Simultaneous tip and base growth mechanism in carbon nanotubes produced by PECVD

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ABSTRACT

Carbon nanotubes (CNTs) with curly and straight segments were synthesized by means of radio-frequency plasma enhanced chemical vapour deposition (RF-PECVD). The origin of this peculiar combination of aligned and misaligned structures within a single CNT is attributed to a simultaneous growth process from the tip and the base of the CNT. Evidences for supporting such a growth mechanism were found by scanning and transmission electron microscopy (SEM and TEM) studies. In addition, energy dispersive X-ray analysis (EDX) provided information about the chemical purity of the active catalyst. The growth kinetics is affected by the particular local conditions surrounding the base and the tip of the CNTs, such as the degree of ion bombardment originated by the presence of plasma.

Keywords: PECVD, VACNTs, VACNFs, CNT growth mechanism, catalyst–substrate interaction.

1 INTRODUCTION

Plasma enhanced chemical vapour deposition (PECVD) has been demonstrated over the years as the preferred method to obtain free-standing vertically aligned carbon nanotubes and nanofibers (VACNTs and VACNFs) [1,2]. This kind of structures show an excellent behaviour in applications such as field emission [3,4] or electrochemistry [5,6]. A full understanding of the growth and alignment mechanisms of these structures is crucial in order to achieve their optimal performance.

Merkulov and co-authors [7] were who firstly proposed a consistent alignment mechanism for CNFs and CNTs grown by PECVD. This model is based on the force that the electric field generated at the plasma sheath exerts on the tip of the growing CNFs. In Merkulov’s article, only CNTs following a tip-growth mechanism grew vertically aligned, while CNFs grown from the base showed random orientations. In contrast, Bower’s article [8] showed VACNTs with their catalyst particle at their base. Although the authors of this work claimed that the electric field was clearly responsible for the alignment, experimental evidences seem ambiguous and unclear presented.

Here, we present CNTs grown from tip and base simultaneously by PECVD. This new kind of structure has been found to provide valuable information on the growth mechanism of these structures, as well as on the factors that determine their alignment with respect to the substrate.

2 EXPERIMENTAL

CNTs/CNFs have been grown on c-Si (100) substrates with a native oxide layer, using a gas mixture of NH₃:C₂H₂=2:1. Ni, Fe and Co have been used as the catalyst materials in our experiments. For this, a 4-5nm thin layer is first deposited by RF magnetron sputtering on top of the substrate. The PECVD system used in this work has been powered by a 300W RF source (Hüttinger) working at 13.56MHz. The deposition temperature ranged from 650ºC to 750ºC. Details of the deposition procedure can be found elsewhere [9].

SEM micrographs of the nanotubes were obtained on a Hitachi H-4100FE operated at 30kV. For TEM analysis, samples were prepared scrapping the films off the substrate, dispersing them in a hexane ultrasonic bath, and placing them onto holey carbon Cu grids. Bright field pictures were taken on a PHILIPS CM30 electron microscope operating at 300kV, while EDX microanalysis was performed on a Hitachi 800MT operated at 200kV equipped with an EDX microprobe.

3 RESULTS AND DISCUSSION

Figure 1a shows SEM and TEM images obtained from various CNT and CNF samples. In figure 1a (sample A) there are mostly VACNFs, although there is a small portion of spaghetti-like CNTs grown among them (marked by arrows). These nanotubes show particular characteristics, as greater length and smaller diameter with respect to the aligned ones. In figure 1b (sample A), TEM pictures of VACNFs reveal a typical bamboo-like structure of their inner cavity, which provides, in addition, a fingerprint of growth direction. Note that in this picture, two CNFs show a particle at both ends. This means that the original Ni catalyst nanoislands broke into two separate fragments during growth, one remaining at the base and the other at the tip. However, only one of the particles appears to be active. EDX analysis performed on both ends of several CNFs revealed a significant Si content, which might be incorporated by temperature-activated diffusion from the silicon substrate. The proportion of Si with respect to Ni was around 10% at the active particles located at the tips, while the percentage at the bottom fragments was slightly
over 30%. Hence, the Si contamination threshold for the inactivation of a Ni catalyst must be within this range (10-30%). Regarding the spaghetti-like CNTs, they were not found in the TEM prepared sample, probably due to its extremely low concentration, although it would be interesting to check the Si content at the active catalyst fragments of these CNTs. In figure 1c, a new kind of structure is shown (sample B). Here, we present nanotubes composed of a partially aligned segment (>5µm), with a VACNF at their tip (~1µm). These two segments are associated to a simultaneous growth from the tip and the base of the nanotube. In figure 1d (Sample C), a TEM micrograph shows clearly a junction of a short VACNF (~200nm) and its spaghetti-like “tail”. The tip segment resembles a CNF grown by a typical PECVD process, while the tail shows a very common structure obtained by thermal CVD. Furthermore, the bamboo structure concavities present inverted orientations, thus highlighting opposite growth start points along the tubules (see inset for the long segment). The great morphological difference found between the two segments of the carbon nanostructure suggests an important variation of the surrounding conditions at their tip and base. On one hand, we must take into account the electric field created at the

Figure 1. a) SEM micrograph of VACNFs. A few CNT (pointed by arrows) grew in a curly fashion, and show a greater length. b) TEM images of the catalyst material found at both edges of the VACNFs. The inset shows their base edges, where the typical bamboo-like growth fingerprints presumably correspond to the tip particles. c) SEM micrograph of CNTs with straight and curly segments. d) TEM image showing a junction which divide a CNTs into two segments: one grown from the tip (left) and one grown from the base (right). The inset highlights the orientation of the bamboo-like structure. Pictures a) and b) corresponds to sample A; picture c) corresponds to sample B and picture d) corresponds to Sample C.
sheath between the plasma bulk and the substrate (cathode). Given that the distance between adjacent tubes is very low compared to their length (<1:10) and the plasma sheath is in the order of several mm, almost all the electric field lines are collected by the tips of the growing nanotubes. Positively ionized species will be electrically attracted by these tips and accelerated against them. It is well established that the role of NH3 is to etch preferentially the amorphous carbon during CNT deposition [10]. Nevertheless, the ion bombardment can also remove building atoms of the nanotube, which results in a slowed down growth process [1]. On the other hand, we can consider that neutral species reach equally the base and the tip of the nanotubes, in this geometry. Consequently, the base of the growing tubules is shielded from high energetic ions but benefits from the extra carbonaceous radicals supplied by the plasma discharge, as CN, CH or C2 [9]. This would explain why in sample B and C the nanotube tails show greater lengths than the tips. Furthermore, it is likely that the small portion of spaghetti-like CNTs in sample A is the result of a base-growth mechanism as well. From a different approach, all these results highly supports Merkulov’s model for the alignment mechanism in CNFs grown by PECVD [7]. SEM images in figure 1c allow us to extract a direct estimation of the growth rates at the tip with respect to the base. If we approximate a constant growth rate with time and consider no deactivation of the catalyst particle during the deposition process, then we obtain that the base-growth is at least 7 times faster in our system under the specified deposition conditions for sample B. This estimation takes into account, for the spaghetti-like segment, the distance from the base of the VACNF to the substrate, which is a lower limit, given that this fragments are not totally aligned. If we apply the same criteria to sample C, then the ratio between base and tip growth rate is as high as 35 (the length of the total nanotube was estimated from another SEM picture). In parallel, this large difference between growth rates gives an idea about how intense is the etching process that takes place on the nanotube tip.

In figure 2, it can be seen possible scenarios for CNT/CNF growth. On step I, the precursor species present in the plasma reach the catalyst nanoisland formed after the annealing process. On step II, carbon atoms from catalytic dissociation of precursor species diffuse along the particle surface and precipitate to form a MWCNT or MWCNF. At this point, the catalyst particle will be lifted-up by the growing tubule (“tip-growth” mechanism) or will remain anchored to the substrate surface because of a strong interaction with it (“base-growth” mechanism). In addition, the particle can fragment into two (or more) parts as a consequence of the tensile stress established along the particle. On one side, the interaction with the substrate retains the particle anchored; and on the other side, the continuous incorporation of new carbon atoms at the catalyst-wall frontiers of the CNT/CNF lifts the particle upwards. This last supposition is highly supported by CNF in-situ growth TEM observations carried out by Helveg S. and co-authors [11]. In the supplementary movie of this reference, it can be clearly seen how a Ni particle attached to the MgAl2O4 substrate is firstly elongated because of the incorporation of new C atoms, and finally it releases the accumulated stress detaching itself from the surface and recovering its initial shape. Finally, on step III, we consider the most feasible processes that take place in our samples. If the catalyst particle keeps its original volume during growth, it will yield a pure base or tip growth (cases 1 and 2, respectively), depending on the interaction between the catalyst and the substrate. If the particle breaks into two or more fragments, the resulting nanotubes will present several morphologies. Case 3 is observed in our sample A, where the CNFs grow mainly from the tip. Finally, the most complex case (4) is when the catalyst material breaks into two active fragments, one located at the tip and the other one at the base of the nanostructure, giving rise to the CNTs shown in samples B and C (figures 1c and 1d). Moreover, these two fragments are continuously subjected to the tensile stress mentioned in step II, so it is possible that new fragments originate and rest encapsulated in the body of the nanotube. In fact, this is the mechanism proposed in [12] for the formation of metallic nanowires encapsulated by CNTs.

A possible cause of the simultaneous growth from the tip and the base described in the case 4 is the effect of temperature on the catalyst particles. At ~700°C, their plastic deformation and further fragmentation are favoured, which does not necessarily imply a melting of the metal, even if we take into account the size correction for its
melting point [13]. In figure 3, it can be seen the transition of the growth mechanism from the case 2/3 to case 4, due to a change in growth temperature, keeping the rest of the deposition parameters unaltered. The length of the nanostructures is found to increase one order of magnitude (~500nm compared more than 5000nm!), and again we found long and partially aligned CNTs with short straight CNFs over them (see inset of figure 3b).

4 CONCLUSIONS

A new kind of CNT-based structure has been presented, which results from a simultaneous tip and base growth mechanism during a PECVD process. SEM and TEM micrographs provided morphological evidences of this kind of growth. EDX elemental analysis was performed directly on the catalyst particles located at both ends of straight Ni-catalysed CNFs. This allowed us to estimate the Si atomic content necessary to inactivate completely Ni as a catalyst, which is between 10 and 30%. From the SEM images obtained of our samples, it has been possible to compare the growth rates of the segments obtained by the tip-growth mechanism and the base-growth mechanism. The highest growth rate ratio found until now in our samples is $R_{\text{tip}}/R_{\text{base}} \approx 35$. Possible growth scenarios were proposed and discussed according to experimental evidences. The main causes of this new kind of simultaneous growth are the high temperature conditions in combination with the catalyst-substrate interaction. In order to obtain VACNFs (regardless of any crowding effect), growth must take place exclusively from their tip, given that the alignment driving force caused by the electric field is only applied at this point.

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