

Anodic aluminum oxide template assisted growth of vertically aligned carbon nanotube arrays by ECR-CVD[☆]

Po-Lin Chen, Jun-Kai Chang, Cheng-Tzu Kuo*, Fu-Ming Pan

Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu 300, Taiwan

Available online 1 July 2004

Abstract

Highly aligned carbon nanotubes (CNTs) have been successfully grown in vertical channels of the anodic aluminum oxide (AAO) template by microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD). Nanoporous AAO templates with hexagonal pore pattern were prepared by the two-step anodization of Al films. Following the electroplating of Co catalyst into the pore bottom, multiwalled CNTs were synthesized in the ECR-CVD system using a gas mixture of CH₄ and H₂. The microstructure of the CNTs was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The CNTs with a very high packing density and a uniform size distribution are well graphitized, and Co particles embedded at their tips implies the tip growth mechanism. The segments of CNTs stretching out of the AAO nanopores still maintain relatively good alignment, and have a very slow growth rate, which allows us to obtain reproducible tube length by tuning the growth time. Field emission measurements of the CNTs showed derivable electron emission properties, attributed to their uniformity in size, good alignment, and good graphitization properties.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Nanotubes; Graphite; Plasma CVD; Field emission

1. Introduction

In the past decade, carbon nanotubes (CNTs) have become one of the most promising candidates for future generations of cold-cathode flat panel displays and various vacuum microelectronic devices because of their excellent field emission properties [1–3]. They exhibit several favorable characteristics as an electron-emitting material, such as a high aspect ratio, small radius of curvature, high chemical inertness, high thermal stability, and high mechanical strength. For the practical application to field emission displays, the growth of vertically aligned CNT arrays on a large area with high packing density and ordered arrangement is necessary. As for this requirement, template methods are widely applied to produce well aligned and

monodispersed CNT arrays. Ordered arrays of CNTs have been fabricated by using nanoporous anodic aluminum oxide (AAO) membranes as the template by several research groups [4–9]. Nanoporous AAO, which consists of vertical pore channel arrays with a hexagonal packing structure, was obtained by anodic oxidation of aluminum in an acidic electrolyte [10,11]. The diameter of the self-ordered nanopores is tunable in the range of 10 to several hundred nanometers, because the pore diameter is dependent upon anodization parameters, such as polarization voltage, bath temperature, electrolyte species, and electrolyte concentration [12], making AAO an ideal template for fabricating ordered arrays of nanostructured materials.

In the fabrication of CNTs assisted by nanoporous AAO templates, the obtained nanotubes generally have a very uniform diameter, vertical alignment, ordered arrangement, and very high packing density, which are the duplicate of the AAO pore channels. Selective growth of CNTs within the AAO nanopores usually requires predeposition processes of metal catalysts in the pore bottom and a high-temperature thermal chemical vapor deposition (CVD) process for catalyst pyrolysis of hydrocarbon precursors to grow CNTs. CVD enhanced by plasma is another potential

[☆] Prime Novelty Statement: The vertically aligned and well-graphitized carbon nanotube arrays can be successfully synthesized in the nanopores of the anodic aluminum oxide template by using the microwave plasma electron cyclotron resonance chemical vapor deposition.

* Corresponding author. Tel.: +886-3-5731-949; fax: +886-3-5721-065.

E-mail address: ctkuo@mail.nctu.edu.tw (C.-T. Kuo).

alternative to dissociate the precursor gases with more efficiency. In this paper, we report on the preparation of CNT arrays in AAO templates by the microwave plasma electron cyclotron resonance CVD (ECR-CVD). It is well known that the microwave plasma ECR-CVD with a high plasma density has the advantages of a high dissociation percentage of the precursor gas and a high uniformity of the plasma energy distribution [13,14], and was generally used for large area dry etching, surface cleaning, or thin film deposition. By using the ECR-CVD instead of the thermal decomposition, we have successfully synthesized well-aligned CNT arrays using the nanoporous AAO membrane as a template.

2. Experimental

For the preparation of the AAO template, an Al film of about 6 μm in thickness was first deposited on the *p*-Si (100) wafer by thermal evaporation. The two-step anodization, which has been reported in detail elsewhere [10,15], was used to prepare ordered pore channel arrays of AAO. Anodization was first carried out in a 0.3 M oxalic acid solution at 21 $^{\circ}\text{C}$ under a constant polarization voltage of 40 V for 30 min. The resulting nanoporous AAO about 4.3 μm in thickness was then removed by wet chemical etching at 60 $^{\circ}\text{C}$ with a mixed solution of H_3PO_4 and CrO_3 , and thereby a relatively ordered indent pattern was produced on the surface of the Al film. The second anodization of the prepatterned Al film was then performed for 5 min under the same anodization condition as the first one. At the end of the second anodization, the voltage was dropped gradually from 40 to 10 V by 1 V steps. The decrease of polarization voltage accompanied the decrease of the alumina barrier thickness under each pore bottom. After the voltage drop process, the pore diameter of the AAO template was widened in a 5% H_3PO_4 solution for 1 h.

Before CNT growth, the Co catalyst was electrochemically deposited at the pore bottom in an electrolyte of 5% $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 2% H_3BO_3 by applying 12.3 V_{rms} ac voltage for 1 min. Finally, the catalyst pretreatment and the CNT growth were all carried out in a microwave plasma ECR-CVD system under 875-G magnetic field strength. The deposition conditions for the CNT growth were microwave power 700 W, -150 V substrate bias, working pressure 0.25 Pa, deposition temperature 600 $^{\circ}\text{C}$, CH_4/H_2 ratio = 11/11 sccm, and deposition time 7–30 min. The morphology and microstructure of the as-grown CNTs were characterized by field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4000) and transmission electron microscopy (TEM) (JEOL JEM-2010F). The field emission measurements were conducted by the simple diode configuration and performed in a high vacuum chamber with a base pressure about 10^{-6} Torr. The distance between the CNTs and anode was about 100 μm .

3. Results and discussion

Fig. 1a shows the top-view SEM image of the nanoporous AAO film after the two-step anodization and pore widening. The self-organized nanopores with a uniform size distribution have a pore diameter about 60 nm and an interpore distance about 100 nm. The AAO nanopores do not show a long-range ordering, but within a pore array domain, ordered nanopore with a hexagonal arrangement is clearly observed. Fig. 1b is the cross-sectional view of the AAO film before Co electroplating. The depth of the straight cylindrical pores is about 740 nm. Moreover, it is obvious that the insulative alumina barrier layer under each pore bottom was removed completely during the pore-widening step. After the Co electroplating uniform catalyst particles were deposited at the AAO pore bottom (see Fig. 1c).

Lee et al. [16] have reported the growth of CNTs in the AAO template with or without deposition of Co in the pore bottom as the catalyst. It was suggested that AAO as well as Co catalyst all play an important role on the pyrolysis of hydrocarbon precursors. CNTs were only grown in the pore channels of the AAO template when Co was not present, and these tubes have a very poor crystallinity [4,9,17]. When the Co catalyst was deposited into the pores, both AAO and Co played important role to assist the growth of the CNTs. Because Co is a much more active catalyst for hydrocarbon decomposition [18], the catalyst role of Co was dominant. The well-graphitized CNTs grew out of the pores due to a high growth rate and entwined above the pores. Fig. 2 shows the side-view SEM images of the Co-catalyzed

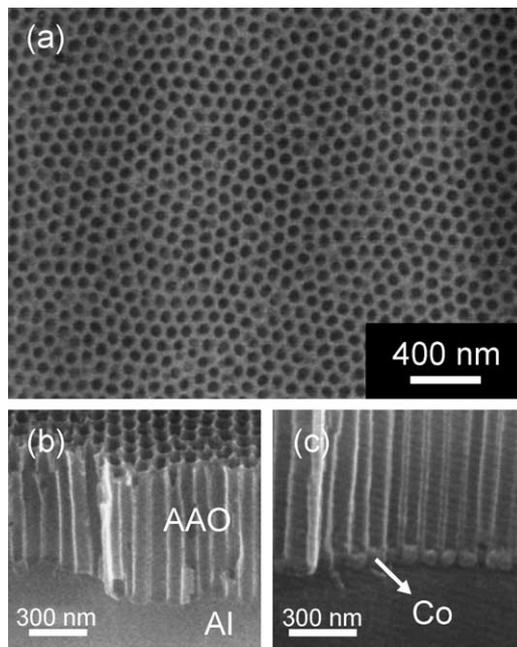


Fig. 1. (a) Top-view SEM image of the nanoporous AAO film after pore widening in a H_3PO_4 solution for 60 min. (b) Cross-sectional view SEM images of the AAO film before Co electroplating and (c) after Co electroplating.

CNTs grown on the AAO template by using the microwave plasma ECR-CVD. Similar to previous works, the CNTs also grew out of the pores as shown in Fig. 2, but the tubes aligned vertically to the AAO surface with little entanglement. In the earlier stage of the growth, the template effect

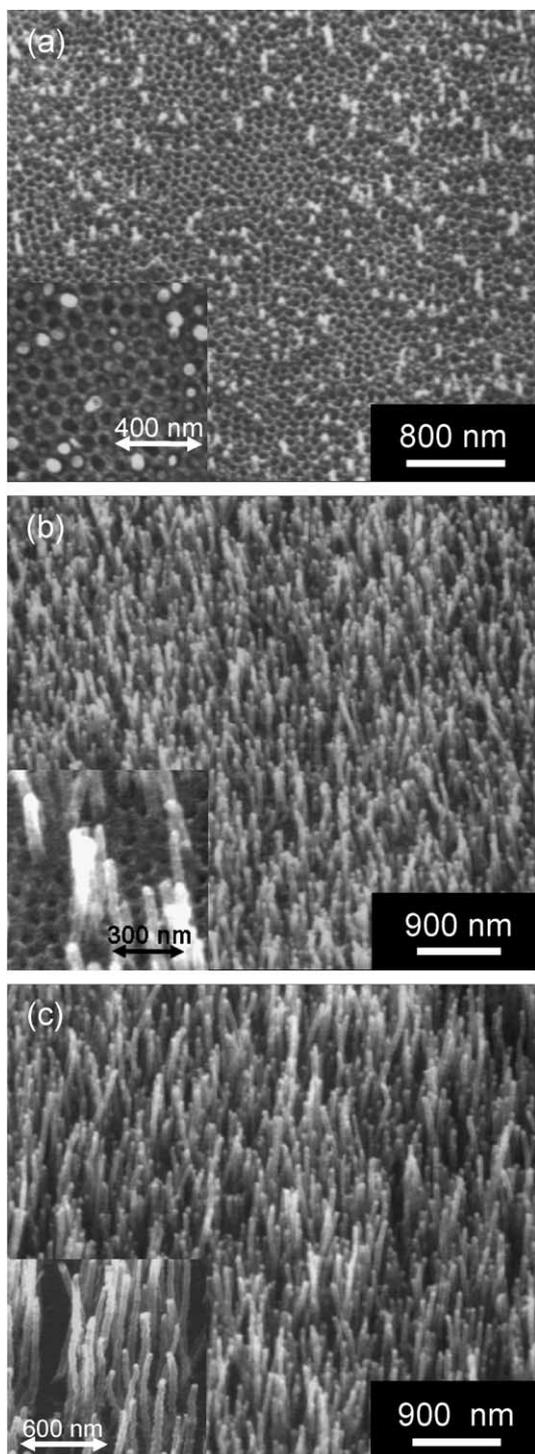


Fig. 2. Side-view SEM images of the Co-catalyzed CNTs grown on the AAO template by using the ECR-CVD for (a) 7 min, (b) 15 min, and (c) 30 min. The insets show the close-up view of the CNTs grown out of the AAO template pores.

of the AAO nanopores constrains the tubes to grow along the axis of the pores, resulting in the growth of the well-aligned tubes. After extending out of the pores, the overgrown CNTs remained the vertical growth direction due to the applied DC bias and the plasma induced electric field (self-bias) in the ECR plasma environment. The electrostatic force would force the exposed CNTs to align with the electric field [19]. By using the AAO template, the CNTs of a very high packing density ($6\text{--}8 \times 10^9$ tubes/cm²) are highly uniform in diameter with an average of about 75 nm, which coincided with the pore size of the AAO template. However, the diameter of tubes is larger than that of the AAO pores before the CNT growth shown in Fig. 1. This is possibly due to water loss in the AAO template from heating during the CVD process resulting in the enlargement of AAO pores [7].

From Fig. 2, it can be clearly seen that the length of the CNTs increases with the growth time. As seen in Fig. 2a, most of the CNTs are shorter than the depth of pore channels after CNT growth of 7 min, and only a few tubes are observed to extend over the pores. After 15 min growth (see Fig. 2b), it is obvious that the almost all the CNTs grew out of the pores, and the overgrowth length was about 300–700 nm. In the case of growth of 30 min (see Fig. 2c), most of the tubes above the template had a length of 700 nm–1.5 μ m. If the growth time was increased further, the tube length would not increase any longer, suggesting the Co catalyst was possibly poisoned. In the fabrication of triode field emitters using CNTs, one of the challenges is to control the length of aligned CNTs in the submicron scale without the overgrowth from the gate hole [20]. The growth rate of CNTs in the AAO template by ECR-CVD is considerably low (~ 60 nm/min), and, therefore, the tube length can be reliably controlled via the growth time. Thus, the CNTs are potentially suitable for the field emitter applications.

The growth mechanism of CNTs prepared by the catalytic decomposition of hydrocarbon vapors has been divided into either tip or base growth [21]. Fig. 3a shows a cross-sectional TEM image of the sample shown in Fig. 2b. It is obvious that the Co catalyst particles are encapsulated at the tips of tubes and covered by graphitic caps. Although residual Co catalyst can also be observed in the tube base, the growth mechanism of the CNTs tends to be the tip growth rather than base growth for the present case. With regard to the base growth, the precursor gases must continuously transport to the Co catalyst at pore bottom. If the gas diffusion is blocked, the catalytic growth of CNTs will be terminated. However, under the experimental condition, the nanopores are compactly filled with multiwalled CNTs and, moreover, the tubes have a closed end. The encapsulated Co nanoparticles at their tips can block the gas diffusion implying that the base growth is unfavorable. In the tip growth, the gas diffusion will not be obstructed because the CNT growing site is at the tip of the tubes.

Fig. 3b shows a selected-area electron diffraction pattern recorded from the overgrown part of the tubes shown in Fig.

3a. Three diffraction rings can be clearly identified to be (002), (100), and (110) of graphite. The diffraction pattern suggests that the tubes have a graphitic form with an interwall distance (d_{002}) of approximately 3.6 Å, which is larger than the interplanar separation of graphite ($d_{002} = 3.35$ Å). The larger interwall distance results from the curvature of the graphitic walls. Fig. 3c is a plan-view high-resolution TEM (HRTEM) image showing a CNT inlaid in a pore of the AAO template. Since the tube has a relatively large diameter, only a part of the tube is shown in this figure. The tube is composed of about 70–80 graphitic walls, and the tube size is strongly defined by the AAO pore geometry. It should be noted that the number of the graphitic layers is independent on the growth time, and this is unlike the layer-by-layer growth mechanism proposed by Yao and Wang [8]. They found that when the AAO was used alone to act as a catalyst to grow CNTs, the thickness of tube walls increased with increasing the growth time, inferring that the graphite was deposited layer-by-layer on the inner wall of the AAO pore. In regard to the Co-catalyzed growth of CNTs, increase of the growth time always leads to the increase the tube length as shown in Fig. 2. Therefore, we believe that the catalyst role of AAO is minor in the presence of Co catalyst under our experimental conditions.

The field emission current density as a function of electric field for the AAO template based CNTs of three different lengths is shown in Fig. 4. It is obvious that the CNTs grown for 30 min (overgrown length: 700 nm–1.5 μm) show better field emission properties than that grown for 15 min (overgrown length: 300–700 nm) and 7 min. The current density of the CNTs grown for 7 min is too low ($< 3 \mu\text{A}/\text{cm}^2$) to be

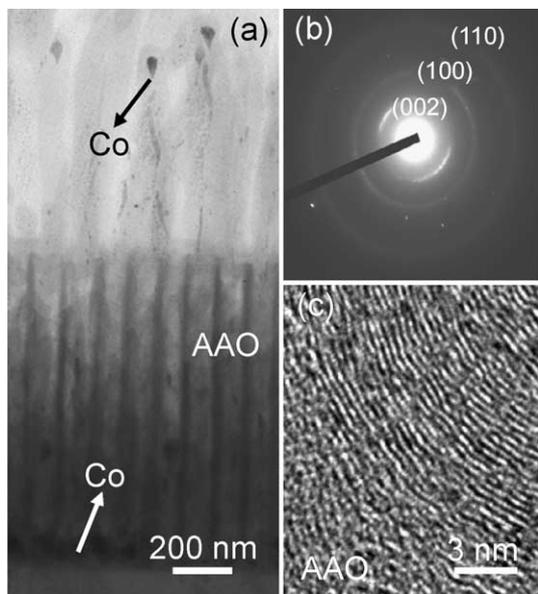


Fig. 3. (a) Cross-sectional TEM image of the very sample shown in Fig. 2b. The surface was covered with an amorphous Si film to protect the exposed CNTs. (b) Electron diffraction pattern recorded from the overgrown part of the tubes shown in panel (a). (c) Plan-view HRTEM image of the walls of a graphitized CNT inlaid in an AAO pore.

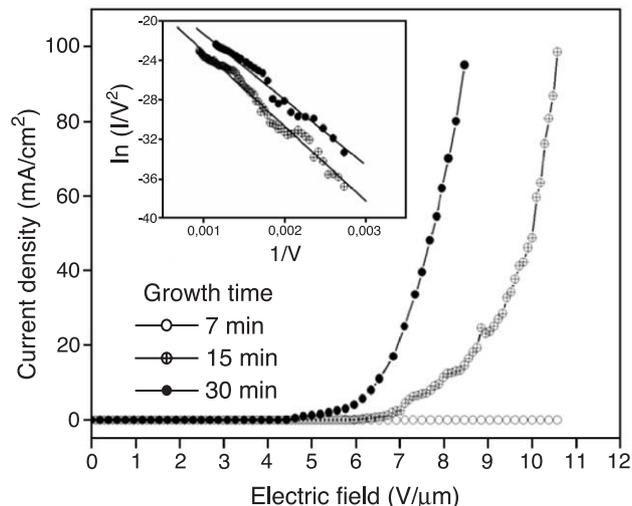


Fig. 4. Field emission current density as a function of electric field for the CNTs grown in the AAO nanopores. The inset shows the corresponding Fowler–Nordheim plots.

observed. The inset in Fig. 4 shows the Fowler–Nordheim (FN) plots of the samples. From these plots, we can obtain the field enhancement factor β , which are derived from the slopes by assuming a CNT work function of 5 eV. The β values calculated for the CNTs grown for 30 and 15 min are 2600 and 1900, respectively. The β values are similar to the values for CNTs grown on an AAO template by Suh et al. [22]. It was concluded that the field emission is optimal ($\beta \sim 2650$) when the exposed tube length is similar to the intertube distance, which was about 100 nm in their work. In our experiments, the tube packing density is obviously lower (CNT filled ratio of pores $\sim 70\%$) and results in higher intertube distances. Therefore, the optimal field emission was obtained at an overgrown length above 1 μm. In order to avoid the field screening effect [23], a lower packing density of CNTs is favorable.

4. Conclusions

We have synthesized vertically aligned CNT arrays, in terms of the AAO templation, by microwave plasma ECR-CVD. Both the AAO template effect and the DC bias as well as the plasma induced self-bias contribute to the vertical alignment of the tubes. The obtained CNT arrays have a very high packing density (as high as 10^9 tubes/ cm^2) and a narrow diameter distribution (about 75 nm), which are in accordance with the pore arrays of AAO template. The tube growth was catalyzed by the predeposited Co catalyst inside the nanopores rather than the AAO template, and the tubes encapsulate Co particles at their tips suggesting the tip growth mechanism. These CNTs are multiwalled and well graphitized and have good field emission properties. They have potential applications for cold-cathode flat panel displays.

Acknowledgements

This work was supported partly by the National Science Council of Taiwan, under Contract No. NSC92-2216-E-009-010, NSC92-2216-E-009-009, and NSC92-2210-M-009-001.

References

- [1] S. Iijima, *Nature* 354 (1991) 56.
- [2] Y. Saito, S. Uemura, *Carbon* 38 (2000) 169.
- [3] N. de Jonge, Y. Lamy, K. Schoots, T.H. Oosterkamp, *Nature* 420 (2002) 393.
- [4] T. Kyotani, L.-F. Tsai, A. Tomita, *Chem. Mater.* 8 (1996) 2109.
- [5] J. Li, C. Papadopoulos, J.M. Xu, M. Moskovits, *Appl. Phys. Lett.* 75 (1999) 367.
- [6] T. Iwasaki, T. Motoi, T. Den, *Appl. Phys. Lett.* 75 (1999) 2044.
- [7] J.S. Suh, J.S. Lee, *Appl. Phys. Lett.* 75 (1999) 2047.
- [8] B.D. Yao, N. Wang, *J. Phys. Chem., B* 105 (2001) 11395.
- [9] E.J. Bae, W.B. Choi, K.S. Jeong, J.U. Chu, G.-S. Park, S. Song, I.K. Yoo, *Adv. Mater.* 14 (2002) 277.
- [10] H. Masuda, K. Fukuda, *Science* 268 (1995) 1466.
- [11] P.-L. Chen, C.-T. Kuo, T.-G. Tsai, B.-W. Wu, C.-C. Hsu, F.-M. Pan, *Appl. Phys. Lett.* 82 (2003) 2796.
- [12] A.P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, *J. Appl. Phys.* 84 (1998) 6023.
- [13] C.-H. Lin, H.-L. Chang, M.-H. Tsai, C.-T. Kuo, *Diamond Relat. Mater.* 11 (2002) 922.
- [14] S.L. Sung, S.H. Tsai, C.H. Tseng, F.K. Chiang, X.W. Liu, H.C. Shih, *Appl. Phys. Lett.* 74 (1999) 197.
- [15] H. Masuda, M. Satoh, *Jpn. J. Appl. Phys.* 35 (1996) L126.
- [16] J.S. Lee, G.H. Gu, H. Kim, K.S. Jeong, J. Bae, J.S. Suh, *Chem. Mater.* 13 (2001) 2387.
- [17] Y.C. Sui, D.R. Acosta, J.A. González-León, A. Bermúdez, J. Feuchtwanger, B.Z. Cui, J.O. Flores, J.M. Saniger, *J. Phys. Chem., B* 105 (2001) 1523.
- [18] S.-H. Jeong, H.-Y. Hwang, K.-H. Lee, Y. Jeong, *Appl. Phys. Lett.* 78 (2001) 2052.
- [19] C. Bower, W. Zhu, S. Jin, O. Zhou, *Appl. Phys. Lett.* 77 (2000) 830.
- [20] Y.-H. Lee, Y.-T. Jang, D.-H. Kim, J.-H. Ahn, B.-K. Ju, *Adv. Mater.* 13 (2001) 479.
- [21] R.T.K. Baker, *Carbon* 27 (1989) 315.
- [22] J.S. Suh, K.S. Jeong, J.S. Lee, I. Han, *Appl. Phys. Lett.* 80 (2002) 2392.
- [23] L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J.-M. Bonard, K. Kern, *Appl. Phys. Lett.* 76 (2000) 2071.