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Growth of Vertically Aligned Carbon Nanotubes Depending on Thickness of Catalyst Films by Plasma-Enhanced Chemical Vapor Deposition

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We attempted to control the diameter and density of vertically aligned carbon nanotubes (VACNTs) using plasma-enhanced chemical vapor deposition. The VACNT diameter was reduced by decreasing the Ni catalyst thickness. Introducing the Mo layer between Ni catalyst and quartz substrate was effective for thin VACNT growth from the thin Ni catalyst film. This result demonstrated that the metal films had to be highly electric-conductive for inducing plasma on the Ni catalyst to grow VACNTs. The maximum density of VACNTs was obtained through the use of optimum plasma pretreatment time.

Keywords: density control; diameter control; Ni catalyst; plasma-enhanced chemical vapor deposition; vertically aligned carbon nanotubes

1. INTRODUCTION

Carbon nanotubes (CNTs) have been studied intensively because of their many characteristics such as high electric conductivity [1], high permissible current density [2], and high mechanical strength in spite of their high flexibility [3]. Furthermore, the growth direction of CNTs is controllable by applying an electric field during chemical vapor deposition (CVD) growth [4]. These characteristics are beneficial to

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prepare various nanostructures for use in scanning probe microscopy (SPM) tips [5–7], field emitters [8–10], wire of ultra large-scale integrated circuits [11], and so on. The required properties for CNTs are different for each purpose. Requirements pertain for CNTs regarding the diameter and density: high density of thin CNTs is necessary for the wire to satisfy high permissible current density and low resistance [11]. In the case of field emitters, low density of thin CNTs is preferred to enhance the electric field at CNT tips [12]. An individual and a thin CNT are necessary for application in an SPM tip.

In this article, we report vertically aligned (VA) CNT growth using plasma-enhanced (PE) CVD. We attempted to control the diameter and density of VACNTs intended to support electronics applications. Diameter control was investigated using various thicknesses of Ni catalyst and introducing a Mo underlayer. Density control was performed by varying the plasma pretreatment time.

2. EXPERIMENTAL

Patterned metals of Ni catalysts and Mo underlayers were deposited on quartz substrates ($5 \times 5\,mm^2$, 0.5 mm thickness) through a metal mask (30 μm thickness, 200 μm pattern width, 100 μm gap) using radio frequency magnetron sputtering. The chamber background pressure was 3.0×10^{-3} Pa, and the pressure during deposition was fixed at 2.0 Pa by feeding Ar gas. The growth conditions were 120°C substrate temperature and 50 W sputtering power for Mo underlayers, and 70°C and 20 W, respectively, for Ni catalysts. The films' deposition rates were 10 nm/min for Mo and 3.5 nm/min for Ni.

The CNTs were grown using DC PECVD method. The reactor tube of the CVD equipment was heated to 500°C. The background pressure was 0.1 Pa. The flow of H_2:Ar (50:50 ccm) was introduced into the reactor tube during heating. Plasma pretreatment was performed by inducing DC glow discharge from immediately before the CNT growth. The DC glow discharge was induced by applying a bias voltage of −250 V between the substrate holder and grounded anodes separated from the substrates by approximately 5 mm. The metal pattern was connected electrically to the cathode of substrate holder by applying Ag paste. The CNT growth was performed by adding 5 ccm of ethylene (C_2H_4) gas. The total pressure was maintained at 2 kPa.

The obtained CNTs were observed using a field emission scanning electron microscope (SEM; S-4500; Hitachi Ltd.) operated at 15 kV and a field emission transmission electron microscope (TEM; HF-2000; Hitachi Ltd.) operated at 200 kV.

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of Ag paste, which electrically connects the Ni/Mo patterns to the cathodes. The respective thicknesses of Ni catalyst and Mo underlayer were 3.5 nm and 10 nm. The specimen of Figure 1(a) was prepared by putting the substrate on the cathode without applying Ag paste. The specimen shown in Figure 1(b) was prepared by electrically connecting the Ni/Mo pattern to the cathode by applying Ag paste. Some particles were observed on the patterns, which were not connected electrically to the cathode. Figure 1(b)

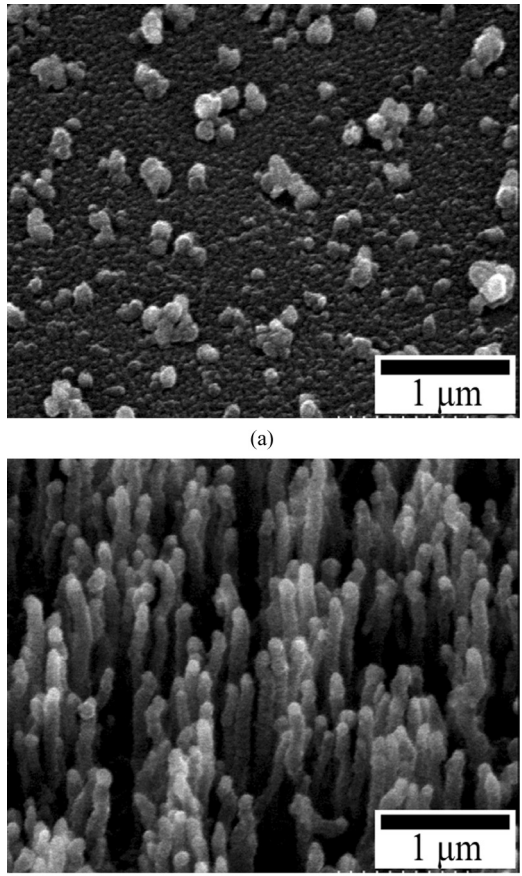


FIGURE 1 SEM images of the surface of the Ni/Mo pattern after CVD. (a) The Ni/Mo pattern was not connected electrically to the cathode. (b) The Ni/Mo pattern was connected electrically to the cathode using Ag paste.

shows that VACNTs were prepared on the patterns by applying Ag paste. Figure 2 shows the VACNTs as observed using TEM. The hollow center and graphitic sidewalls were visible. In this case, the number of walls was 25, and the CNT internal and external diameters were *ca*. 4.6 nm and *ca*. 26 nm, respectively.

In the case of PECVD method, a cathode dark space is used mainly for preparing CNTs [13]. The cathode dark space contains many positive ions and radicals. The active species reduce the activation energy for a catalytic reaction. In addition, the voltage drop takes place mostly in the cathode dark space because of its high impedance. The positive ions are accelerated using an electric field; some of them bombard the cathode of catalyst films. These impacts generate catalyst particles from continuous catalyst films [14–16]. The CNTs are aligned using an applied strong electric field. The thickness of the cathode dark space was estimated using the Child-Langmuir law [17]. The estimated thickness of the cathode dark space was 0.21 mm. Therefore, the DC glow discharge was not induced on a quartz substrate with 0.5 mm thickness although the

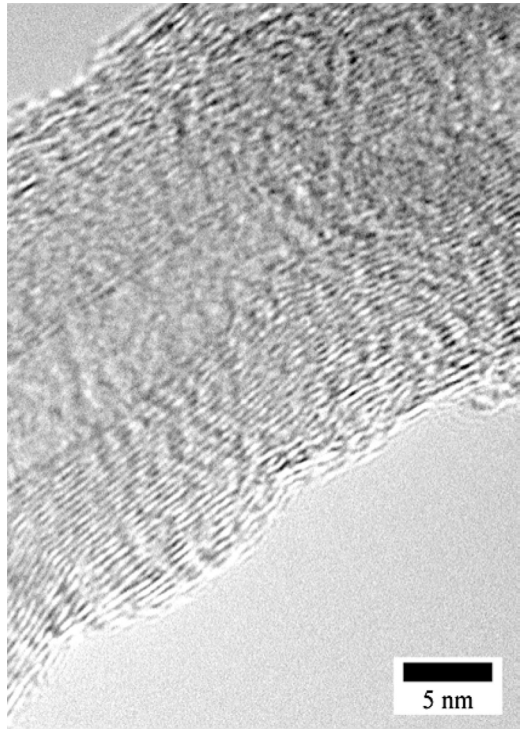


FIGURE 2 Typical TEM image of a VACNT.

substrate was placed on the cathode. The catalysts should be connected electrically to the cathode to induce plasma on the catalysts.

Figure 3 depicts SEM images of VACNTs with various Ni thickness. The Ni thickness, the pattern resistance from the Ag paste, and the diameter and the density of the grown VACNTs are listed in Table 1. The pretreatment was maintained for 1 min. The VACNT diameter was decreased by reducing the Ni catalyst thickness. Figure 3(a) shows that no CNTs grew from 3.5 nm of Ni thickness. Although the Ni thickness was equal to that shown in Figure 3(a), the smallest VACNT diameter was obtained by introducing the Mo underlayer, as shown in Figure 3(d).

The VACNT diameter was reduced by reducing the Ni catalyst thickness. The continuous Ni catalyst films were broken into fine particles using thermal and plasma pretreatment. The CNT diameter is determined by the catalyst particle diameter. In addition, the catalyst particle diameter depends on the initial thickness of the catalyst films [18,19]. However, VACNTs did not grow when the catalyst films were too thin, i.e., 3.5 nm. The pattern conductivity was reduced because

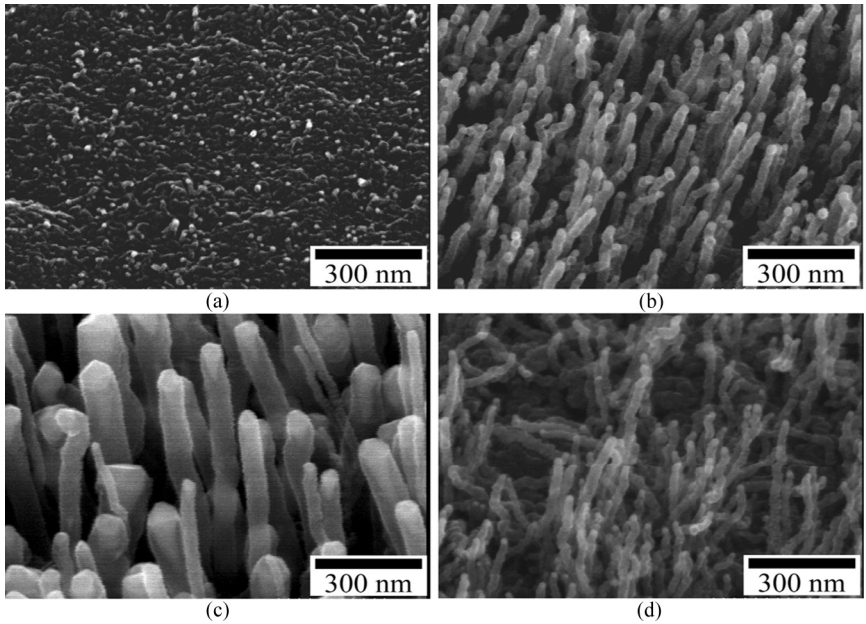
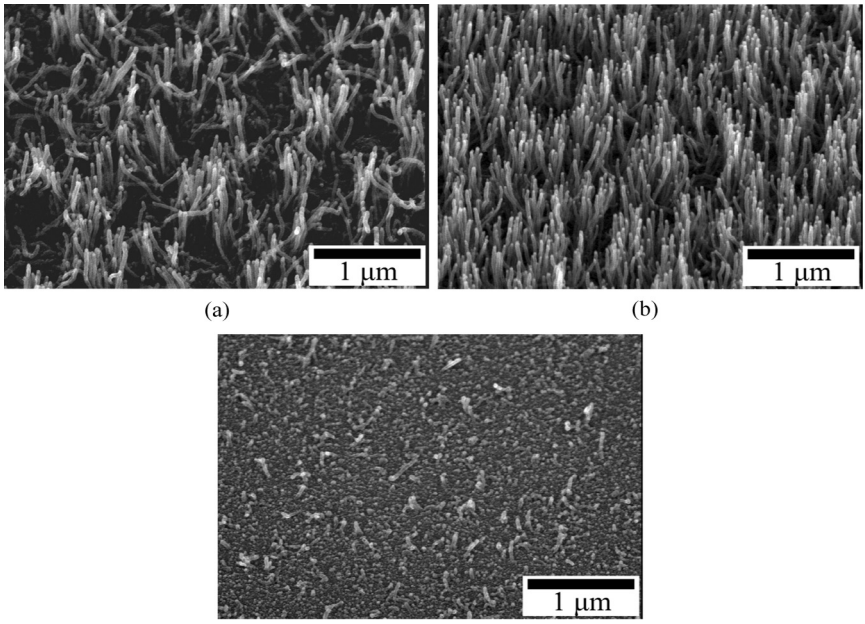


FIGURE 3 SEM images of VACNTs grown from various Ni catalyst thickness. The Ni catalyst film thicknesses were (a) 3.5 nm, (b) 35 nm, (c) 350 nm, and (d) 3.5 nm with a 10 nm Mo underlayer.

TABLE 1 Summary of the Obtained VACNTs with Various Ni Catalyst Thicknesses

	(a)	(b)	(c)	(d)
Thickness of Ni [nm]	3.5	35	350	3.5 with 10 nm Mo
Pattern resistance from Ag paste [Ω]	>60 M	360 k	12 k	300 k
VACNT diameter [nm]	×	40	40–150	30
VACNT density [μm^{-2}]	×	100	30	90

the Ni catalysts formed fine particles. The resistance of the 3.5 nm Ni patterns was greater than 60 MΩ. Therefore, the plasma was not induced on the 3.5 nm Ni patterns during CNT growth because of their high resistance. By introducing the Mo underlayer, VACNTs with smallest diameters were obtained from 3.5 nm Ni patterns. The densities of VACNTs grown from 3.5 nm Ni patterns were slightly less than those of 35 nm Ni. Although the Ni catalysts were thin, plasma was induced on Ni catalysts because of the conductive Mo underlayer



(a) (b)

(c)

FIGURE 4 SEM images of the VACNTs at different plasma pretreatment times of (a) 0.5 min, (b) 1 min, and (c) 5 min.

and Ag paste. Therefore, introducing an Mo underlayer is effective for preparing VACNTs with small diameter and low density.

Figure 4 shows SEM images of samples with different plasma pretreatment times. The Ni catalyst and Mo underlayer were 3.5 nm and 10 nm thick, respectively. The pretreatment times were (a) 0.5 min, (b) 1 min, and (c) 5 min. In fact, VACNTs with *ca*. 30 nm of diameter grew from the films, which had been pretreated for 0.5 and 1 min. For pretreatment time of 5 min, poorly aligned CNTs with 20–35 nm diameter and 80–450 nm of length grew sparsely. The respective densities of the VACNTs are shown in Figure 5: they were (a) $50\,\mu m^{-2}$, (b) $90\,\mu m^{-2}$, and (c) $20\,\mu m^{-2}$.

The CNT density was increased by extending the pretreatment time from 0.5 min to 1 min. The plasma induces catalyst films to form fine particles, as discussed above. Many catalyst particles were produced during the extended pretreatment time. However, the CNT density was decreased by extending the pretreatment time to 5 min. The Ni catalyst and Mo underlayer were removed through the use of longer pretreatment times. Sparse CNTs were prepared because a small amount of Ni catalyst remained at the pattern. Short and the poorly aligned CNTs were prepared because the resistance of the Mo underlayer was increased as a result of the reduced thickness.

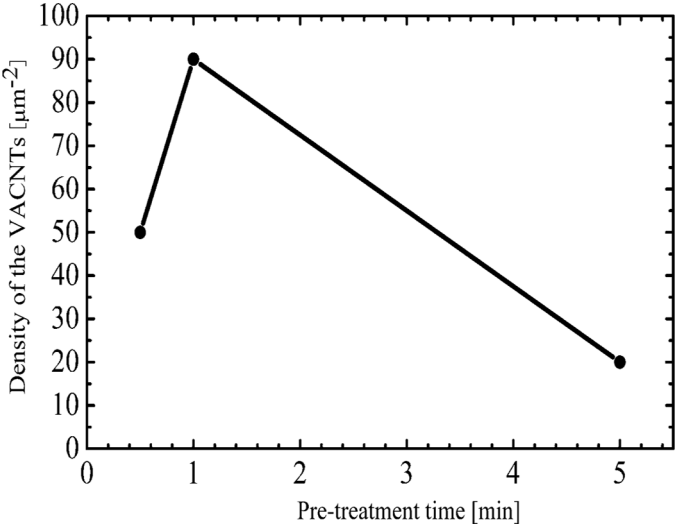


FIGURE 5 Density of the VACNTs as a function of plasma pretreatment time.

4. CONCLUSIONS

We attempted to control the density and the VACNT diameter using DC PECVD. It was important for VACNT growth that the DC plasma be induced onto the Ni catalyst. The VACNT diameter was reduced by decreasing the Ni catalyst thickness. Introducing the Mo underlayer was effective for thin VACNT growth from the thin Ni catalyst film. The VACNT density was maximized by plasma pretreatment time of 1 min. Longer or shorter pretreatment time than 1 min yielded a lower VACNT density.

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