was observed using a cathode emission profiler (Tokyo Cathode Laboratory, CEPS-MFE). The measurement condition was optimized based on previous works [14][15]. Emission profiles were obtained by scanning the anode hole (20 μm; diameter) over the emitter surface.

The sample was attached to the cathode stage, which was covered with a thin metal foil with a 4 mm-diameter hole in order to measure the central area of the cathode stage. The gap between anode and the sample surface was fixed at 0.3 mm.

3. RESULTS AND DISCUSSION

Raman spectra were obtained at the range from 100 to 1800 cm^{-1}. Figure 2 shows the Raman spectra of the samples in the high frequency area from 1200 to 1800 cm^{-1} in order to determine the purity of SWNTs. The peak at 1593 cm^{-1} due to G-band, which is originated from graphite, are observed on sample 120 and sample 180. The multi-peak G-band feature, which is unclear for MWNTs due to the large tube diameters, reveals that SWNTs are synthesized in the samples [16]. The peak at 1350 cm^{-1} due to the D-band, which represents the extent of disorder in the sp^2 arrangement of carbon atom, is also observed in sample 120 and sample 180. The G-band and the D-band are slightly observed on sample 60. On sample 240, the peaks due to carbon nanotubes are hardly observed. The purity of SWNTs is estimated by the relative intensity of the G-band and the D-band (G/D ratio). The G/D ratio of sample 120 is the highest among these four samples. This result indicates that optimum plating time is 120 s under the conditions used in this study. No peaks assigned to radial breathing mode were observed in low frequency area most probably due to the limited amount of the products (not shown here).

Figure 3 shows the SEM images of sample 120. No mesopores on the surface can be observed because the mesopore-diameter of 2.5 nm is too small to observe. In Fig. 3 (A), the white bright lines represent the bundles of SWNTs floating over the mesoporous silica surface, and the gray lines represent the bundles of SWNTs attached to the surface. Many gray lines observed in the image indicate that high-density SWNTs are formed on the mesoporous silica film. The white particles can not be observed on the surface. This result supports that aggregated Co does not exist on the mesoporous silica surface. In Fig. 3 (B), the dark area in the lower part of the image represents Si substrate. The white layer, thickness of which is about 300 nm, represents Au and Ti layer. The black

layer on the white layer represents the mesoporous silica film. White lines on the surface represent the bundles of SWNTs. In our previous work, sputtered Co film under mesoporous silica film was distorted and transferred onto the surface of the mesoporous silica film [9]; it was concluded that Co layer was distorted and transferred onto the surface during the reduction process for the activation of the catalyst at 750 °C. Figure 3 shows that the Co particles are not transferred or aggregated on the surface of the mesoporous silica film. In this work, since Co catalyst is deposited on the surface of the conductive substrate after the calcination process, Co catalyst is not transferred or aggregated on the surface of the mesoporous silica film without complete oxidation. This sample has optimized structure for field emitter as shown in Fig. 1.

Areal distributions of electron emissions from sample 120 before and after the growth of SWNTs are shown in Fig. 4. The height of the peaks indicates the local current density. A total current in Fig. 4 (A) was 0.36 mA, and that in Fig. 4 (B) was 0.0007 mA. A number of emission sites were observed in sample 120 with SWNTs. No emission site was observed in the sample without SWNTs. These results reveal that the emission of electron in Fig.4 (A) is due to SWNTs. The distribution of the emission current in the scanning area was not uniform, because the synthesis of SWNTs was not so uniform in the scanning area. Emission is hardly observed in the right part of the scanning area. It is ascribable to partial cracks of the Au layer, which occurred during the calcination process or CVD process. Still, the cracks could be observed by an optical microscope (not shown here). These results revealed that SWNTs attached to the conductive substrate. The field emission curves (*I*-*V*) are shown in Fig. 5. Closed circle denotes sample 120 after ACCVD (with SWNTs) and open circle denotes sample 120 before ACCVD (without SWNTs). The emission current density was 0.5 mA/cm^2 at 5.8 V/μm. The turn-on electric field (E_{to}) at the field emission current density of 10 μA/cm^2 was 4.2 V/μm. This value is lower than those (4.8 V/μm) previously reported with SWNTs emitters [5].

The Fowler-Nordheim plot (FN plot) was employed to interpret the field-emission current. Figure 5 shows the FN plot of the data from sample 120. A linear relationship in Figure 5 confirms that the current was a result of the field emission. The field enhancement factor β is calculated from the FN

plot. The slope of linear correlation corresponds with $\alpha=6.8308\times10^{9}\phi^{3/2}d/\beta$, where the work function ϕ of SWNTs is 4.88 eV [14] and the distance d between the anode and the cathode is 0.3 mm. The field enhancement factor β is thus estimated as 1500 from the slope of the FN plot (1.46×10^{4}).

Compared with randomly grown MWNTs ($\beta\approx1700$) [18], diamond tips ($\beta\approx1000$) prepared by ion sputtering [19], SWNTs film ($\beta\approx3400$) on Teflon-coated metal surface [20], and SWNTs aligned on a gold plate ($\beta\approx3000$)[5], this β value is closer to those of MWNTs or diamond tips , and lower than that of SWNTs. It might be caused by over-growth of bundles of SWNTs on the mesoporous silica film, as observed by FE-SEM (Fig.3). The field emission property might be improved by the removal of over-grown SWNTs.

4. CONCLUSIONS

We directly synthesized SWNTs on a conductive substrate and observed their field emission. Co catalysts were selectively deposited at the bottom of the mesoporous silica film formed on the conductive substrate by the electroplating method. It is found that the mesoporous silica film prevents the aggregation of catalysts. The electrical contact between the conductive substrate and Co catalysts are kept after the synthesis of SWNTs. The SWNTs show a turn-on electric field of 4.2 V/μm and the field enhancement factor of ca. 1500. Our direct synthesis approach is a promising one to fabricate field emitters using SWNTs.

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FIGURE CAPTIONS

Figure 1. A schematic diagram of preparation of mesoporous silica film and synthesis of SWNTs

Figure 2. Raman spectra of (a) sample 60, (b) sample 120, (c) sample 180, and (d) sample 240 after ACCVD process

Figure 3. (A) Top and (B) cross-sectional surface FE-SEM images of sample 120 after ACCVD process

Figure 4. Areal distribution of the emission of electrons from (A) sample 120 after ACCVD (with SWNTs) and (B) sample 120 before ACCVD (without SWNTs)

Figure 5. Field emission curves of samples. Closed circle denotes sample 120 after ACCVD (with SWNTs) and open circle denotes sample 120 before ACCVD (without SWNTs). (Insets) The Fowler-Nordheim plots

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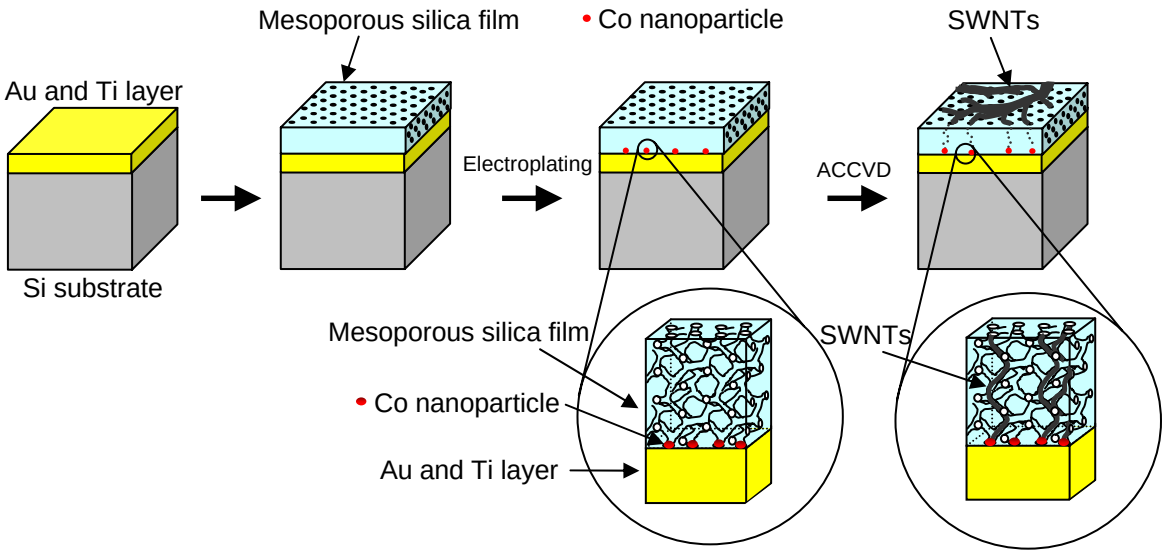
Au and Ti layer
Si substrate
Mesoporous silica film
Electroplating
Co nanoparticle
ACCVD
SWNTs
Mesoporous silica film
Co nanoparticle
Au and Ti layer
SWNTs

Figure 1

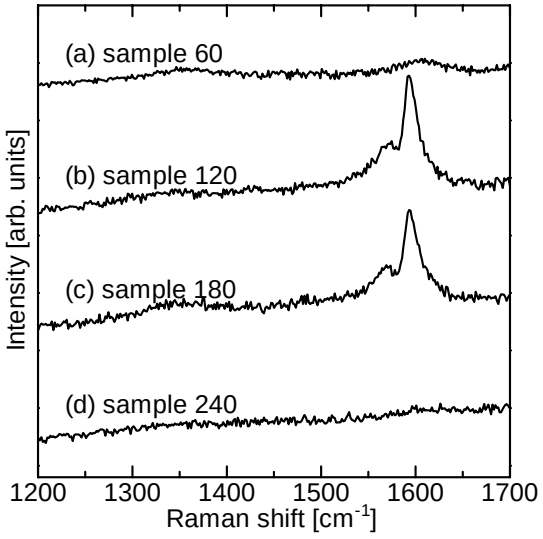
(a) sample 60
(b) sample 120
(c) sample 180
(d) sample 240
Intensity [arb. units]
1200
1300
1400
1500
1600
1700
Raman shift [cm-1]

Figure 2

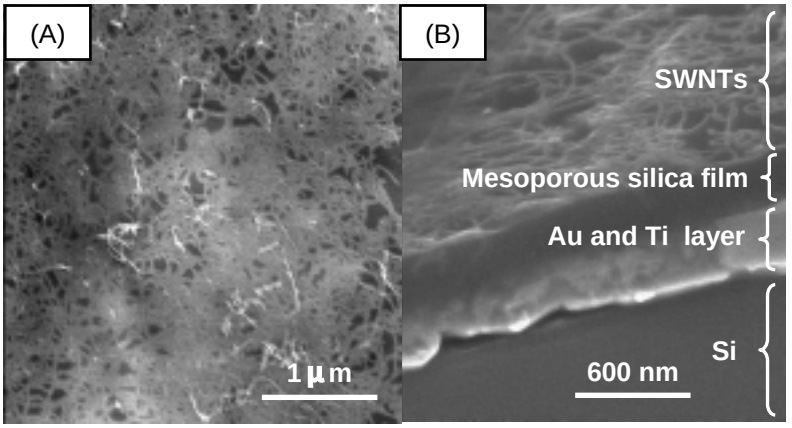

Figure 3

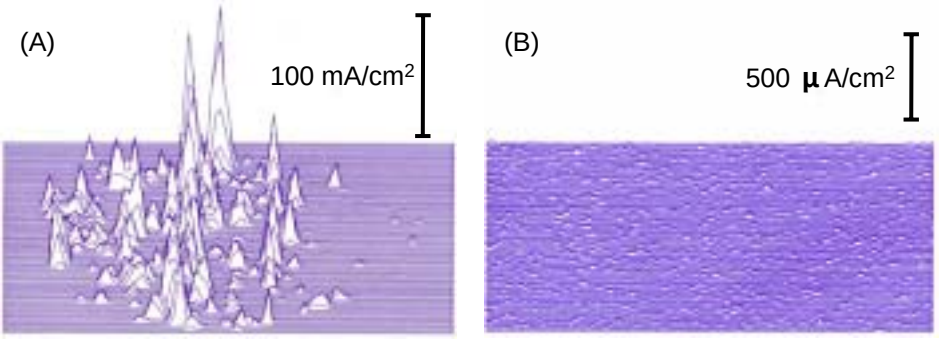

Figure 4

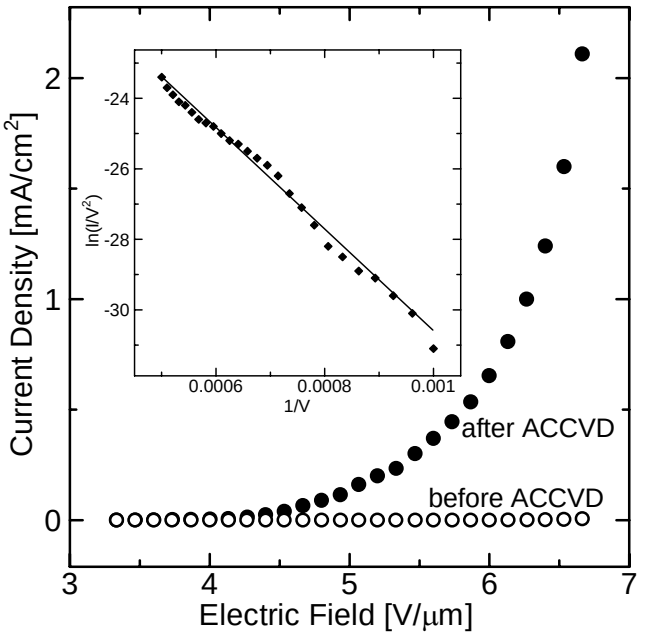
Current Density [mA/cm^2]
Electric Field [V/μm]
after ACCVD
before ACCVD
ln(I/V^2)
1/V
-24
-26
-28
-30
0.0006
0.0008
0.001
0
1
2
3
4
5
6
7

Figure 5