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AN ARRAY OF INTERCONNECTED-OPENED-ENDED MULTI WALL CARBON NANOTUBES GROWN ON AAO TEMPLATE

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Abstract. *The uniform and high ordered array of interconnected-opened-ended multi wall carbon nanotubes (MWNTs) are synthesized into nanopores of anodic aluminum oxide (AAO) templates by thermal chemical vapor deposition (CVD) method without using metallic catalyst. The morphologies and quality of MWNTs are characterized by SEM, and Raman spectroscopy. The results show that at optimized growth conditions, the high quality interconnected-opened-ended MWNTs are successfully synthesized.*

I. INTRODUCTION

Carbon nanotubes (CNTs) have drawn much attention because of their unique physical properties and wide variety of applications such as hydrogen storage, high power electrochemical capacitor, field emitters, electronic device and gas sensor [1-5]. In order to be application in microelectronic devices as well as to decrease the cost of device, it requires the CNTs to be synthesized with a uniform size, high alignment, ordered, and high purity. A simple and effective method to control the dimensions and orientation of CNTs is using AAO templates because the AAO template has uniform and straight channels with controllable dimensions. Almost recent reports, MWNTs were grown in the pore channels of AAO with metallic catalyst, therefore, the MWNTs had closed-end and outgrew from the pores of template [6-7], resulting in a wide distribution in length and made them difficulty in application. Based on the change in their conductivity when exposed to gaseous molecules, carbon nanotubes were used for detecting different gases, such as H_2, , O_2, CO, NO_2 [8-12]. Opened-end MWNTs grown on AAO templates were used for gas sensors applications and reported to have higher gas adsorption capacity and higher sensitivity compare to others [13], in which, the inner tubes were used as adsorption sites. However, to use the inner MWNTs as adsorption sites, the oxygen plasma and/or ion milling were used to remove the top-carbon-layer to open the tips of MWNTs and then a metal electrode was deposited for electrical measurements [14]. For my best known, the growth of an array of interconnected-opened-end of MWNTs has not been reported yet.

In this paper, we report a simple method to grow uniform interconnected-opened-end MWNTs array by using AAO templates. Details about the optimizations growth conditions for synthesizing an array of interconnected-opened-ended MWNTs will be reported and discussed.

II. EXPERIMENTAL

The schematic diagram of fabrication uniform interconnected-opened-end MWNTs by using AAO templates is described in the Fig.1. The fabrication includes: a) synthesis of

AAO template on p-type silicon substrate, b) growth of MWNTs on the pore of AAO template by thermal CVD method. The AAO template was synthesized on a p-type silicon substrate by using a two-step anodization process [14]. Brief; an aluminum layer with a thickness of 2 μm was deposited from a 4 inch target (purity of 5N) on silicon wafer by r.f. sputtering method. Then after, the Al/Si wafer was annealed at 500°C in N_2 for 30 min to enhance the adhesion between Al and substrate. The anodizations were carried out in a solution of 0.3 M oxalic acid maintained at 10°C. The first anodization was done by applying a constant voltage of 45 V for 800 seconds. However, the AAO formed after the first anodization process had low quality and could not used to grow MWNTs, therefore it was etched away by using a mixed solution of 6 wt.% phosphoric acid and 1.8 wt.% chromic acid maintained at 60°C for 2h. The second anodization was carried out for 1400 seconds in the same condition with the first anodization to obtain a regular array of AAO channels. The pores of AAO were then widened by etching in a 0.1 M solution of phosphoric acid for 30 min to get the AAO template.

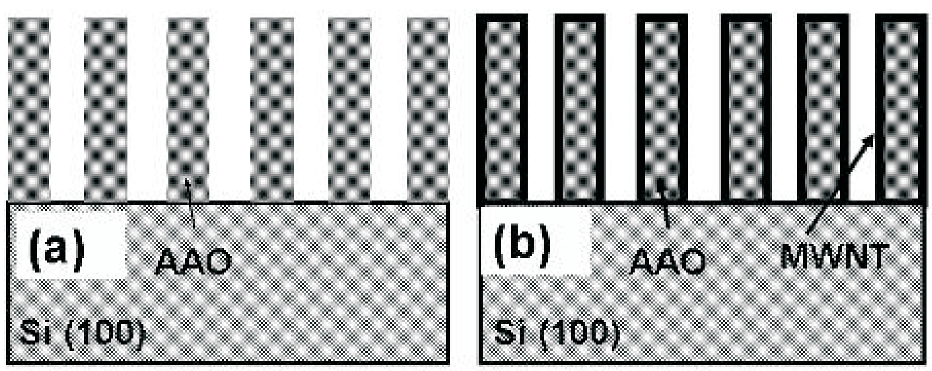

Fig. 1. The Schematic diagram of fabrication interconnected-opened-ended MWNTs.

MWNTs were synthesized via a thermal chemical CVD method without using metallic catalyst. In detail, the AAO template was placed in the central region of a horizontal quartz tube having inner diameter of 7.5 cm and a length of 150 cm. Then the tube furnace was evacuated out by using a rotary pump to 10^{-3} Torr. After that H_2 gas was filled in the chamber, then the temperature was raised up to growth temperatures (700, 800, 900, 1000, 1200^{o}C) with a heating rate of 15°C/min. Once the temperature was achieved, a mixed gas of C_2H_2 and NH_3 was introduced in the tube furnace to generate MWNTs on the surface and wall of AAO template. After growing, the quartz tube was evacuated again to 10^{-3} Torr until the temperature decreased to room temperature. The growth conditions were optimized to obtain an array of interconnected-opened-ended MWNTs. The morphologies and qualities of AAO template and synthesized MWNTs were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4700), micro Raman spectroscopy (Ar-ion laser, 514.532 nm wavelength).

III. RESULTS AND DISCUSSION

Fig. 2 shows the surface and cross section SEM images of AAO template after pore widening in 0.1 M solution of phosphoric acid for 30 min. The AAO had a very clean surface without any detectable dirty particles (Fig. 2(a)). The nanopores had a nearly perfect circular structure with uniform size and hexagonal distribution. The diameter and inter-pore distance were about 60 nm and 100 nm, respectively. The cross section image shows straight pore-channel with parallel arrangement down to silicon substrate (Fig. 2(b)). The AAO template with a thickness of about 1μm showed good adhesion to silicon substrate.

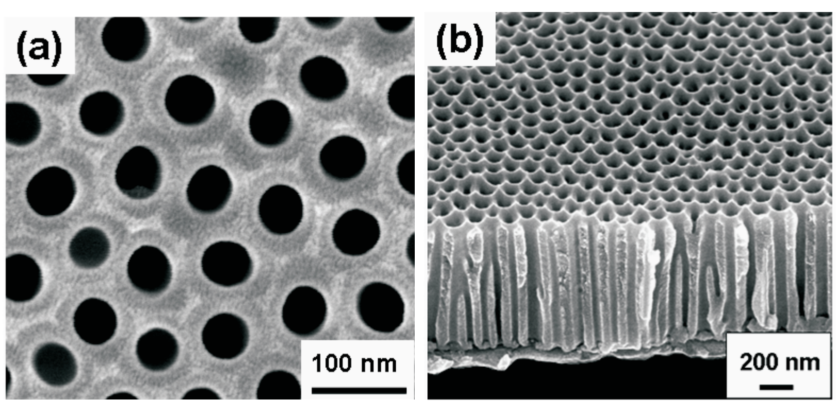

Fig. 2. The surface (a) and cross section SEM images of AAO template.

The growth of MWNTs on AAO template was reported depending on temperatures as well as gases flowing rates. To investigate the effect of growth temperature on the growing rate, the growth time and gases flowing rate were kept at 30 min and C_2H_2/NH_3=80/20 sccm, respectively. The morphologies of MWNTs grown at different temperatures (700-1200°C) are showed in Fig. 2 (a)-(d), respectively. There were not any detectable MWNTs grown at 700°C (Fig. 3(a)). Under the recent experimental conditions for the synthesis

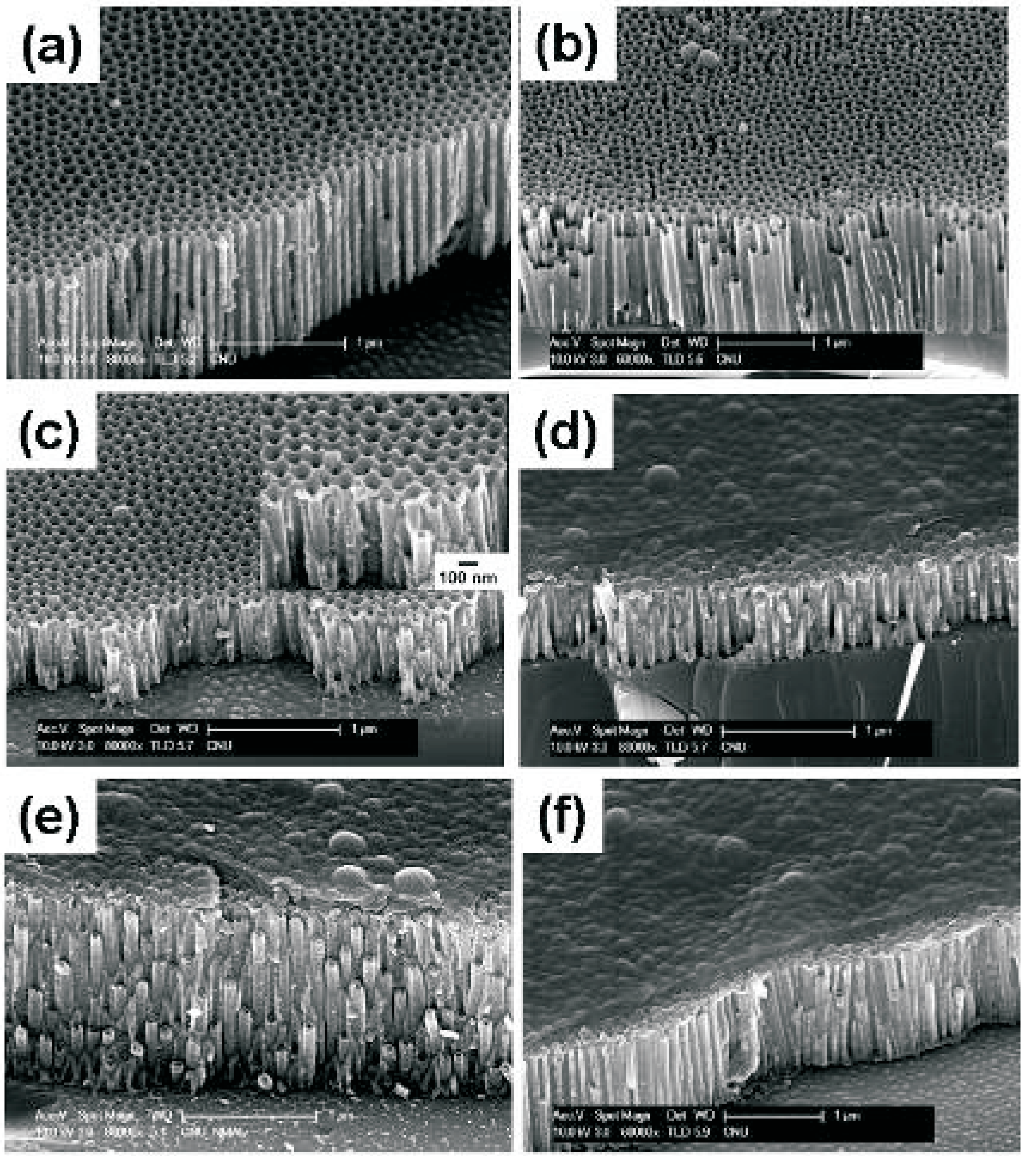

Fig. 3. SEM images of MWNTs grown at different temperatures with gases flow rate C_2H_2/NH_3=80/20 sccm for 30 min: (a)-700 ^{o}C, (b)-800^{o}C, (c)-9000°C, (d)-1000°C, (e)-1100 ^{o}C, (f)-1200°C.

of MWNTs it was opined that the MWNTs were formed on AAO through pyrolytic deposition of the carbon source [15]. Therefore, it was possibility that, at temperature of 700°C, the thermal energy was not high enough to break the C-H bonding in C_2H_2 and/or the growth time was not long enough to generate MWNTs. At higher temperature of 800 ^{o}C, the MWNTs were grown on all the nanopores of AAO template (Fig. 3(b)). But the

MWNTs were grown separately in the nanopores and there was not observable top-carbon-layer connected the MWNTs together. By increasing the growing temperature to 900˚C, we could clearly observe the top-carbon-layer that connected the MWNTs together to form an array of interconnected-opened-ended MWNTs (Fig. 3(c)). This MWNTs would be used as opened-electrode for electrical and gas sensing measurements as well as a template for deposition of nanowires. However, if increased the grown temperatures to 1000, 1100, and 1200˚C, the top-carbon-layer became thicker and it closed the mouths of MWNTs (Fig. 3(d)-(f)). It was known that the growth rate of MWNTs and the top-carbon-layer increased with increasing of growth temperatures, therefore, at temperature of 1000˚C or higher (1200˚C), the top-carbon-layer was thick enough to totally close the mouth of MWNTs. However, to get higher quality of MWNTs, it required the MWNTs to be grown at higher temperature. In this work, out system was limited at temperature of 1200˚C due to the melting of quart tube furnace. Therefore, to synthesize high quality MWNTs with interconnected-opened-end, we fixed the growth temperature at 1200˚C and decreased the growth time. Fig. 4 (a)-(c) showed the SEM images of MWNTs grown at 1200˚C for 15, 5 and 2 min, respectively. It was observed that the interconnected-opened-end MWNTs were achieved at growth time of 5 min. Note that, in all cases, the MWNTs were formed on the nanopores of the AAO with diameter and length limited by the size (∼60 nm) and length (1μm)of nanopore-channels and no growth outside the pores was detected. This result was contrary to the MWNTs gown by using a metal catalyst, whereas the MWNTs grew out of the pores of AAO.

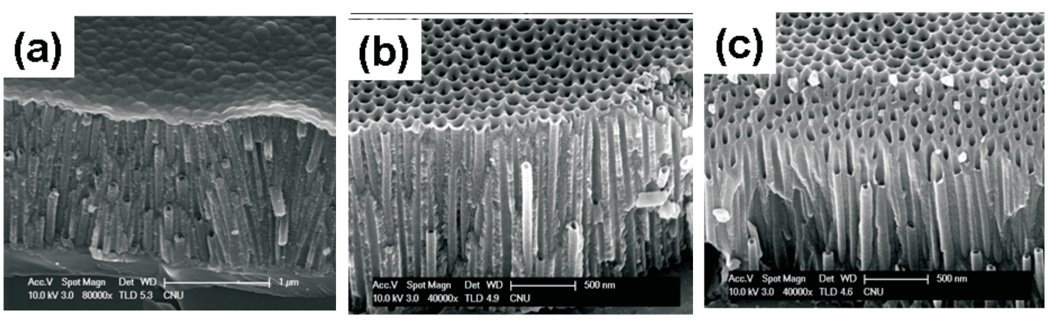

Fig. 4. SEM images of MWNTs grown at temperature of 1200˚C, C_2H_2/NH_3=80/20 sccm for (a)-15 min, (b)-5 min, (c)-2 min.

The crystallinity of MWNTs was known depending on the growth temperatures, at higher growth temperature; the crystallinity of interconnected-opened-ended MWNTs was higher. Raman spectroscopy was employed to characterize the quality of synthesized MWNTs. Fig. 5 (a)-(b) shows the Raman spectra of interconnected-opened-ended MWNTs grown at 900 and 1200˚C, respectively. Both Raman spectra showed two main peaks, at 1288 and at 1592 cm^{-1}, which are designated as the tangential modes of carbon nanotubes [16]. The former band corresponds to the defect-induced Raman band and is known as the defect mode, A_{1g} or D-band associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The latter peak, also known as G-band, represents the Raman-allowed E_{2g} mode of graphite and is related to the vibration of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, such as in graphite layer. The intensity ratio (I_G/I_D) of G-band and D-band represents the quality of MWNTs. The I_G/I_D ratio of MWNTs grown at 1200°C was 1.156, higher than that of MWNTs grown at 900 ^{o}C (0.957), indicating higher crystallinity of MWNTs.

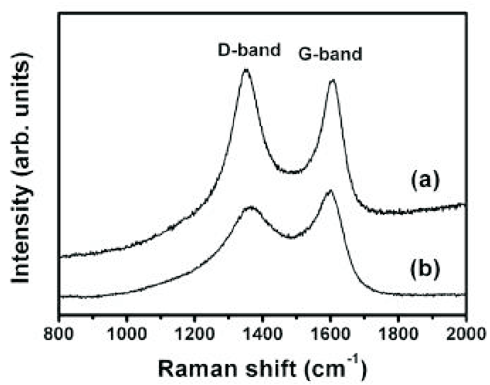

Fig. 5. Raman spectra of interconnected-opened-ended MWNTs grown at: (a)-900°C, and (b)-1200°C.

IV. CONCLUSION

We have successfully synthesized an array of interconnected-opened-ended MWNTs on AAO template by thermal CVD method without using metallic catalyst. Both low quality and high quality of interconnected-opened-ended MWNTs were successfully synthesized. The crystallinity of MWNTs grown at 1200°C is higher than that of MWNTs grown at 900°C. The synthesized interconnected-opened-ended MWNTs are expected to be applied for gas sensors applications as well as templates for nanowires deposition.

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