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Communications

Packing Density Control of Aligned Carbon Nanotubes

Soo-Hwan Jeong,† Ok-Joo Lee,† Kun-Hong Lee,*,† Sang-Ho Oh,‡ and Chan-Gyung Park‡

Departments of Chemical Engineering and Materials Science and Engineering, Pohang University of Science and Technology, San31, Hyoja-Dong, Nam-Ku, Pohang, Kyungbuk 790-784, Korea

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Carbon nanotubes (CNTs) are the material of interest for many potential applications, including electron field emitters,[1] quantum wires,[2] molecular filters,[3] and artificial muscles.[4] Control of the packing density of CNTs, which stand normal to a substrate, is very important to fundamental characterization and potential applications in some microelectronic devices such as CNT-based field emitters. For instance, the packing density of aligned CNTs has a paramount effect on emission characteristics due to the field screening effect.[5,6] Here, we report a simple method to control the density of aligned CNTs.

Densely packed aligned CNTs have been prepared by common techniques, such as thermal[1] or plasma-enhanced chemical vapor deposition.[7] Alternatively, template-based techniques, especially anodic aluminum oxide (AAO) nanotemplates, have been applied to grow aligned CNTs.[8] In the fabrication of CNTs using AAO nanotemplates embedded with Co catalysts, the length and the packing density of CNTs are the same as those of AAO nanotemplates[6,8,9] (as high as 10^8-10^{11} pores cm^{-2}). However, not only do these CNTs have poor crystallinity but also the density of CNTs is very high, which is the direct consequence of the high density of pores in the AAO templates. In our previous works,[6,10] we showed that there was a competition in the pyrolysis of C_2H_2 with the AAO nanotemplate between CNTs growth by the Co catalysts and amorphous carbon deposition on the pore wall by the AAO nanotemplate itself. On the other hand, as can be seen in our work[10] and another work,[11] well-graphitized CNTs were overgrown out of the pores of AAO nanotemplates in a hydrogen-added atmosphere. Hydrogen is a well-known inhibitor of the deposition of amorphous carbons so that CNTs with the same pore diameter can grow out of the pores of AAO nanotemplates. However, control of the packing density of aligned CNTs was not possible in this case.

* To whom correspondence should be addressed. E-mail: ce20047@postech.ac.kr.
† Department of Chemical Engineering.
‡ Department of Materials Science and Engineering

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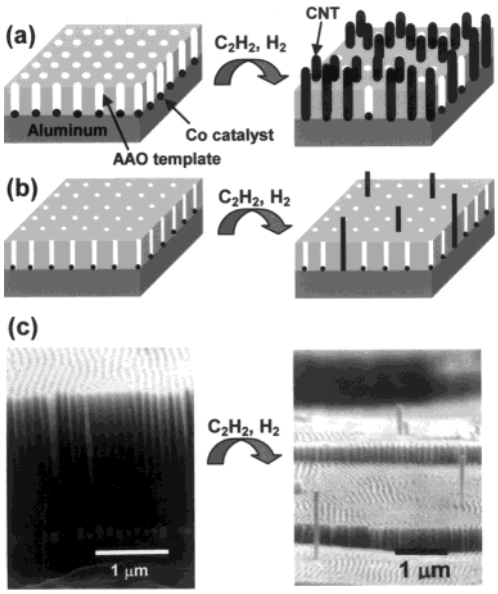

Figure 1. Schematic of the fabrication process. (a) Growth of high-density CNTs with a low aspect ratio of AAO pores. (b) Growth of low-density CNTs with a high aspect ratio of AAO pores. (c) SEM images of an AAO template embedded with Co catalyst (left-hand side) and density-controlled CNTs (right-hand side).

In this communication, we report a simple method to control the packing density of aligned CNTs in AAO nanotemplates. The key idea of this method is to utilize the competition between the catalytic reaction of C_2H_2 with Co catalysts and amorphous carbon deposition on the pore surface of AAO nanotemplates.

This idea was realized by preparing AAO templates of different aspect ratios. An illustration of the fabrication process and the scanning electron microscope (SEM) image of density-controlled CNTs in this work are shown in Figure 1a−c), respectively.

The process starts with the preparation of AAO templates. Two-step anodization was chosen to prepare highly ordered AAO templates.[12] Briefly, a cleaned and electropolished Al sheet of high purity (99.999%) was first anodized at 40 V in 0.3 M oxalic acid solution at 15 °C for 12 h. After chemically etching the AAO film in a mixture of phosphoric acid and chromic acid solution, anodization was performed again under the same conditions for 10 or 20 min, which results in the formation of a highly ordered AAO template with a pore depth of 1 and 2 μm, respectively. At the end of the second anodization, a voltage drop from 40 to 14 V by 1-V steps was required to decrease the thickness of the barrier alumina layer at the bottom of the pores, which is important for facilitating the following uniform electrodeposition of Co. After the voltage drop process, the pore diameters of the AAO templates were adjusted to 40 or 80 nm by widening the pores in 0.1 M phosphoric acid. The thickness of the barrier layer reduced further during this step. Co catalysts were electrochemically deposited at the bottom of the pores.[6] The left photograph of Figure 1c shows the scanning electron microscope (field emission SEM, Hitachi S-4200) image

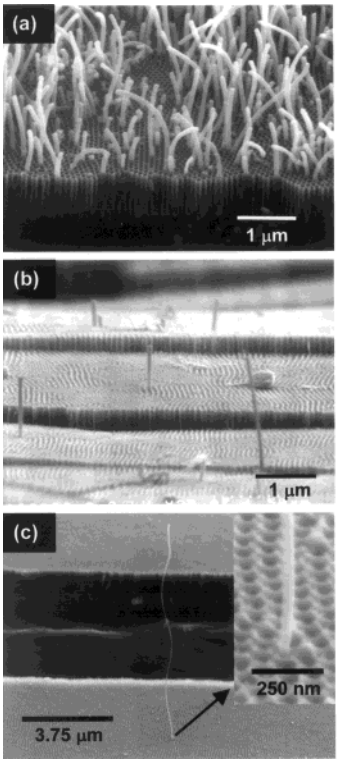

Figure 2. SEM images of the CNTs grown with the AAO templates of different aspect ratios in a gas mixture of 10% C_2H_2, 20% H_2, and 70% Ar at 650 °C for 20 min. (a) Sample A, (b) sample B, and (c) sample C.

of the AAO template with electrodeposited Co. It is observed that Co particles can be electrodeposited at every pore with a uniform height. CNTs were grown with three samples. One is a AAO template with 1-μm pore depth and 80-nm diameter (hereafter, sample A), another is a AAO template with 2-μm pore depth and 80-nm diameter (hereafter, sample B), and the last is a AAO template with 2-μm pore depth and 40-nm diameter (hereafter, sample C). It should be noted that all samples have the same packing density of pores due to the same anodizing voltage. The pore density is approximately 10^{10}/cm^2.

The Co particles were reduced in a gas mixture of 10% H_2 and 90% Ar at 500 °C for 1 h. Next, CNTs were grown by catalytic pyrolysis at 10% C_2H_2 and 20% H_2 in an Ar carrier gas for 20 min, at 650 °C in a tube reactor. The total flow rate was 200 sccm. Finally, the C_2H_2 and H_2 flow was stopped, and the samples were cooled to room temperature in an Ar atmosphere.

As shown in Figure 2, the packing density of CNTs changes dramatically depending on the diameter and depth of the templates. Estimated densities of sample A, sample B, and sample C from the SEM images are $2-3 \times 10^9$, $2-3 \times 10^7$, and $1-2 \times 10^5$ CNTs/cm^2, respectively. This figure also reveals that the diameter of CNTs is almost the same as that of the pores in the AAO template. The CNTs initially align vertically to the surface of the template. With an increase in growth time, the length of CNTs increased and CNTs became curved. However, the packing density of CNTs did not change.

Figure 3 is a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010F) image and an electron diffraction pattern of CNT shown in Figure 2a.

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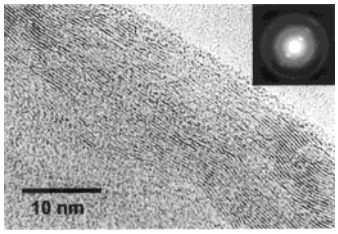

Figure 3. HRTEM image of a CNT (sample A). Inset: Electron diffraction pattern of CNT.

As the CNTs have a relatively large diameter, only the right half of a CNT is shown in this figure. Well-ordered graphitic layers are clearly seen on the right side while part of a hollow core appears on the left corner. The tube wall thickness was found to lie in the range of 14−17 nm, suggesting that it is composed of approximately 40−50 graphitic walls. The interwall distance (d_{002}) was 3.5 Å, which is larger than the interlayer distance of graphite ($d_{002} = 3.35$ Å), as occurs in multiwall CNTs because of the curvature of the walls. The electron diffraction pattern also confirms that the ordered graphitic layer is oriented parallel to the tube axis.

Several important characteristics of this method should be noticed: The merits include the simple adjustable parameter of the aspect ratio of the AAO pores, which can be easily controlled by varying the anodizing and pore-widening time. This method does not require lithography and is therefore simple and inexpensive. In addition, it is not limited to a small area and can produce aligned CNTs with a wide range of densities. The process can also be directly applied on a variety of substrates including silicon wafers.[6] The above-mentioned properties are very important to the fundamental characterization and potential applications of CNT-based microelectronic devices.

The mechanism of CNTs' growth by the catalytic pyrolysis of hydrocarbon has been postulated as involving either base or top growth.[13] In our experimental conditions, CNTs grow in the top growth mode.[10] At the initial stage of our experiment, CNT growth and carbon deposition on the pore wall occur simultaneously. As the synthesis continues, the deposited carbon on the internal pore surface prevents the liftoff of Co catalysts at the tip of the growing CNTs, resulting in short CNTs inside the pores. However, the CNTs, which have already escaped from the pores, can continuously grow. Although the Co catalysts at the bottom of the AAO template are uniformly deposited and have similar dimensions, the Co catalyst particles are not exactly the same. Therefore, it is understandable that the activities of the deposited cobalt catalysts are different from each other. Moreover, CNT growth in numerous pores has a statistical fluctuation. Therefore, some pores can overgrow the CNTs while others cannot.

The mean free path of C_2H_2 molecules is ≈174 nm under the experimental conditions. Therefore, C_2H_2 flow in a cylindrical pore of an AAO nanotemplate proceeds in Knudsen diffusion. C_2H_2 molecules collide mainly with the pore walls so that the effect of pore geometry is amplified; in other words, carbon deposition on the pore walls would be more noticeable in an AAO template of smaller and deeper pores. In this context, the number of CNTs, which are able to escape from the pores of an AAO template, are strongly affected by the length and diameter of the pores in an AAO template. To quantify this geometric effect on the packing density of CNTs, further investigation is required.

In summary, a simple method to control the packing density of aligned CNTs is proposed. This method takes advantage of the difference in the catalytic activity of Co catalysts and AAO nanotemplates and the large aspect ratio of pores in AAO templates. This approach should open novel possibilities for the fundamental characterization and applications of microelectronic devices such as CNT-based field emitters.

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