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Well-aligned carbon nanotube array grown on Si-based nanoscale SiO_2 islands

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Abstract

Well-aligned carbon nanotube (CNT) array grown on Si-based nanoscale SiO_2 islands was obtained by microwave plasma-enhanced chemical vapor deposition under low temperature of 520°C. Atomic force microscope observation and Raman spectroscopic analysis disclosed the formation of the CNTs. The SiO_2 islands formed by excess anodization of Si-based Al film were found to be the growth points of the CNTs, which was confirmed by the C–V curves without charge characteristics. Position-controllable growth of CNTs was attempted on silicon substrate so as to explore significant applications in nanoelectronics and nanodevices.

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1. Introduction

In the recent years, using anodic porous alumina (APA) templates, a series of carbon nanotube (CNT) arrays [1–3] on different substrates have been synthesized because of their promising applications in field-emission (FE) devices and nanoelectronics [4,5]. The APA template has highly ordered pore arrangement, controllable pore diameter and channel length, and fine insulating property [3,6]. These are all very useful for applications of CNT arrays in nanoelectronics and nanodevices.

However, an important problem is how to control growth position, diameter, and direction of each CNT [7]. The growth of CNTs in pattern may be obtained by controlling the positions of the deposited catalyst [8–10]. The diameter of CNTs can also be changed by controlling the size of catalyst [11]. Generally, the growth of CNT arrays needs catalyst (such as Co and Ni) to be pre-deposited in the nanopores of the APA templates

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by electrochemical method as the growth points [1–3]. The catalyst plays an important role in position- and size-controllable growth of CNTs. However, the existence of the catalyst is not beneficial to integration with Si-based microelectronics. Further, the synthesis temperature of CNTs is usually so high (more than Al melting point of 660°C) that most of electric connections cannot work very well [1]. Recently, we fabricated a Si-based SiO_2 nanoscale island array using the APA template. Ge^+ implantation and subsequent annealing lead to formation of a Si-based nanoscale light source array, which will be useful in nano-optoelectronics [12].

In this paper, we utilize the APA template to fabricate well-aligned CNT array on Si-based nanoscale SiO_2 islands at 520°C by microwave plasma-enhanced chemical vapor deposition (MW-PECVD) [13]. The catalyst is not necessary for our present experiments. The SiO_2 islands at the bottoms of the APA channels formed by excess anodization of Si-based Al film were used as starting growth points. The morphology and bonding structure of the Si-based CNT array were investigated in terms of atomic force microscope (AFM) observations and Raman spectroscopy, respectively. The C–V characteristics of this CNT array embedded in the APA film shows that the CNTs are well graphitized and connected with SiO_2 islands.

2. Experiments

The substrates used in our work were p-type $\langle 1\,0\,0 \rangle$-oriented silicon wafers with a resistivity of 5 Ω cm. A layer of Al film with a thickness of 440 nm and a purity of 99.99% was deposited onto the Si wafer by electron beam evaporation. Anodization with a platinum plate as a cathode was carried out in sulfuric acid of 15 wt% under a constant DC voltage of 40 V. By monitoring anodic $I-t$ curve, anodization of Al/Si system can easily be controlled in situ. Through excess anodization, we fabricated a Si-based nanoscale SiO_2 island array at the bottoms of nanopore channels of the APA template [12]. To remove barrier layer, the anodization time was prolonged and subsequently the samples were immersed into a 5 wt% phosphoric acid solution for several minutes. Anodization process of Al film includes two steps [11]: oxidation of Al and dissolution of the resulting products such as Al $(OH)_3$ or AlOOH, which are a part of barrier layer. When anodization proceeds to the interface between Al film and the substrate, Al is exhausted and Si starts to be anodized in sulfuric acid solution. Dissolution of barrier layer would proceed continuously. When the SiO_2 islands are formed, the barrier layer is basically dissolved. Immersion of the samples into phosphoric acid solution might ensure complete dissolution of the barrier layer and enlarge the nanopore sizes of APA film.

3. Results and analysis

Fig. 1(a) shows a schematic diagram of Si-based nanoscale SiO_2 island array covered with APA

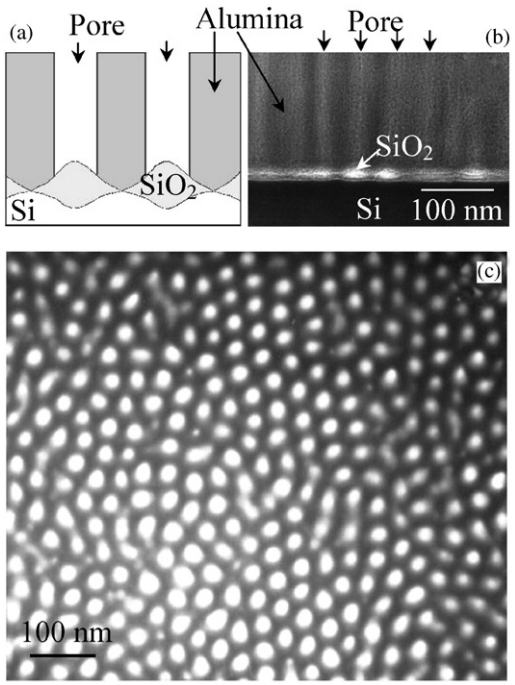

Fig. 1. (a) A schematic diagram of Si-based nanoscale SiO_2 islands. (b) A cross-sectional and (c) a planar images of Si-based APA film. The nanoscale SiO_2 islands are located at the bottoms of APA channels.

film. The cross-sectional and planar transmission electron microscope (TEM) observations are shown in Figs. 1(b) and (c), respectively. The APA film has uniform, ordered nanopore arrangement. The mean diameter of nanopores is about 30 nm and the distance between two nanopores is about 50 nm. The nanoscale SiO_2 islands are located at the bottoms of APA nanopore channels, also displaying high ordering. Formation mechanism of the SiO_2 island array has been reported in our previous literature [12]. We expect these SiO_2 islands to be the starting points for growing the CNTs.

The CNTs were grown on the APA template with ordered nanopore array using MW-PECVD under low temperature of 520°C [13]. The mixture gases, as precursors, were led into the system from the top of the quartz tube. The flux of the mixture gases was monitored by a digital mass flow controller. The total pressure in the chamber during synthesis was kept constant. The microwave generator operating at 2.45 GHz was continuously variable up to a maximal output of 800 W. To estimate the temperature in the growth zone of carbon nanotubes, a piece of hard glass with strain point of 520°C, as a probe, was placed close to the sample. An AFM image of the fabricated samples is shown in Fig. 2(a). Some grew patches with sizes of 35–60 nm can be observed on the sample surface. To confirm the formation of a CNT array, the sample was further annealed at 600°C in mixture gas (O_2: N_2 = 1:16) for 90 min. This process will remove surface coating (tip) of the CNTs. The corresponding AFM image is shown in Fig. 2(b). Obviously, the image clearly shows the existence of the CNTs with open-tip (by the white arrow). This can be observed more clearly in Fig. 2(c), a magnified image with open-tip CNT array. From Fig. 2(c), it can be seen that the CNTs have an outer diameter of about 30 nm, consistent with the inner diameter of alumina nanopores. They are well aligned and close-packed each other.

Raman scattering has been proved to be a useful tool to identify the formation of the CNTs [14–18]. In the current work, Raman spectra were obtained on a Renishaw RM1000 system. A typical result is shown in Fig. 3(a). As a comparison, the Raman

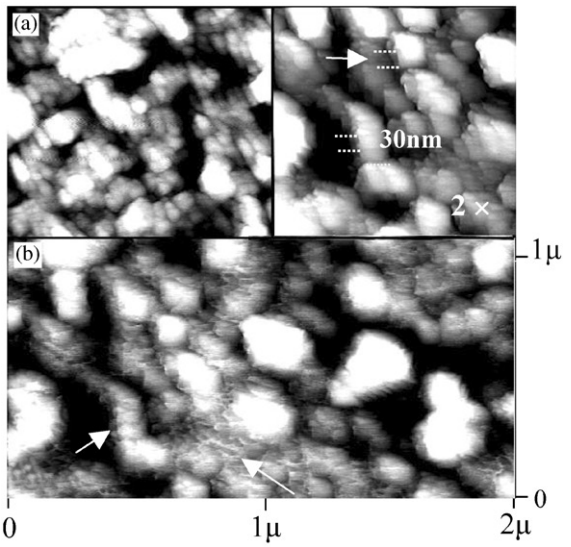

Fig. 2. The AFM images of the CNT array. (a) As-made and (b) the annealed samples at 600°C in mixture gas (O_2: N_2 = 1:16) for 90 min. (c) A magnified AFM image (magnification: 2×). The open-tip CNTs can clearly be observed (by the white arrows).

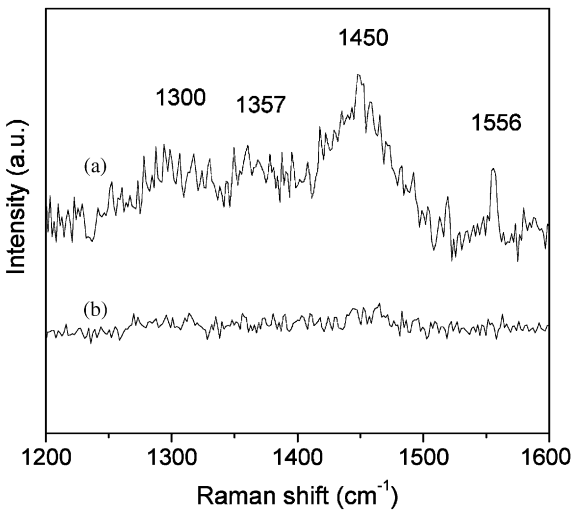

Fig. 3. The Raman spectra of: (a) the CNT array grown on Si-based SiO_2 islands and (b) Si-based APA film.

spectrum of the APA membrane without CNTs is displayed in Fig. 3(b). Fig. 3(a) shows four Raman vibration bands at 1300, 1357, 1450, and 1556 cm^{-1}. The 1556 and 1357 cm^{-1} bands correspond to G-band and D-band of the typical

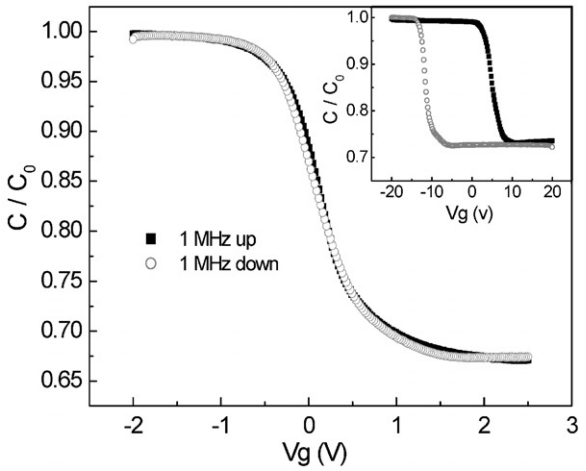

Fig. 4. The C–V curves of the CNT array grown on Si-based SiO_2 islands, displaying no charge characteristics. C/C_0 is normalized capacitance. The inset shows the C–V curves of Si-based APA film. The charge feature is pronounced.

first-order Raman spectrum of CNTs, respectively. The G band at 1556 cm^{-1} is noteworthy, because its peak position is lower than that reported previously (1581 cm^{-1}) [14]. Since the position of the G-band is slightly dependent on domain sizes of graphite planes formed, a downshift of the peak position of the G-band may be due to different crystalline sizes of the CNTs in our samples. The 1300 cm^{-1} band is also D-band, belonging to the disorder-induced mode A_{g1}. The 1450 cm^{-1} band is related to a kind of interphase between graphite and diamond. The appearance of D- and G-bands in the Raman spectrum implies the formation of the CNTs in our samples.

It was known that multi-wall CNTs generally have fine conductibility, whereas the APA film is a kind of fine insulator. According to these properties, we may also identify the formation of the CNTs from the C–V curves of the samples. Fig. 4 shows the typical up and down C–V curves of the Si-based APA membrane deposited with CNTs on nanoscale SiO_2 islands. We know that the Si-based APA film is easily charged (see the inset). After embedded with the CNTs into nanopores, the charge feature vanishes. The C–V curve displays characteristic of SiO_2/Si structure [19]. This result indicates that the CNTs are really grown on the SiO_2 islands. The SiO_2 islands at the bottoms of APA channels are the starting growth points of the CNTs. The CNTs are used as conducting nanowires. They are connected with nanoscale SiO_2 on the Si substrate. Therefore, the C–V curve of this kind of structures is similar to that of SiO_2/Si structure.

Why is not pre-deposited catalyst necessary for the formation of CNTs in our experiments? This can be explained as follows: The alumina on the template surface and/or on the walls of pores may act as a catalyst to be involved in the fabrication of CNTs [1,2]. Our experiments found that partial γ-Al_2O_3 has been formed in the film with annealing temperature of 520°C [20]. The γ-Al_2O_3 can decompose hydrocarbons to lead to the growth of CNTs. Furthermore, in the current experiments we also used microwave plasma to grow the CNTs. Microwave plasma is of an action for decomposing hydrocarbons and therefore also beneficial to the CNTs growth from nanoscale SiO_2 islands. Generally, catalyst particles have two functions, catalysis and determination of growth points for the CNTs [11]. In our experiments, nanoscale SiO_2 islands determine the CNT positions through nanopore channels, whereas both microwave plasma and γ-Al_2O_3 play a role as catalysis.

4. Conclusion

We have obtained well-aligned CNT array on Si-based nanoscale SiO_2 islands by MW-PECVD under low temperature of 520°C. The AFM observation and Raman spectroscopic analysis have revealed the morphology and bonding structure of this kind of CNTs. The SiO_2 islands formed by excess anodization of Si-based Al film are the starting growth points of the CNTs. This kind of Si-based CNT array is expected to have significant applications in nanoelectronics and nanodevices.

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References

[1] J. Li, C. Papadopoulos, J.M. Xu, Appl. Phys. Lett. 75 (1999) 367.
[2] W. Hu, D. Gong, Z. Chen, L. Yuan, K. Saito, C.A. Grimes, P. Kichambare, Appl. Phys. Lett. 79 (2001) 3083.
[3] Z. Yuan, H. Huang, L. Liu, S. Fan, Chem. Phys. Lett. 345 (2001) 39.
[4] W.A. de Heer, A. Chatelain, D. Ugarte, Science 270 (1995) 1179.
[5] C. Dekker, Phys. Today 52 (1999) 22.
[6] A.P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, J. Appl. Phys. 84 (1998) 6023.
[7] S.J. Tans, A.R.M. Verschueren, C. Dekker, Nature 393 (1997) 49.
[8] J. Kong, H.T. Soh, A.M. Cassell, C.F. Quate, H. Dai, Nature 395 (1998) 878.
[9] A.F. Morpurgo, J. Kong, C.M. Marcus, H. Dai, Science 286 (1999) 263.
[10] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tomler, A.M. Cassell, H. Dai, Science 283 (1999) 512.
[11] C.L. Cheung, A. Kurtz, H. Park, C.M. Lieber, J. Phys. Chem. 106 (2002) 2429.
[12] J.P. Zou, Y.F. Mei, J.K. Shen, J.H. Wu, X.L. Wu, X.M. Bao, Phys. Lett. A 301 (2002) 96.
[13] X.Z. Wang, Z. Hu, Q. Wu, X. Chen, Y. Chen, Thin Solid Films 390 (2001) 130.
[14] W.Z. Li, H. Zhang, C.Y. Wang, Y. Zhang, L.W. Xu, K. Zhu, S.S. Xie, Appl. Phys. Lett. 70 (1997) 2684.
[15] A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodríguez-Macías, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fisher, A.M. Rao, P.C. Eklund, R.E. Smalley, Appl. Phys. A 67 (1998) 29.
[16] W. Li, H. Zhang, C. Wang, Y. Zhang, L. Xu, K. Zhu, S. Xie, Appl. Phys. Lett. 70 (1997) 2684.
[17] M.A. Pimenta, A. Marucci, S.A. Empedocles, M.G. Bawendi, E.B. Hanlon, A.M. Rao, P.C. Eklund, R.E. Smalley, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. B 58 (1998) R16016.
[18] C.A. Cooper, R.J. Young, M. Halsall, Composites Part A 32 (2001) 401.
[19] S.H. Choi, R.G. Elliman, Appl. Phys. Lett. 75 (1999) 968.
[20] J.H. Wu, X.L. Wu, N. Tang, Y.F. Mei, X.M. Bao, Appl. Phys. A 72 (2001) 735.