F. Ahmadzade · S. Safa · P. Balashabady

Growth of Vertically Aligned Carbon Nanotubes by DCPECVD System and the Effects of C_2H_2 Concentration and Plasma Current on the Growth Behavior of CNTs

Received: 17 October 2009 / Accepted: 2 April 2010 / Published online: 6 January 2011
© The Author(s) 2010. This article is published with open access at Springerlink.com

Abstract A direct current plasma enhanced chemical vapor deposition (DC PECVD) apparatus was designed and constructed to synthesize high purity vertically well-aligned carbon nanotubes (VACNTs) at relatively low temperatures. The effect of C_2H_2 concentration and plasma current on CNT growth was investigated. The DC PECVD synthesis of CNTs consisted of two steps: (1) reduction with gaseous H_2 and NH_3 to form catalyst nanoparticles, and (2) subsequent CNT growth in the presence of gaseous H_2 and C_2H_2 . High-resolution transmission electron microscopy images confirmed the presence of multi-walled carbon nanotubes (MWCNTs). Their graphitic structure was then confirmed by Raman spectroscopy. Scanning electron microscopy (SEM) results illustrated the relationship between the plasma, C_2H_2 concentration and CNT growth. Deviation of acetylene flow rate from an optimal rate led to deterioration of CNT growth. Comparing SEM images of CNTs grown with and without plasma showed that plasma had an important role in VACNT formation.

Keywords Carbon nanotubes · PECVD · Vertical-aligned growth · MOSFET

الخلاصة

من أجل تحضير أنابيب كربون نانوية بحالة نقية و منسقة عموديا عند درجات حرارة منخفضة نسبيا تم تطوير جهاز بلازما بتيار مباشر و معزز لترسيب البخار كيميائيا. وتم - في ما بعد- بحث تأثيرات تركيز الأسيتيلين و تيار البلازما في نمو أنابيب الكربون النانوية. وتم - إلى جانب ذلك - تحضير أنابيب الكربون النانوية بالطريقة المطورة بوجود البلازما على خطوتين: أولاها تتضمن الاختزال بغازات الهيدروجين و الأسيتيلين لتكوين جزيئات نانوية ، وتتمثل ثانيهما في النماء بوجود غازات الهيدروجين و الأسيتيلين. وقد أظهرت صور المجهر الإلكتروني الماسح عالي الدقة وجود جدران متعددة لأنابيب الكربون النانوية و تم تأكيد الشكل الغرافيتي لها باستخدام أطياف رامان. وأكثر من ذلك أكدت نتائج المجهر الإلكتروني الماسح الصلة القوية بين البلازما و كمية الأسيتيلين و بين نمو أنابيب الكربون النانوية ، وأن أي حيود يؤدي في سرعة تدفق الأسيتيلين المثالية إلى تدهور في نمو أنابيب الكربون النانوية. وأظهرت المقارنة للرسومات الدقيقة لأنابيب الكربون النانوية بوجود و عدم وجود دور أساسي للبلازما في تكوين أنابيب الكربون النانوية المنسقة عموديا.

1 Introduction

Since 1991, when carbon nanotubes (CNTs) were discovered by Iijima [1], different methods, including electrical arc discharge, laser ablation and chemical vapor deposition (CVD), have been suggested for their

F. Ahmadzade · S. Safa (✉) · P. Balashabady
Agricultural, Medical and Industrial Research School,
Science and Technology Research Institute, P. O. Box 31485-498, Karaj, Iran
E-mail: sda.safa@gmail.com

Fig. 1 Schematic of the purpose built DC PECVD apparatus

synthesis [2–6]. CVD is advantageous because of its high product purity and yield, selective growth and ability to facilitate well-aligned CNTs [7,8]. Plasma-enhanced CVD (PECVD) allows the efficient growth of high purity vertically aligned carbon nanotubes (VACNTs) at lower temperatures [9]. Many applications of CNTs have been reported, including their use as probes in atomic force microscopy (AFM), as electron emitters for field emission displays (FED), as nanofillers for composite materials, as electrodes for fuel cells and as nanoscale electronic devices for micro-/nano-electro mechanical systems (MEMS/NEMS) [10–13].

VACNTs can be used for various electrical purposes, including as flat pageant and metal–oxide–semiconductor field-effect transistors (MOSFET). In the present study, the effects of plasma current and acetylene (C_2H_2) gas concentration on CNT growth behavior have been evaluated using a purpose-built PECVD apparatus. The primary objective was to ascertain the optimal plasma current and inlet gas ratio, in which VACNTs could be synthesized in high yield.

2 Experimental

2.1 PECVD System

Well-aligned CNTs were produced using a purpose-built PECVD apparatus, shown schematically in Fig. 1. Features of this system include the main reactor chamber, vacuum pumps, power supplies, and heating and cooling systems. A gas mixer was employed at the main chamber gas inlet to thoroughly mix the entering gases. The direct DC plasma between the Si substrate (cathode) and a steel mesh plate (anode) was enhanced with a 1 KW DC power supply.

2.2 Techniques

CNT morphology was investigated using scanning electron microscopy (SEM). Raman spectroscopy was carried out using a Jobin Yvon LabRam HR-800, in Stokes mode with 532 nm frequency-doubled Nd:YAG laser

Table 1 Gas flow rate during growth step at constant plasma current of 50 mA

Sample number	S ₁	S ₂	S ₃	S ₄	S ₅
Acetylene flow (sccm)	140	120	110	100	90
Hydrogen flow (sccm)	60	80	90	100	110

Table 2 Plasma current in growth process at H₂:C₂H₂ = 100/100

Sample number	P ₁	P ₂	P ₃	P ₄	P ₅
Plasma current (mA)	20	30	50	70	0

excitation. A SIMS analysis was performed to estimate the thickness of the oxide layer on the silicon wafer. Transmission electron microscopy (TEM: CM200 FEG Philips) operated at 200 kV was used to characterize CNTs.

2.3 CNT Preparation

The n-type silicon substrates were cleaned in an ultrasonic ethanol/acetone bath for 5 min. It was necessary to initially oxidize the silicon surface layer to suppress the formation of Si–Ni bimetallic species during the coating procedure. Samples were placed in a conventional cylindrical resistive furnace and heated to 800°C for 2 h to allow the oxide layer to form. The oxidized Si substrate was then placed in a sputtering chamber, the base pressure reduced to 8×10^{-4} Pa, and the Ni target then sputtered using a Kaufman ion gun at a 30 sccm Ar flow rate (working pressure and temperature were 12×10^{-4} Pa and 400°C). The oxide layer thickness was estimated to be approximately 8 nm by SIMS profile analysis. A thin layer (40 nm) of Ni film was deposited onto the SiO₂/Si substrate during ion beam sputtering.

Samples were then introduced to the DC PECVD system, and a typical two stage CVD process was carried out:

- The coated Ni was reduced with a 1:1 H₂ : NH₃ corrosive gas at 10 mbar and 750°C, under 8W DC plasma irradiation for 5 min. During reduction, the Ni layer changed to Ni islands which became active sites for CNT nucleation.
- The second stage was CNT growth on catalyst nanoparticles with varying ratios of acetylene and hydrogen inlet gases, for 20 min. Acetylene was used as a substitute for gaseous ammonia, and gas flow rates and plasma conditions are summarized in Tables 1 and 2, respectively.

Finally, samples were slowly cooled to room temperature under a hydrogen atmosphere.

3 Results and Discussion

Figure 2 shows SEM images with corresponding Raman spectra at different C₂H₂ concentrations. In the Raman spectra, low frequency absorptions between 200 and 300 cm⁻¹ arose from the radial breathing mode (RBM). Frequencies at $\approx 1,350$ and $\approx 1,580$ cm⁻¹ were assigned to G and D bands, respectively. The G band is reported to be related to graphitic structure (sp² hybridization), and the D band related to defects and disorder [13].

It is clear from Fig. 2a that at a C₂H₂ flow rate of 90 sccm, CNT formation was limited to the initial stage of growth. At a C₂H₂ flow rate of 140 sccm, the surface was covered by a thick layer of graphite and amorphous carbon as indicated by the Raman spectrum (Fig. 2c). The optimal flow rate was found to be 100 sccm, where dense vertical aligned carbon nanotubes were observed covered with nickel particles on their extremities (Fig. 2b). A low acetylene precursor concentration led to a low surface carbon concentration and resulted in limited CNT growth. Tanemura et al [14] reported that at high acetylene concentration, the catalyst surface could be covered or reacted with carbon forming metallic carbide. In that case, C₂H₂ fragments showed a greater tendency to form graphite or amorphous structures rather than CNTs.

Samples were prepared at various plasma currents (Table 2) to evaluate its effect on CNT growth. Figure 3 shows SEM images and corresponding Raman spectra of these samples. CNT formation only took place at a plasma current of 50 mA. Low quantities of CNTs without a well-defined shape were observed at higher

(a)

(b)

(c)

Fig. 2 SEM images and corresponding Raman spectra of samples prepared at acetylene flow rates of **a** 90, **b** 100 and **c** 140 sccm at 10 torr. The inset presents the radial breathing mode (RBM) and corresponding CNT diameter

Fig. 3 SEM images and corresponding Raman spectra of samples prepared at various plasma currents of **a** 20, **b** 50 and **c** 70 mA, at an acetylene flow rate of 100 sccm. Insets present the RBM and corresponding CNT diameters

Fig. 4 SEM image of a CNT network randomly grown on the silicon surface

Fig. 5 TEM image of MWCNTs prepared at an acetylene flow rate of 100 sccm

currents. Such behavior was rationalized by the inherent relationship between plasma current and surface carbon concentration, where higher plasma current led to a higher surface carbon concentration.

A sample was prepared where CNT growth was attempted at the same flow rate but in the absence of DC plasma (P5). A CNT network on the surface was clearly observed in the absence of DC current (Fig. 4). Studies have been carried out to ascertain the effect of DC plasma on the formation of VACNTs [15]. The Fig. 3 insets suggested that thicker single-walled CNTs (SWCNTs) would be formed at higher plasma current. The tendency to form multi-walled CNTs (MWNTs) was particularly noticeable at higher plasma current. SWCNT diameter was estimated using the equation $\nu = 223.75/d$ [16], where ν is the RBM frequency in cm^{-1} and d is SWNT diameter in nm. Figure 5 shows TEM micrographs of sample P4, in which MWNTs with an average diameter of ≈ 7 nm were formed.

4 Conclusions

VACNT growth on Ni/SiO₂/Si substrates was investigated using a purpose built DC PECVD reactor. The Ni layer acted as a catalyst after being transformed into islands on the surface by reduction. Our reactor was able to form VACNTs under suitable plasma current and acetylene flow rate conditions in a mixture of gaseous C₂H₂ and H₂.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

1. Iijima S (1991) Helical microtubules of graphitic carbon. *Nature* 354:56–58
2. Saito Y, Tani Y, Miyagawa N, Mitsuhashi K, Kasuya A, Nishina Y (1998) High Yield of single wall carbon nanotube by ARC discharge using Rh-Pt mixed catalyst. *Chem Phys Lett* 294:593–598
3. Iijima S, Ichihashi T (1993) Single-shell carbon nanotubes of 1- μ m diameter. *Nature* 603:603–606
4. Guo T, Nikolaev P, Thess A, Colbert DT, Smalley RE (1995) Catalytic growth of single walled carbon nanotubes by laser vaporization. *Chem Phys Lett* 243:49–53
5. Yudasaka M, Komatsu T, Ichihashi T, Iijima S (1997) Single-wall carbon nanotube formation by laser ablation using double targets of carbon and metals. *Chem Phys Lett* 278:102–105
6. Birkett R, Cheetham AJ, Eggen BR, Hare JP et al (1997) Transition metal surface decorated fullerenes as possible catalytic agents for the creation of single walled nanotubes of uniform diameter. *Chem Phys Lett* 281:111–115
7. Liu J, Dai H, Hafner JH, Colbert DT, Samlley E, Tans SJ, Dekker C (1997) Nanotubes as nanoprobe in scanning probe microscopy. *Nature* 385:780–785
8. Wei YY, Eres G, Merkulov VI, Lowndes DH (2001) Effect of catalyst film thickness on carbon nanotube growth by selective area chemical vapor deposition. *Appl Phys Lett* 78:1394–1396
9. Hesamzadeh H, Ganjipour B, Mohajerzadeh S, Khodadadi A, Mortazavi Y, Kiani S (2004) PECVD growth of carbon nanotubes using a modified tip-plate configuration. *Carbon* 42:1043–1045
10. Nguyen CV, Ye Q, Meyyappan M (2005) Carbon nanotube tips for scanning probe microscopy: fabrication and high aspect ratio nanometrology. *Meas Sci Technol* 16:2138–2145
11. Wu Y, Qiao P, Chong T, Shen Z (2002) Carbon nanowalls growth by microwave plasma enhanced chemical vapor deposition. *Adv Mater* 14:64–68
12. Lechuga LM (2006) Micro- and nanoimmunosensors: technology and applications. *Anal Bioanal Chem* 384:44–48
13. Popov VN (2004) A simple purification for single-walled carbon nanotubes. *Mat Sci Eng R* 43:61–65
14. Tanemura M, Iwata K, Takahashi K, Fujimoto Y, Okuyama F, Sugie H, Filip V (2001) Growth of aligned carbon nanotubes by plasma-enhanced chemical vapor deposition: optimization of growth parameters. *J Appl Phys* 90:1529–1532
15. Meyyappan M, Delzeit L, Cassell A, Hash D (2003) Carbon nanotube growth by PECVD: a review. *Plasma Source Sci Technol* 12:205–216
16. Bando S et al (1998) Effect of the growth temperature on the diameter distribution and chirality of single-wall Carbon nanotubes. *Phys Rev Lett* 80:3779–3784