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Synthesis of multi-walled carbon nanotubes by combining hot-wire and dc plasma-enhanced chemical vapor deposition

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ABSTRACT Multi-walled carbon nanotubes (MWCNTs) have been grown on 7 nm Ni-coated substrates consisting of crystalline silicon covered with a thin layer (10 nm) of TiN, by combining hot-wire chemical vapor deposition (HWCVD) and direct current plasma-enhanced chemical vapor deposition (dc PECVD), at 620 °C. Acetylene (C₂H₂) gas is used as the carbon source and ammonia (NH₃) and hydrogen (H₂) are used either for dilution or etching. The carbon nanotubes range from 20 to 100 nm in diameter and 0.3 to 5 μm in length, depending on growth conditions: plasma intensity, filament current, pressure, C₂H₂, NH₃, H₂ flow rates, C₂H₂/NH₃ and C₂H₂/H₂ mass flow ratios. By combining the HWCVD and the dc PECVD processes, uniform growth of oriented MWCNTs was obtained, whereas by using only the HWCVD process, tangled MWCNTs were obtained. By patterning the nickel catalyst, with the use of the HW dc PECVD process, uniform arrays of nanotubes have been grown as well as single free-standing aligned nanotubes, depending on the catalyst patterning (optical lithography or electron-beam lithography). In the latter case, electron field emission from the MWCNTs was obtained with a maximum emission current density of 0.6 A/cm² for a field of 16 V/μm.

KEYWORDS: Carbon nanotubes; Hot-wire assisted direct current plasma-enhanced chemical vapor deposition

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], there has been widespread interest in their use in a multitude of applications in nanoscale devices. Numerous studies have shown that multi-walled carbon nanotubes (MWCNTs) always exhibit metallic behavior and, due to their high aspect ratio (length/radius), can emit electrons in the neighborhood of their tips. These interesting electronic properties allow MWCNTs to be useful as new materials for the development of electron-field-emitting flat panel displays [2,3]. Although aligned CNTs are not strictly necessary for these applications, the use of aligned/micro-patterned forms of CNTs has been shown to offer additional advantages for the development of low threshold field (electric field required for an electron field emission) nanotube-based flat-panel displays.

In the beginning, CNTs have been produced by arc-discharge or laser ablation. These high-temperature methods were the most useful because they could produce large amounts of nanotubes, but their common drawback was the number of impurities incorporated in the material, whose type and amount depended on the deposition technique. Along with controlling the CNT morphology and structure, many practical applications require as well the precise control of their orientation, alignment and density. Thus, the high-temperature methods have been replaced by several low-temperature chemical vapor deposition (CVD) techniques (<800 °C), which are most promising in terms of CNT deterministic growth. These techniques include thermal CVD [4,5], direct current (dc) plasma-enhanced CVD (dc PECVD) [6,7], microwave PECVD [8–10], hot-wire (HW) dc PECVD [11–13], and HWCVD [14–16]. In all these techniques, substrates (c-Si or SiO₂ coated c-Si) were coated with a suitable transition metal catalyst, primarily Fe, Co or Ni.

The present paper focuses on the synthesis of MWCNTs in a reactor combining both HWCVD and dc

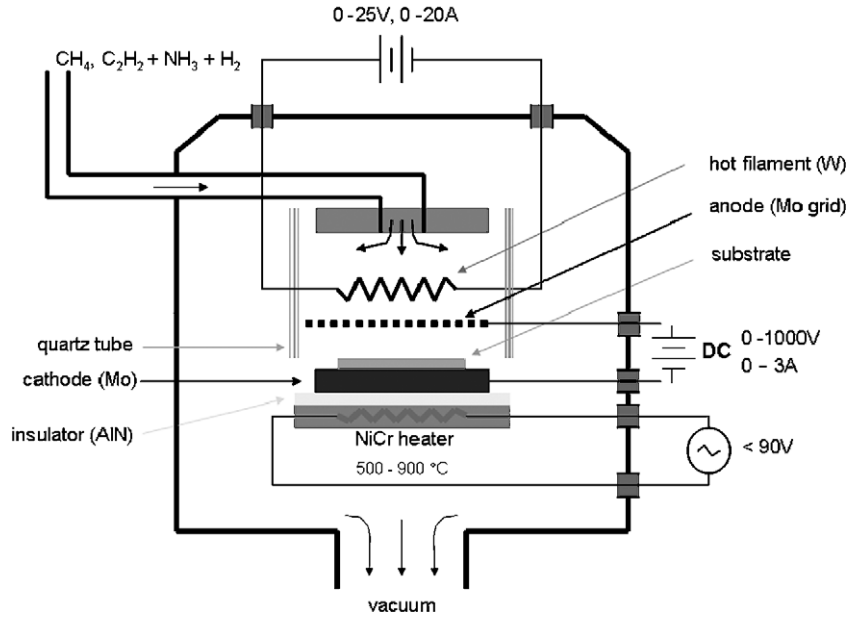


Fig. 1. Schematic cross-section of the experimental HW dc PECVD set-up.

PECVD techniques, using the $C_2H_2/NH_3/H_2$ gas mixture. The idea is that by comparing these two CVD processes separately or not, under identical deposition conditions, it should be possible to get a new insight into the understanding of the complex mechanism of CNT nucleation and growth. Thus, optimized growth conditions should be found, providing aligned MWCNTs with uniform diameters and lengths. Moreover, using patterning techniques such as optical or electron lithography in order to precisely locate the catalyst on the surface, this work shows that patterned arrays of aligned nanotubes can be deposited to ensure a significant electron emission current.

2. Experimental details

A stainless steel reactor (Fig. 1) containing one tungsten filament (0.38 mm in diameter) and two molybdenum electrodes has been designed for the growth of carbon nanotubes. The tungsten filament coil is powered by a direct current (dc) source around 13 A (250 W), allowing the filament temperature to stabilize at 1800 °C. The cathode (substrate-holder) can be negatively dc-biased compared to the anode (Mo grid) up to -450 V (with current densities between 1.5 and 4 mA/cm²). The distance between the tungsten wire and the cathode is fixed to 15 mm. An Ni-Cr heater, in thermal contact with the cathode but electrically

Table 1
Growth conditions for dc PECVD, HWCVD and combined HW dc PECVD processes

Sample	Gas mixture, $C_2H_2/NH_3/H_2$ (%)	Pressure (mbar)	T_s (-C)	dc-PE activation, V_{A-C} (V) $\times J_C^a$ (mA/cm ²)	HW activation, P (W)/ T_f (-C)
1	10:00:90	1	620	486 \times 1.5	–
2	10:20:70	1	620	365 \times 1.5	–
3	10:40:50	1	620	360 \times 1.5	–
4	10:60:30	1	620	370 \times 1.5	–
5	10:90:00	1	620	375 \times 1.5	–
6	10:00:90	1	620	–	250/1800
7	10:50:40	1	620	–	250/1800
8	10:90:00	1	620	–	250/1800
9	10:20:70	1	620	375 \times 1.5	75/1100
10	10:20:70	1	620	375 \times 1.5	150/1500
11	10:20:70	1	620	375 \times 1.5	250/1800
12	10:10:80	1	620	405 \times 1.5	250/1800
13	10:05:85	1	620	420 \times 1.5	250/1800
14	10:00:90	1	620	490 \times 1.5	250/1800
15	7.5:2.5:90	3	660	375 \times 3	250/1800
16	15:05:80	3	660	400 \times 4	250/1800

For all samples, the substrate consisted of Ni (7 nm)/TiN (10 nm)/Si(100), and the growth time was set to 15 min.

^a V_{A-C} : potential drop between the anode and the cathode; J_C : current density of ions impinging on the cathode.

insulated from it, can heat the cathode up to 700 °C. The base pressure of the deposition chamber is as low as 10^{-7} mbar. In the gas mixture used, acetylene is the deposition gas whereas ammonia and hydrogen are the etching gases. During the growth, a pressure ranging from 1 to 5 mbar is maintained in the reactor.

The nickel catalyst (7 nm thick) and the TiN diffusion barrier (10 nm thick) films were deposited onto doped silicon substrates. The diffusion barrier layer prevents the formation of NiSi_x via Ni diffusion above 300 °C and maintains Ni particles for the catalytic nucleation and subsequent growth of the carbon nanotubes. Upon annealing to the growth temperature in the range 500 to 700 °C, under H_2 flow, with the help of the thermally activated HWCVD process (W filament heated at 1800 °C), the

nickel thin film was found to break up into nanoparticles which seed the growth of the MWCNTs. Owing to the studies of other groups [5,7,9], it has been shown that the thickness of the initial Ni thin film and the growth temperature determine the size and density of the nanoparticles formed after annealing, and hence control the diameter and density of the nanotubes. After reaching the working temperature, the nanotube growth was initiated by introducing NH_3 and C_2H_2 into the chamber and igniting the glow discharge plasma using a 1 kW dc generator between the anode and the heated substrate-holder, the distance between these electrodes being 8 mm.

The surface morphology of the grown MWCNTs was investigated with a FEG high resolution scanning electron microscope whereas the carbon bonding and the micro-

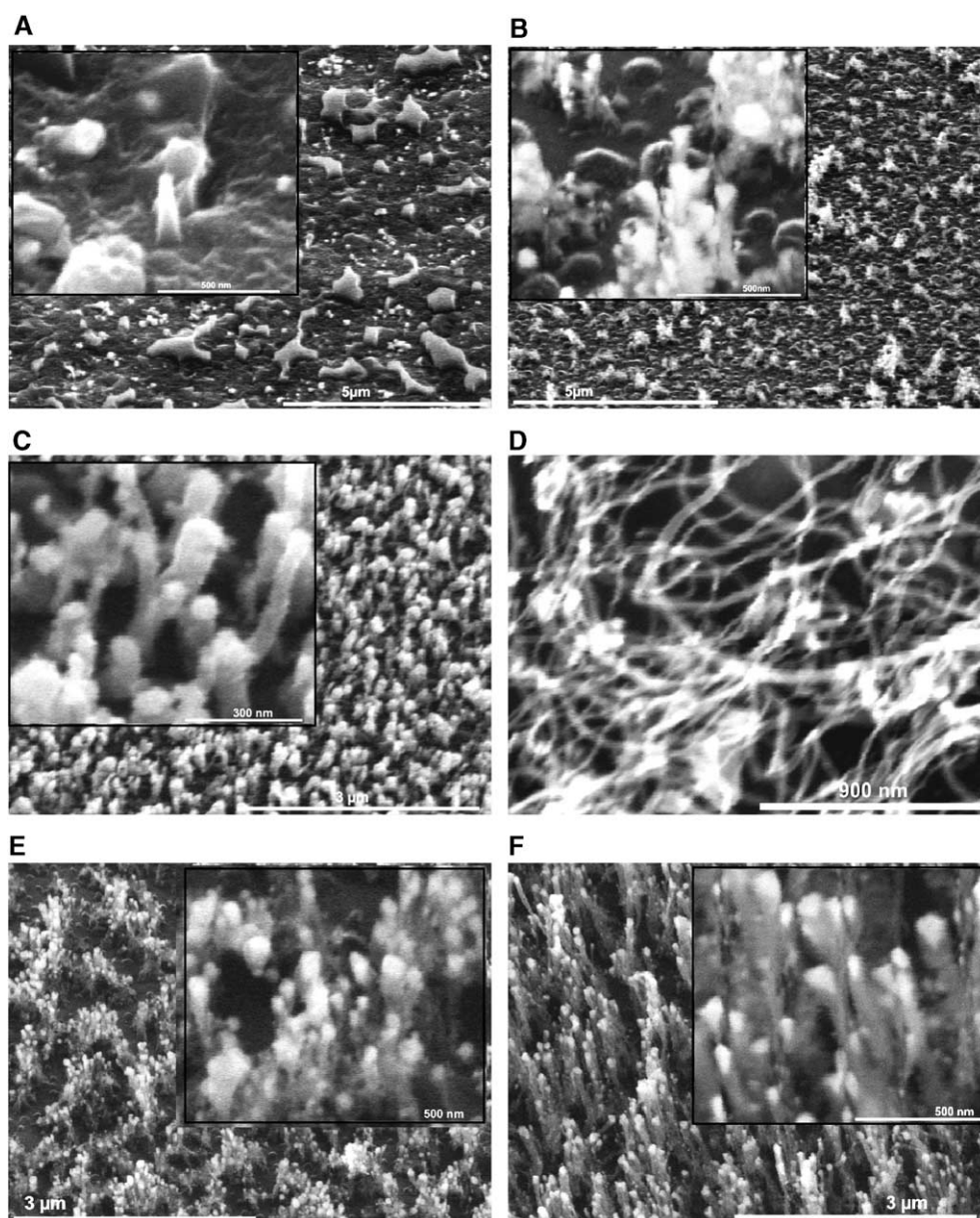


Fig. 2. Sequence of SEM images (observation angle 45°) on: (A) sample 1; (B) sample 2; (C) sample 5; (D) sample 7; (E) sample 12; (F) sample 13.

structure were assessed by Raman spectroscopy and transmission electron microscopy, respectively. Electron field emission was carried out using a triode set-up in a vacuum chamber working at 10^{-6} Torr.

3. Results and discussion

Different types of growth processes, namely dc PECVD, HWCVD and combined HW dc PECVD were investigated as function of gas mixture composition, total pressure, activation power and geometrical configuration. Various $C_2H_2/NH_3/H_2$ ratios were used with a total gas flow rate of 100 sccm (see the growth conditions in Table 1, samples 1 to 14). All syntheses were performed at 620 °C and 1 mbar total pressure with 15 min deposition time.

The dc PECVD growth mode was first studied for gas mixtures containing 10% acetylene and an increasing ammonia content diluted in hydrogen (see Table 1, samples 1 to 5). The dc PECVD process generates radicals and ions impinging on the cathode. Moreover, the dissociation energy for NH_3 is lower than for H_2 (a bias of 325V [17] is sufficient), so that atomic H is easily produced by the plasma. The current density of ions impinging on the cathode has been maintained to a fixed value of 1.5 mA/cm^2 while the potential drop between the electrodes could vary freely (current regulation mode) between 360 V and 480 V. Fig. 2A is the SEM image corresponding to sample 1 prepared with no ammonia and high bias voltage: the deposited layer exhibits a large roughness with scarce whiskers. The associated Raman spectrum (Fig. 3) exhibits two intense D and G peaks around 1350 and 1590 cm^{-1} with two additional small bands around 1160 and 1500 cm^{-1} , indicative of many sp^3 C defects. The graphitic contribution may be ascribed to the high voltage which generates some etching species. When 20% ammonia is introduced in the gas mixture (sample 2, Table 1), formation of bundles of carbon nanotubes with diameters ranging from 15 to 50 nm and lengths of a few hundreds of nanometers can be observed, scarcely distributed on the surface (see SEM micrograph of Fig. 2B): a thinner carbon layer is deposited and Ni nanoparticles are identified on tips of CNTs. The associated Raman spectrum (Fig. 3) exhibits weaker and broadened D and G peaks, compared with the peaks of sample 1. The smaller amount of carbon deposition as well as the growth of some bundles of CNTs can be correlated with the higher concentration of the activated etching species (H , NH_2) generated by the presence of ammonia which is easily decomposed by the dc discharge, as discussed previously. By increasing the amount of ammonia introduced in the gas mixture (samples 3 to 5, Table 1), an increased formation of carbon nanotubes is observed: Fig. 2C shows, for the sample 5 prepared with 90% NH_3 , a surface uniformly covered by aligned carbon nanotubes with diameters ranging from 15 to 100 nm and lengths ranging from 100 to 300 nm. The corresponding

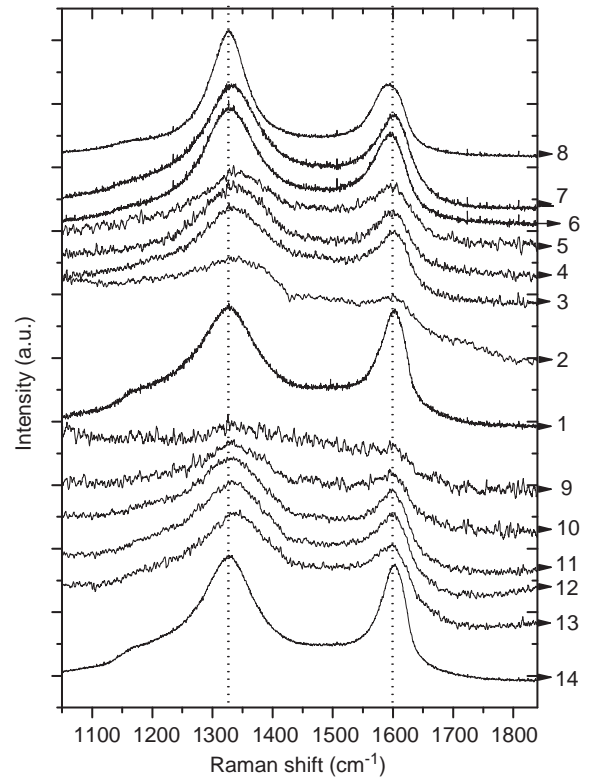


Fig. 3. Sequence of Raman spectra recorded for samples 1 to 14 (see Table 1).

Raman spectra (Fig. 3) confirm, through the decrease of the I_D/I_G ratio when $[NH_3]$ increases, the improvement of the CNT structure: both the amount of amorphous carbon and of defective structure in CNTs decrease.

The HWCVD growth mode was studied for gas mixtures containing 10% C_2H_2 and an increasing amount of NH_3 diluted in H_2 (Table 1, samples 6 to 8). The HWCVD process generates atomic hydrogen and C_nH_n radicals with $n=1,2$ [18], depending on the filament temperature T_f . When T_f is set at 1800 °C, the various gases are mostly dissociated at the contact of the tungsten wire or close to the wire. For these samples, dense tangled and curled up nanotubes are observed by SEM (Fig. 2D). The diameters of the nanotubes range from 15 to 60 nm and their lengths are several micrometers. The corresponding Raman spectra (Fig. 3) show, first the highly graphitic nature of the deposited samples, then the increase of the I_D/I_G ratio when $[NH_3]$ increases, which could suggest that NH_2 radicals generated at high concentration deteriorate the CNT structure.

The use of both the dc plasma and the hot-wire leads to a high rate of transformation of gas molecules in the gas mixture into ions, radicals and activated molecules. So with the HW dc PECVD process, we first investigated the influence of the filament temperature (samples 9 to 11), taking as $C_2H_2/NH_3/H_2$ ratio the ratio of sample 2 (Table 1). Apart from the fact that sample 9 is equivalent to sample 2 because NH_3 and H_2 molecules are not significantly dissociated when the filament temperature T_f is as low as

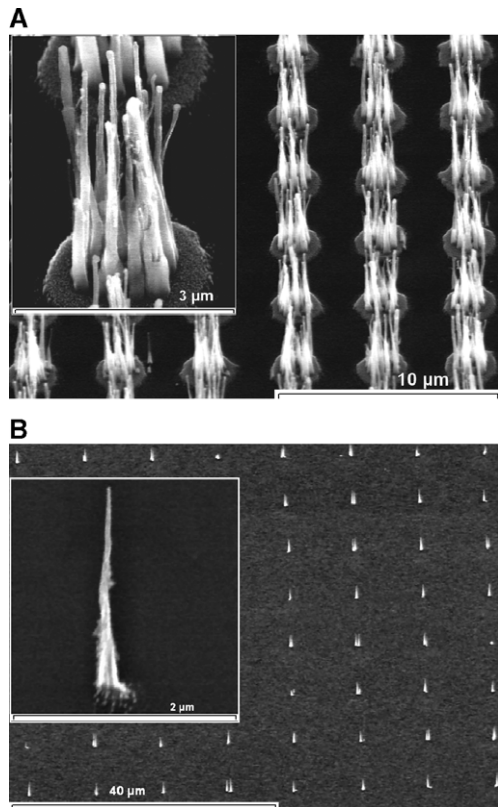


Fig. 4. Sequence of SEM images (observation angle 45°) on: (A) sample 15; (B) sample 16.

1100 °C, increase of T_f results in the formation of CNTs with a small amount of amorphous carbon due to the efficient etching effect of H radicals, as observed in the Raman spectra (Fig. 3). Setting T_f at 1800 °C and increasing the H_2/NH_3 ratio improves the CNT growth: Fig. 2E and 2F corresponding to samples 12 and 13, respectively, show the SEM micrographs of dense aligned carbon nanotubes with lengths ranging from 500 to 700 nm and diameters ranging from 15 to 100 nm. The interpretation of these HW dc PECVD results is very similar to that of the HWCVD results. The length of the nanotubes has been observed to increase rapidly when the current density impinging on the cathode (correlated with the total pressure) increases: for instance, carbon nanotubes of 5 μm length are obtained using 3 mbar pressure corresponding to a current density in the dc-discharge of 3 to 4 mA/cm².

Using HW dc PECVD process at 3 mbar pressure and $T_s=660$ °C, we have performed growth of CNTs on patterned substrates with Ni dots of different sizes. For sample 15 (Table 1) deposited on a patterned substrate with 1 μm Ni dots realized by UV lithography, we observed several MWCNTs with diameters less than 100 nm growing on each dot (Fig. 4A), whereas for sample 16 deposited on a patterned substrate with 100 nm Ni dots realized by electron-beam lithography, we observed only one MWCNT on each Ni dot (Fig. 4B). The first I–V characteristics performed on sample 16, consisting of an array of individual

MWCNTs, gave an onset electric field of 6 V/Am and a maximum emission current density of 0.6 A/cm² for a field of 16 V/Am. Further work is necessary, taking into account the uniformity of the nanotube length, the spacing between nanotubes, etc., in order to get efficient electron emission useful for cold-cathode flat panel FEDs or vacuum micro-electronic sources [2,3,19].

4. Conclusions

Since the first paper dealing with the preparation of CNTs by an activated CVD process [4], many workers tried to control the growth of aligned CNTs by the use of various CVD methods and to understand the mechanisms of CNT nucleation and growth.

The present study has been restricted to the use of two specific CVD methods: the hot-wire CVD and the dc plasma-enhanced CVD, working separately or in a combined action. Fixing the diffusion barrier thickness, the catalyst thickness, the substrate temperature and the pressure in the reactor, only the relative composition of the gases, the filament temperature and the potential drop between the anode and the cathode could vary in the experiments. In these conditions, we observed that using the dc PECVD process exclusively, with a potential drop of around 400 V, for which radicals and ions impinging on the cathode were generated, growth of aligned carbon nanotubes was favored. Moreover, the CNT structure was improved when ammonia replaced molecular hydrogen as the etching gas. When the HWCVD process was used exclusively with a filament temperature of 1800 °C, for which a high concentration of atomic hydrogen was generated, dense tangled and curled up localized carbon nanotubes have been grown. However, contrary to what was observed with dc PECVD, the CNT structure was deteriorated when increasing ammonia content. Thus, combining HWCVD and dc PECVD, we observed that growth of dense aligned carbon nanotubes could be obtained if ammonia content was minimized.

The last part of this work was focused on the possibility to grow aligned MWCNTs on patterned substrates, using the HW dc PECVD process, in order to get rid of the screening effect which is deleterious for the field emission properties. First attempts of growth have been realized on an array of 100 nm Ni catalyst dots realized by electron beam lithography: individual MWCNTs have been grown on each dot, thus a maximum emission current density of 0.6 A/cm² has been measured for a field of 16 V/Am. Further work should be necessary for these results to be useful for electronic applications.

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