Diameter Controlled of Carbon Nanotubes Synthesized on Nanoporous Silicon Support

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Abstract. Carbon nanotubes (CNTs) have been successfully synthesized on nanoporous silicon template (NPSiT) using botanical source, camphor oil. Diameter of CNTs synthesized was controlled by pore size of NPSiT prepared by photo-electrochemical anodization method. The diameter of CNTs grown on different NPSiT corresponded to the pore diameter of NPSiT. FESEM images showed self-organized bundles of fiber-like structures of CNTs with diameter of around 20nm which were successfully grown directly on nanoporous silicon while raman spectra obtained ratio of I_D/I_G at 0.67.

Keywords: Carbon nanotubes; Nanostructured porous silicon template; two-stage hot filament thermal chemical vapor deposition system; diameter of nanotubes

1. Introduction

Carbon nanotubes (CNTs) have attracted great attention in science and technology field since discovered by Iijima (1991) \cite{1}. They are known due to their extraordinary mechanical, chemical, electronic and optoelectronic properties such as stronger than steel, harder and higher thermal conductivity compared to diamond and higher electrical conductivity than copper \cite{1, 2}. Its various extraordinary properties are applicable in various applications especially in nanoelectronics and field emission devices which require the modification of carbon nanotubes with well orientation, internal structures and morphologies features \cite{1, 3}.

Recently, researchers have tried to synthesize carbon nanotube on various substrates in order to control their geometry and features. Earlier work focused on synthesis of CNTs on substrate in random
orientation. [2]. Further approach had been verified in order to control the trend orientation of CNTs growth, as well as applying the external electric or magnetic field during the deposition of CNTs [3]. Additionally, diameters and lengths of tubes were considered as most controllable properties of CNT during fabrication process [4].

Study of growth condition such as diameter of nanotubes can clarify the size of catalytic nucleate particle, energy gap of the semiconducting nanotubes, as well as interaction between nanotubes [5]. As reported the diameter of nanotubes can be controlled by modulating growth temperature, growth time and pressure [6].

Previous studies reported that the diameter of carbon nanotubes can be easily controlled by nano support materials such as porous anodic aluminum oxide (AAO) template, where the diameter of nanotubes correspond to the pore size [7]. AAO was mostly used as template to fabricate nanomaterials including nanowires and nanotubes because of the well uniformity of pores [8-13]. Instead of AAO, porous silicon was used as template in this study because of the limitation of AAO in terms of its high cost. Silicon on the other hand, has its own advantages in device application because of its visible luminescence and lower cost [14].

This paper will report on the synthesis of carbon nanotubes on nanostructured porous silicon template using botanical hydrocarbon (camphor) by two-stage hot filament thermal chemical vapor deposition system. From observation, it can also be seen that changing the series of porous silicon template contributed to diameter distribution of carbon nanotubes synthesis.

2. Experimental

2.1. Preparation of Nanostructured Porous Silicon Template

NPSiT was prepared by photo-electrochemical anodization technique [15] on boron doped p-type Si wafer (1 0 0) orientation with resistivity of 1 Ωcm-1. The cleaning process of silicon wafer was carried out by immersion in acetone (CH3COCH3) and methanol (CH3OH) for at least 5 minutes at 40 °C in ultrasonic bath then followed by H2O: HF (40%) in ratio of 10:1 for at least 2 minute after rinsing with deionized water. The wafer then went through etching process where it was placed in Teflon cell with electrolyte consisting of ethanol: HF (48%) in 1:1 ratio with illumination of halogen lamp. Aluminum foil was attached behind the Si wafer during anodization process to increase the uniformity of anodic current flow. The etching process was carried out for 20, 30, 40 and 50 min at 20 mA/cm2 current density. The NPSiT was then rinsed in deionized water, dried under the dry nitrogen stream and stored at room temperature or in desiccators to avoid oxidation.

2.2. Preparation of Carbon Nanotube (CNTs) on Nanostructured Porous Silicon Template

A 100 cm long and 5 cm diameter of quartz tube serves as a thermal chemical vapour deposition (TCVD) reactor and placed horizontally inside a double stage tube furnace system. The camphor white oil as carbon source and ferrocene powder as catalyst were filled in separate alumina boats and placed at the middle of the first furnace while the NPSiT was placed in alumina boat at the center of the second furnace. The quartz tube was closed with end cap and connected to nitrogen gas supply through the inlet and exhaust through the outlet. Before the furnace is switched on, the nitrogen gas was flowed inside the furnace to remove the atmospheric air from tube reactor for 5 minutes and was reduced to 150 sccm of flow rate. The second furnace was first switched on at temperature of 800°C and stabilized for 15 minutes then followed by first furnace at temperature of 180 °C to allow camphor white oil and ferrocene powder to vaporized with flow of gas. Deposition time of CNTs on NPSiT was
around 1 hour and when completed, the furnace was switched off and cooled down in ambient temperature.

3. Results and Discussion

2.2. Morphological features

The morphological study and cross-section of porous silicon template and carbon nanotube growth on template was visualized using Field Emission Scanning Electron Micrograph (FESEM). Figure 1 (a) showed FESEM micrograph of nanostructured porous silicon template (NPSiT) at 3 kV, x100 (plan view) and 5 kV, x5 magnification (cross-section) while figure 1 (b) showed carbon nanotubes deposited on porous silicon layer respectively at 5 kV, x1 and 5 kV, x100 magnification (high resolution).

Micrographs of NPSiT in figure 1(a) showed the pore size distribution of samples prepared by electrochemical anodization etching of p-type Si wafer for 20, 30, 40 and 50 minutes at a current density of 20 mA/cm$^2$. The variation of average diameter pore and nanotubes of the NPSiT with different etching time is shown in figure 2.

Results showed that the sample prepared at 30 minutes and 20mA/cm$^2$ (1a,ii) have uniformed pore size which are about 20 nm, and the thickness of NPSi is about 17 μm while sample prepared at 20 minutes of etching time have very small pores and cannot be detected in the measurement but estimated to be around 1-10 nm size. The pore size increases as etching time increases up to 30 minutes. As the etching time was increased further, the average pore size decreased from 20 to 9 nm. The result agrees as reported [16], this is due to the Beale models which showed etching behaviors of silicon wafers in etchant and the resultant characteristic pore morphology of p-type NPSiT.

Micrographs of CNTs grown on NPSiT prepared by thermal chemical vapor deposition (double stage tube furnace system) for 1 hour of synthesis time at 800 °C are illustrated in figure 1(b). FESEM images showed that the carbon nanotubes was successfully synthesized on nanostructures porous silicon template respectively using botanical precursor, camphor white oil and presence of ferrocene as catalyst. The top view of FESEM images (1 b i, ii, iii) showed uniform growth of dense CNTs from entire template with different diameter of nanotubes respectively. Results indicate that the diameter of carbon nanotubes corresponds to the size of pores shows in figure 2. Carbon nanotubes have the biggest diameter and in random orientation as shown in figure 1(b,i) while figure 1 (b, ii) showed that carbon nanotubes were grown in self-organized bundles of fiber like structures and has lowest diameter of nanotubes of around 20 nm. As the etching time of template increases further, the diameter of carbon nanotubes growth gradually increases and most of them form spiral like structure.

These results agreed as reported by [7], the diameter of carbon nanotubes synthesis correlate with nanostructured pore size of template. Additionally, as referred from [7], CNTs growth depends on the catalytic behavior of template pores.
Figure 1. (a) Plan view and cross-section view of FESEM micrograph of the NPSi with magnification of ×200 and ×5 K at 20 mA/cm² for i) 20 min, ii) 30 min, iii) 40 min, and iv) 50 min of etching time; (b) FESEM micrograph of CNT grown on NPSiT respectively with magnification of x1 and x100 (high resolution).
Figure 2. The variation curves of an average pore diameter and nanotubes diameter as a function of etching time.

2.2 Raman spectroscopy

Figure 3. (a) Raman spectra of CNTs grown on respective NPSiT for various etching time (20, 30, 40 and 50 minutes); (b) Variation curve $I_D/I_G$ ratio of CNTs grow on respective NPSiT.

Figure 3 (a) showed the raman spectra of CNTs grown on NPSiT at different parameter of template from 20 to 50 minutes etching time and constant current density (20 mA/cm$^2$) in the range 100-4000 cm$^{-1}$. Raman characterization was carried at room temperature under 20 mW of power at 514 nm of wavelength with illumination of Ar laser.

Raman spectroscopy was used to determine the characteristic of overall graphitic structures growth. Raman spectra represent the G ($\sim 1573$ cm$^{-1}$) and D (1348cm$^{-1}$) bands which were initiated from well-graphitized carbon and disorder-activated band respectively. It can be observed that the ratio of D and G band ($I_D/I_G$ ratio) for CNTs growth on NPSiT prepared at 30 minutes and 20 mA/cm$^2$ (figure 3,a II) has the lowest value of 0.67. The variation trend of the $I_D/I_G$ ratio is shown in figure 3 (b). The trend showed that the amount of $I_D/I_G$ ratio is smaller in crystalline sample (<1). The $I_D/I_G$ ratio for CNTs synthesized on NPSiT prepared at 20 minutes is about 0.8 and decreased sharply to 0.67 when template was change (30 minutes). The values increased gradually as the etching time of template was increased further, which is around 0.9 at preparation time 50 minutes. Therefore, it can be said that this experiment can only run for template prepared up to 50 minutes etching time at fix current density. As reported previously[17], smaller $I_D/I_G$ ratio corresponds to fewer defects. Raman spectra
showed no peak present at 0-500 cm\(^{-1}\) where refer to \[18\], radial breathing modes (RBM) is present at 186 cm\(^{-1}\) which means that there are no single wall CNTs obtained.

4. Conclusion

We have presented a simple method of growing multi-walled carbon nanotubes (MWCNTs) at smallest diameter corresponding to the diameter of nanostructured porous silicon template by using an economical, biomass and ecologically-friendly carbon source namely camphor white oil. Previous research focused more on TCVD parameters such as flow rate of gas, concentration of catalyst, temperature and synthesis time to control the diameter of nanotubes. This work is more on the controlled diameter of template which effects the diameter of nanotubes grown.

FESEM images showed the lowest diameter of nanotubes around 20nm deposited on NPSiT prepared at 30 minutes etching time at 20 mA/cm\(^2\). Raman spectra revealed that the smallest defect of disorder crystallinity of carbon nanotubes was grown at 30 minutes etching time of NPSiT. Therefore, the best template to synthesize high quality, smallest diameter and aligned orientation is NPSiT prepared at 30 minutes of etching time and 20mA/cm\(^2\) of current density.

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