

Plasma composition during plasma-enhanced chemical vapor deposition of carbon nanotubes

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Neutral species and positive ions were extracted directly from a $C_2H_2:NH_3$ plasma used to grow vertically aligned carbon nanotubes (CNTs) and analyzed by mass spectrometry. We observe that NH_3 suppresses C_2H_2 decomposition and encourages CNT formation. We show that the removal of excess carbon, essential for obtaining nanotubes without amorphous carbon deposits, is achieved through gas phase reactions which form mainly HCN. We determine an optimum $C_2H_2:NH_3$ gas ratio which is consistent with previous observations based upon postdeposition analysis. We find, in contrast to thin film growth by plasma-enhanced chemical vapor deposition, that the optimum condition does not correspond to the highest level of ionization. We also provide evidence that C_2H_2 is the dominant precursor for CNTs in our experiments. © 2004 American Institute of Physics. [DOI: 10.1063/1.1782256]

Carbon nanotubes have attracted great interest among researchers since their discovery.¹ Their physical and electronic properties, combined with their chemical inertness, makes them potentially useful as electron-field emitters,² nanoelectrodes,³ filter media,⁴ and superhydrophobic surfaces.⁵ Plasma-enhanced chemical vapor deposition (PECVD), combined with a suitable metal catalyst, has been used to coat substrates with “forests” of well-aligned multi-walled nanotubes (MWNTs), or intricate patterns of MWNTs when the catalyst layer is patterned using lithography. It is important that the synthesis of MWNTs is performed without the deposition of amorphous carbon (*a-C*), which prevents the formation of carbon nanotubes (CNTs) by poisoning the growth catalyst, and can cause short circuits on the substrate surface. One method to prevent the deposition of *a-C* is to combine the carbon source (hydrocarbon gas) with a hydrogen-rich gas (typically NH_3 or H_2) which produces reactive species to remove the excess carbon. Despite experimental evidence and the vast amount of research which has been performed on the growth of CNTs, there is little in the literature which reports detailed plasma analysis. Measurements of neutral species extracted from vacuum chamber gases have previously been presented^{6–8} but we are not aware of any previously reported measurements either of ion species or of neutral species extracted from inside the plasma itself. In this letter, we report on *in situ* measurement of the plasma used for PECVD growth of carbon nanotubes.

CNTs were grown using a dc PECVD setup with the substrate located on a resistively heated graphite stage. The substrate temperature was measured using a thermocouple attached directly to the upper surface of the stage. Gas flow rates were controlled independently using mass flow controllers and the combined gases were fed into the chamber through a metal pipe which was grounded, acting as an anode for the plasma discharge. A dc plasma was generated

using an Advanced Energy MDX 1K dc power supply, with tungsten heaters in the graphite stage forming the cathode. The chamber was maintained at vacuum using a rotary pump, with a base pressure of 7×10^{-2} mbar. Our standard deposition procedure consists of loading Si substrates coated with a thin catalyst film onto the graphite stage and heating to 520 °C in NH_3 (200 sccm flow rate, achieving a pressure of 2.5 mbar). At this temperature, the thin film catalyst agglomerates into particles suitable for seeding nanotube growth. The dc plasma is then immediately initiated, and C_2H_2 is added into the gas flow as the carbon feedstock for the growth of MWNTs. During growth, NH_3 is believed to be generating active species for removing unwanted *a-C*. The results obtained by growing CNTs in this particular system have previously been reported.^{9,10} It was demonstrated that well-aligned nanotubes were grown for C_2H_2 concentrations between 4% and 20%, that at 29% C_2H_2 the nanotubes became more obelisk-like, and that by 38% there are no longer any tubes at all, but carbon tip structures resembling a miniature mountain range. These results are shown in Fig. 1. It was also reported that the nanotube growth rate peaked at around 20% C_2H_2 content. This growth condition gave a clean, *a-C*-free substrate.¹⁰ The heater temperature is regulated to maintain the temperature stably at 650 °C throughout the deposition. The chamber pressure is set to 5.3 mbar by throttling the pump. The plasma dc bias is maintained at 600 V, with current typically around 100 mA. Our base gas

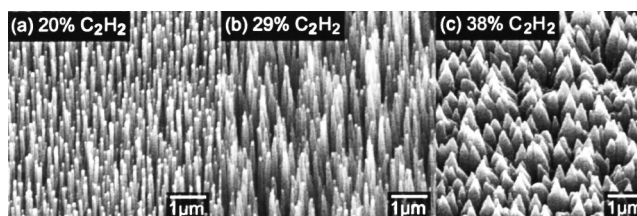


FIG. 1. SEM image of CNTs grown with (a) 20% C_2H_2 , (b) 29% C_2H_2 , (c) 38% C_2H_2 .

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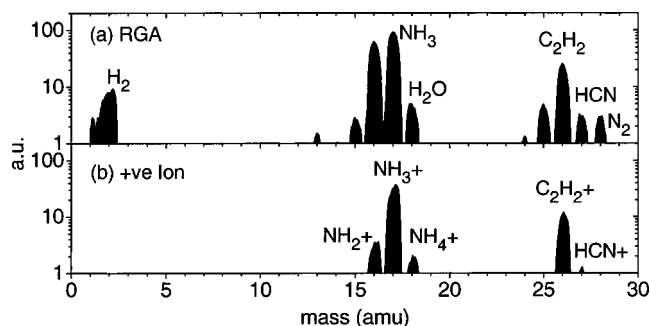


FIG. 2. Mass spectra. (a) RGA spectrum, (b) positive ion spectrum.

flow rates are 200 sccm NH_3 and 59 sccm C_2H_2 . C_2H_2 thus makes up approximately 23% of the combined flux.

Mass spectrometry was performed on species extracted 15 mm from the graphite cathode/stage using a Hiden EQP High Energy plasma analyzer. The tip of the analyzer was immersed in the plasma and differentially pumped to 1×10^{-6} mbar during the measurements. Neutral molecules were analyzed using residual gas analysis (RGA), whereas positive ions were investigated using secondary ion mass spectrometry. Background noise was subtracted from the ion data. A RGA mass spectrum for neutral species at standard conditions is shown in Fig. 2(a), and a mass spectrum for positive ion species is shown in Fig. 2(b). The species in the RGA spectrum are consistent with the cracking patterns of C_2H_2 (base peak at 26 u) and NH_3 (base peak at 17) and also indicate the presence of H_2 , HCN , H_2O , N_2 , and CO_2 .¹¹ Signal levels at higher masses were far less significant, but included the mass signature of the rotary vacuum pump oil. The principal species in the ion spectrum are consistent with ions derived from NH_3 , C_2H_2 , and HCN . Note that whilst these figures only show masses up to amu30, data were recorded up to 100 u.

To investigate why optimal growth occurred at around 20% C_2H_2 , we varied the volume flow rate proportion of C_2H_2 in the $\text{NH}_3:\text{C}_2\text{H}_2$ plasma between 0% and 70% whilst maintaining other parameters at their standard setting. The overall level of the RGA signals differed significantly between measurements, and it was necessary to normalize the data in order to make comparisons between measurements. To do this, the absolute signal for each mass point was divided by the measured "total gas flux" for the measurement. The calculated gas composition derived from the normalized data is shown in Fig. 3(a), which includes the "ideal" line for comparison. The major neutral species detected, aside from NH_3 and C_2H_2 , were H_2 , N_2 , and HCN . This is consistent with data reported by other authors.⁷ The data for H_2 and HCN are shown in Figs. 3(b) and 3(c). The dominant ions detected were NH_3^+ and C_2H_2^+ . Other detected species were NH_2^+ , NH_4^+ , HCN^+ and C_2H^+ . It is possible that the C_2H_2^+ data also contain a small amount of CN^+ , which has the same mass number. The ion measurements are presented in Figs. 3(d)–3(f).

We first investigate the role of NH_3 in CNT growth. The production of *a*-C-free CNTs requires a controlled deposition of carbon. This is achieved through the combination of rate-controlled dissociation of a carbon-rich gas (in our case C_2H_2) and removal of excess carbon species which would otherwise lead to amorphous carbon deposits. There has been some discussion in the literature regarding the carbon re-

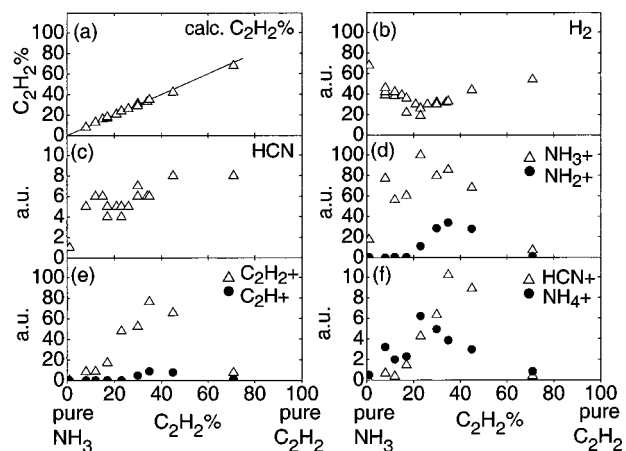


FIG. 3. RGA and Ion data. (a) Calculated vs actual $\text{C}_2\text{H}_2\%$, (b) H_2 , (c) HCN , (d) NH_3^+ and NH_2^+ , (e) C_2H_2^+ and C_2H^+ , (f) HCN^+ and NH_4^+ .

moval reaction, and the role of NH_3 . It has been widely reported that atomic hydrogen is the active species, generated by electron impact dissociation of H_2 in plasma.^{8,12} H_2 as well as NH_3 has been reported to act as a source for atomic hydrogen¹² and generation of H from an $\text{NH}_3:\text{C}_2\text{H}_2$ dc plasma has been shown in simulation studies.¹³ It has also been shown that NH_3 is a more effective generator of atomic hydrogen than H_2 as the addition of NH_3 to a CH_4/H_2 mixture enhances hydrogen formation.⁸ The efficacy of NH_3 in CNT production has been attributed to the preferential decomposition of NH_3 suppressing the decomposition of C_2H_2 , and to the incorporation of nitrogen into Ni catalyst particles forming Ni_3N during annealing, changing the composition and structure of the catalyst surface.¹⁴

Our results show preferential decomposition of NH_3 taking place. A graph of H_2 for varying gas ratio is shown in Fig. 3(b). H_2 is generated by the decomposition of either NH_3 or C_2H_2 . To the left of this figure, where the plasma is predominantly NH_3 , it can be seen that the amount of H_2 generated increases as the amount of NH_3 increases. This indicates that in this region, the H_2 is derived from decomposition of NH_3 . To the right of the figure, where the plasma is predominantly C_2H_2 , we see that the amount of H_2 generated rises as the amount of C_2H_2 rises. In this region, therefore, H_2 is derived from the decomposition of C_2H_2 . The explanation for this behavior is that at high NH_3 ratios, NH_3 decomposes preferentially over C_2H_2 due to its weaker bonds. This allows the C_2H_2 to decompose slowly, generating the controlled amounts of carbon necessary for CNT formation and giving rise to clean, well-aligned carbon nanotubes. At high C_2H_2 ratios, there is insufficient NH_3 to effectively suppress C_2H_2 decomposition, resulting in high levels of carbon generation and deposition of *a*-C onto the substrate. NH_3 therefore has two key roles in the formation of CNTs: not only does it generate atomic hydrogen species to remove excess carbon, it also suppresses the decomposition of C_2H_2 , limiting the amount of carbon generated at source.

We next consider the process for removing excess carbon. The key reaction product found in our results was HCN . Figure 3(c) shows that large amounts of HCN are generated where there are plentiful supplies of both C_2H_2 and NH_3 . The figure also shows that a purely NH_3 plasma does not generate significant HCN , despite the presence of a graphite (carbon) stage. This lack of HCN indicates that the carbon

removal process must be a predominantly gas phase reaction transforming excess carbon in the gas phase into HCN, rather than a reaction removing carbon from the substrate surface.

The data indicate an optimum region for CNT growth, consistent with our previously reported observations. We have shown that H₂ is derived from NH₃ at low C₂H₂ fraction, and from C₂H₂ at high C₂H₂ fraction due to the interaction between the two gases. This leads to a minimum in H₂ generation at around 23% C₂H₂, shown in Fig. 3(b). Figures 3(d)–3(f) show that ion intensity is greatest at around 40% C₂H₂. Not only do the signals for the base ions NH₃⁺, C₂H₂⁺, and HCN⁺ peak here, but the subsidiary ions NH₂⁺ and C₂H⁺ are only present close to this peak. This suggests that these subsidiary ions are only generated when the ionization level is high. At this point, we see *a*-C on the substrate as well as on the CNTs. The most reactive condition therefore favors the deposition of *a*-C. In contrast, we have previously shown that the growth rate of clean CNTs is at a maximum at around 20% C₂H₂. This is close to our observed minimum in H₂, and we suggest that this is the optimum condition for CNT growth. At this point, species which remove carbon are at a minimum and C₂H₂ decomposition is low, giving rise to steady, controlled deposition of CNTs.

Finally, there has been discussion in the literature regarding the nature of the carbon precursor for the formation of CNTs. In this work, we were unable to detect C₂, CH₄, or other higher carbon species within our data and thus conclude that, in our case, C₂H₂ is the dominant precursor for CNT formation. Other authors⁸ have also detected the presence of C₂H₂ in a CH₄/H₂/NH₃ plasma yielding CNTs, and it has been reported that C₂H₂ is the most efficient carbon feedstock for the growth of carbon filaments.¹⁵

In conclusion, our results provide direct experimental insight into the plasma chemistry during the growth of MWNTs by PECVD. The role of NH₃ in suppressing C₂H₂ decomposition and encouraging CNT formation has been clearly demonstrated. The data also indicate that excess carbon is removed predominantly in the gas phase. We have shown that undesirable *a*-C deposition occurs when ionization is at a maximum, and that optimum clean CNT production takes place at a lower C₂H₂ ratio of around 23%, where

H₂ is at a minimum. This is in contrast with most thin film growth, where the condition with maximum ionization is preferred. Lastly, our results indicate that C₂H₂ is the dominant detected precursor for CNT growth. The results support what we have observed in practice: a region where CNTs grow, and an optimum point where the carbon deposition and removal processes balance to give a maximum in the growth rate for clean CNTs.

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