Influence of morphology of catalyst thin film on vertically aligned carbon nanotube growth

Young Min Shin, Seung Yol Jeong, Hee Jin Jeong, Sung Jin Eum, Cheol Woong Yang, Chong Yun Park, Young Hee Lee*

Department of Physics, Institute of Basic Science, and Center of Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Republic of Korea

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Abstract

We have investigated how the morphology of transition metals prepared by radio-frequency magnetron sputtering influences on the vertically aligned carbon nanotube growth during thermal chemical vapor deposition (CVD). By changing the catalyst morphology systematically with sputtering temperature, pressure, and time, we were able to control the density, diameter, and length of the aligned carbon nanotubes at a given thermal CVD growth condition. We found that the sputtering temperature and pressure determine the grain size and density of the transition metals that control the diameter, length, and density of carbon nanotubes. Formation mechanism of nucleation seeds for carbon nanotubes in terms of these variables is further discussed.

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1. Introduction

Carbon nanotubes (CNTs) have been synthesized with various methods such as arc discharge [1,2], laser vaporization [3], and chemical vapor deposition (CVD) [4–9,14]. Among these methods, CVD technique has an advantage to control the structure of CNTs through various parameters. Transition metals such as nickel (Ni), cobalt (Co), and iron (Fe) have been used as a catalyst to grow the CNTs. Typical hydrocarbon source gases are effectively decomposed with an assistance of the metal catalyst at relatively low temperature. It has been known that the morphology of transition metals is of critical importance for the CNT growth [4–5,7–10]. Therefore, control of the surface morphology of the catalytic metal is an
essential ingredient prior to the CNT growth. Furthermore, the diameter, density, and length of CNTs can be controlled by the catalyst morphology. The Co thin film deposited on Si substrate by thermal evaporator has been further dipped in HF solution to control the nucleation sites of catalyst prior to the CNT growth [11]. However, the film uniformity in large area, adhesion of catalyst to the substrate, and wet etching process are serious drawbacks for application to field emission displays. Several groups have tried to control the catalyst surface by NH₃ pre-treatment during the CNT growth [4–6]. One can also use porous surface to control the morphology of the transition metals [12]. We would like to minimize the growth parameters during the CVD process by preparing the catalyst film in advance without further post-treatment. We introduce here the radio-frequency (RF) magnetron sputter to prepare the uniform thin film of catalyst. This method is useful not only for the preparation of a large area substrate but also for the formation of strong adhesion layers on the substrate. Moreover, it can be easily adopted in the current technology. It has been successfully used for the CNT growth [8,9]. In this study, we have modified systematically the catalyst surface morphology with various RF power densities using RF magnetron sputtering method in order to control the CNT length, diameter, and density.

2. Experimental procedure

Ni thin films were deposited onto TiN/p-type doped Si (1 0 0) substrate using the RF Magnetron sputtering technique with Ni target (100 mm diameter, 5 mm thickness, purity 99.99%). The TiN thin film between Ni transition metal and silicon substrate was introduced (i) to effectively protect the formation of silicide, (ii) to form strong adhesion between Ni and Si substrate, and (iii) to use it for an electrode with high conductivity.

Before the deposition of Ni thin films, the sputter chamber was pumped to a base pressure of 1×10⁻⁶ Torr. TiN/p-type-doped Si (1 0 0) substrate was heated by a heating plate of graphite. The chamber pressure was then adjusted to several working pressures by feeding Ar gas. The target-to-substrate distance was kept at 100 mm. Prior to the deposition of Ni, a pre-sputtering process was performed to clean the target surface for 10 min. During the sputtering, the RF power for Ni target was fixed at 20 W. The power dependence on the Ni morphology has been described elsewhere [8]. The Ni film thickness was maintained less than 100 nm during the whole process. The Ni-coated TiN/Si substrate was moved into a thermal CVD chamber without any pretreatment. The CNT growth condition was fixed at a certain (optimized) condition to study the influence of Ni surface morphology deposited at various conditions. The CNTs were grown on Ni-coated TiN/Si substrates using thermal CVD at 650 °C with a gas mixture with C₂H₂ (20%) and Ar (80%). The chamber pressure was kept at 5.5 Torr. The CVD chamber was heated by halogen lamps with a heating rate of 54 °C/min till the temperature reached the growth temperature of 650 °C. The growth temperature was fixed during the growth time of 20 min.

The surface morphologies of Ni thin film were investigated using a non-contact mode of atomic force microscope (AFM). The length and density distributions of CNTs were observed by scanning electron microscope (SEM). High-resolution transmission electron microscope (HR-TEM, JEOL-JEM3011, 300 keV) was also used to measure the quality and diameter of CNTs. For HR-TEM measurement, the peeled nanotubes were suspended in butyl alcohol, and dispersed simply by stirring with a glass stick. The solvent containing the nanotubes was dripped onto a micro-grid covered with a copper. The micro-grid was dried in vacuum oven before it was loaded into the TEM chamber.

3. Results and discussions

Fig. 1 is the AFM images in contact mode, which show the surface morphologies of the Ni films prepared at different sputtering temperatures. In these cases, we fixed the chamber pressure at 5 mTorr and the sputtering time for 4h. Small Ni grains are uniformly distributed over the substrate. It is in fact the RF power density that is the most critical variable for the grain formation.
We tried to maintain the lowest RF power to have Ni grains with smaller diameter during Ni deposition (in this case 20 W). The Ni grain morphology determines the quality of the CNT growth, as we will discuss later. The grain size and number density of the Ni film increase gradually with the increasing sputtering temperatures up to 240 °C. However, after 240 °C, the grain sizes keep increasing, while the number density of the grains decreases. At higher sputtering temperature, Ni grains were not uniformly distributed, as shown in Fig. 1d, which is also evidenced by the root-mean-square (RMS) height in Fig. 1f. Fig. 1e summarizes the grain-size changes as a function of the sputtering temperatures, showing an abrupt increase at 500 °C. Ni atoms ejected from the sputter target at a given RF power reach the substrate surface and then either migrate by the thermal diffusion and interact with other adatoms or re-evaporate from the surface. The substrate temperature determines the thermal diffusion length on the surface, which seriously influences the grain size. At room temperature, the migration of Ni atoms deposited on the surface may be negligible due to the small diffusion length, i.e., diffusion-limited. The grain formation is mostly determined by an initial adsorption of Ni clusters and smaller grain sizes are expected, as observed at
relatively low temperature ranges in Fig. 1. On the other hand, high temperature will cause an increase of the thermal diffusion length and therefore Ni grains start aggregating, enlarging the grain size.

Figs. 2a–d show the oblique (45°) SEM images of vertically aligned carbon nanotubes grown on the substrate with Ni dots that were deposited with the previously described conditions. The CNT length and density increase with sputtering temperatures up to 240 °C, but decrease at higher temperatures, as summarized in Fig. 2e and f. In particular, we observed that at 500 °C, (i) the CNT lengths were relatively short compared to the CNTs grown at other conditions and (ii) the CNTs were no longer aligned due to the low Ni grain density. It strongly suggests that the formation mechanism of the vertically aligned CNTs is the steric hindrance between nanotubes, which is invoked by the high number density of Ni grains.

In general, the catalytic growth of CNTs by CVD involves an efficient decomposition of hydrocarbon gases, incorporation of carbon atoms into the grain of the transition metals, and

![Fig. 2. SEM images (45° tilted) of vertically aligned CNTs synthesized on Ni films deposited at the sputtering temperature of (a) room temperature, (b) 120 °C, (c) 180 °C, (d) 240 °C, and (e) lengths and (f) densities of CNTs as a function of the sputtering temperature.](image-url)
diffusion of carbon atoms in the transition metals to form the nucleation seeds. Figs. 3a and b show the HR-TEM images of CNTs with different sputtering temperatures at 400°C and 500°C, respectively. The outer diameter of the CNTs grown on Ni grains formed at 400°C is less than 20 nm and the inner diameter is less than 10 nm, as shown in Fig. 3a. The CNTs are straight with relatively fewer defects on the walls in spite of low growth temperature (650°C) during the CVD. Unlikely, the CNT walls grown on Ni grains formed at 500°C are not well defined with a lot of defects and the diameters ranging from 30 to 40 nm, as shown in Fig. 3b. No clear inner hollowness is observed and sometimes bamboo types are formed. We observed completely filled nanotubes or fibers in many cases. These observations suggest that the diameters of the CNTs are controlled by the grain sizes of the Ni film, as expected. Diffusion of catalytically decomposed carbon atoms is limited within the Ni grain. The growth temperature determines the diffusion length of the carbon atoms. The carbon diffusion length is short at low growth temperature. If the grain size is small enough, the carbon atoms can diffuse over the whole region of the grain uniformly to form a solid nucleation seed of hexagons. When the grain size is large at low temperature, the diffusion length is relatively short and hence carbon atoms may not be supplied uniformly over the whole region of the grain. Therefore, there will be less chance to form a nucleation seed and more chance to form defects on the tube walls.

We now change the sputtering pressure, while fixing the substrate temperature at 180°C and sputtering time for 5 hours. Figs. 4a and b show the AFM images of the Ni films at different pressures. At 20 mTorr, the grain size is around 20 nm, which is smaller than that shown in Fig. 1. The Ni grain size decreases with increasing sputtering pressure, whereas the number density...
Fig. 4. AFM images of Ni thin films deposited at the sputtering pressure of (a) 5 mTorr, (b) 10 mTorr, (c) 15 mTorr, and (d) 20 mTorr, and (e) average grain size and (f) height RMS of roughness as a function of sputtering pressure.

Fig. 5. SEM images (45° tilted) of vertically aligned CNTs synthesized on Ni films deposited at the sputtering pressure of (a) 5 mTorr, (b) 10 mTorr, and (c) lengths and (d) densities of CNTs as a function of the sputtering pressure.
of the Ni grains increases. The Ni grains are uniformly distributed over the substrate area, similar to those shown in Fig. 1. While the sputtering yield, defined as the number of Ni atoms ejected per incident Ar particle, is constant at a given RF power density, the arriving Ni atoms on the surface will reduce at higher sputtering pressure due to larger scattering rate with Ar ions during the flight according the Thornton model [13].

Figs. 5a and b show the CNTs grown at different sputtering pressures of 5 and 20 mTorr, respectively. The CNT length and the number density keep decreasing with increasing sputtering pressures. When the grain size is small, small amount of carbon atoms will be supplied to the Ni grain. In the situation where the carbon supply is not enough or the CNT growth temperature is low, the CNT growth rate on a smaller grain would be slower in spite of short diffusion length [14]. The CNT density will be lower due to the lower chance of forming nucleation seeds by the insufficient supply of carbon atoms. We confirmed this assertion by changing the CVD condition. We tried to grow the CNTs using the substrate with the smallest grains we could get (Fig. 4b). With increasing flow rate of acetylene gas, the CNT density was significantly increased due to higher chance of forming nucleation seeds.

Fig. 6a and b show the AFM images at different deposition times of 2 and five hours, while fixing the sputtering pressure at 5 mTorr and temperature at 180 °C. When the Ni film thickness is less than the grain size, the grain size of the Ni thin film is proportional to the film thickness [12]. In our case, the Ni film thickness at 2 h of sputtering time is 50 nm and the grain size is 40 nm. In this region, the grain size is not proportional to the film thickness. The grain size in fact decreases with increasing sputtering time, as shown in Fig. 6c. The grain size ranges from 40 to 30 nm in our sputtering time limit. The Ni grains are uniformly distributed over the whole surface of the substrate. We observed that the CNTs were vertically grown in this range, as shown in Fig. 7. It is also noted that an optimum grain size exists for the vertically
aligned CNT growth. In this work, the grain size less than 30 nm or greater than 60 nm, the CNTs fail to grow vertically. These criteria are of course the growth–temperature dependent.

4. Summary

We have prepared the Ni thin films at various conditions using the RF magnetron sputter for the vertically aligned CNT growth. We have demonstrated that the control of the surface morphology of the Ni film is a crucial factor in growing vertically aligned CNTs. Several sputtering parameters have been measured. At high sputtering temperatures, Ni grains were large with large size distributions due to the aggregation of Ni grains. The length and density of the grown CNTs were reduced compared to the CNTs grown at other sputtering temperatures. Ni grain size decreases with increasing sputtering pressure, giving rise to the reduction of the CNT length and the number density. In the case of the grain size less than 30 nm or greater than 60 nm, the CNTs fail to grow vertically. Therefore, optimum grain size exists for the vertically aligned CNT growth.

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