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### Role of Gas-phase Reactions and Thermal Gradient Control in Carbon Nanotube Synthesis

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# ABSTRACT

We investigate the role of precursor thermal rearrangement and surface catalytic reactions in the synthesis of vertically aligned carbon nanotubes (VA-CNTs) by acetylene-based, chemical vapor deposition (CVD) and demonstrate a millimeter-long growth of single-walled CNT (SWNT) without water assistance. A substrate heater was used to create an ascending temperature gradient from gas injection to catalyst substrate. Whereas temperature of catalyst substrates primarily determines their catalytic activity, it is a thermal condition of a gaseous mixture in the CVD chamber that also influence growth yield and structural features of as-grown CNTs. Employing Egloff's characterization, [1] we discuss the importance of various gas thermal zones in producing high-quality nanotubes with augmented growth efficiency. We continue to report production of millimeter-long, VA-SWNT having a mean diameter of  $1.7 \pm$ 0.7 nm, catalyzed by iron on an alumina support. Important finding is that a million of aspect ratio of SWNT arrays can be produced, without water assistance, via combined action of an ascending temperature gradient toward catalyst substrate and low partial pressures of acetylene carbon feedstock. Our results do not only emphasize the role of precursor thermal rearrangement in CNT synthesis, but also offer a practical route to the modulation of such complex phenomena for an ultrahigh-yield growth of narrow VA-SWNT.

# INTRODUCTION

VA-CNTs find use in many applications including MEMS/NEMS, nanofluidic membranes, electrical and gecko brush contact, field emitters and fuel cell electrodes. Each application has a requirement such as height of a CNT forest, uniformity in height, and diameter and wall number of average nanotube comprising the CNT forest. Despite the importance, exact control of VA-CNT structure and quality is yet far-fetching. For the controlled synthesis of VA-CNT, therefore, a detailed understanding of the growth process is crucial.

Studies about VA-CNT growth have mostly focused on action and control of catalyst. Recently, however, there is growing interest in the research community about the role of thermal rearrangement of carbon precursors in the mechanism of nanotube growth. CVD conditions of VA-CNT synthesis usually incorporate high temperatures, sub-atmospheric to atmospheric pressures, carbon source and reducing gases (hydrocarbons and hydrogen), inert carrier gas (argon, helium, nitrogen, etc.) and catalyst. Reactions in the gas phase, or pyrolysis, have been assumed a complete decomposition that yields atomic carbon as a reactant for heterogeneous catalysis for the CNT synthesis. An imbalance between carbon flux and catalytic activity could cause fast catalyst carburation and poisoning, leading to an early termination of the growth. Efforts have been made to overcome this early termination of the growth, such as moisture addition. [2] It is quite recent that researchers have begun to pay attention to detailed reaction products from the gas pyrolysis. Hart and colleagues have studied ethylene pyrolysis identified methylacetylene and vinylacetylene as important carbon intermediates from ethylene pyrolysis. [3] Ma *et al.* [4] have reported that thermal treatment of pure acetylene at temperatures above 600 °C could facilitate CNT growth, attributing the growth enhancement to the production of unsaturated carbon chains such as vinylacetylene. Additional studies have been limited due to the complex nature of multiple thermal reactions and lack of practical methods for systematic modulation of the reactions.

Here, we investigate the effect of gas thermal reactions on the VA-CNT synthesis by imparting thermal gradient to acetylene-based precursors. We will study the growth yield (height of VA-CNT), quality and diameter distribution of as-grown CNTs. Obtained findings will be applied to demonstration of VA-SWNT growth up to one millimeter with maintaining a diameter distribution of  $1.7 \pm 0.7$  nm. Speculative explanation on the role of possible gas reactions responsible for the growth results will be presented.

# EXPERIMENT

We synthesized VA-CNT in a vertical, cold-wall CVD reactor. The precursor gas is introduced to the CVD reactor through a shower head inlet to allow uniform flow field. Flow of the precursor gas impinges on the catalyst substrate 4 centimeters below and heated by a resistive heater from underneath. This gas flow is reminiscent of an impinging jet that allows for uniform boundary layer thickness in the radial direction on a 10-cm-diameter holder for the catalyst substrates. The total flow rate of precursor of 505 sccm was divided as 5 sccm of acetylene, 200 sccm of hydrogen and 300 sccm of argon. Throughout the growth, total pressure of the chamber was maintained at 480 mbar. We used two types of catalyst deposited by an e-beam evaporation technique. A thick bimetallic catalyst of iron (10 nm) and molybdenum (10 nm) atop an alumina layer on a 500-micrometer-thick silicon piece was used to study the role of gas phase reactions in VA-CNT growth. Once an optimal condition for the growth was obtained, we switched to a thin monometallic catalyst of iron 0.2 nm in thickness. All catalyst thicknesses are nominal values from crystal monitor reading of the e-beam evaporator. In the course of CVD, the substrate temperature was detected by an IR pyrometer of which feedback controlled the heater underneath the catalyst substrate. The PID control maintained the IR-detected substrate temperature at the preset point. Upon loading catalyst substrates, vacuum and flow were hold at the set values. Subsequently, thermal ramping at rates of 300 °C/min increased the substrate temperature to a value for reduction and annealing of oxidized catalysts. Upon 10 minutes of hydrogen annealing, acetylene was introduced to the chamber to begin CNT growth. On completion of growth the heater was turned off, and all the gases were switched off except argon for cooling the substrates. Growth time was 15 min and 1 hour for thick and thin catalysts, respectively. The resulting CNTs were analyzed by SEM (Zeiss Ultra 55, 5 keV), high-resolution TEM (Philips CM 12, 100 keV) and Raman spectroscopy (Renishaw, 785-nm excitation).

# RESULTS AND DISCUSSION

The use of a single heater underneath the catalyst substrate can result in an ascending thermal gradient in the direction from gas shower head inlet to catalyst substrate. Approximately 200 °C of difference in gas temperature was measured for the sweep of substrate temperatures between 670 and 775 °C. Outside of this temperature window no VA-CNT was observed, and

sparse network of CNT was not included to our study. Therefore, the range of gas temperatures in this study spans from 470 to 775 °C bracketing the polymerization and slight decomposition constituents of acetylene pyrolysis. Since hydrogen is present all the time in the precursor gas mixture, thermal hydrogenation of acetylene cannot be ignored completely. It is likely that thermal hydrogenation could turn acetylene primarily to ethylene. An important variable in the consideration of thermal rearrangement during acetylene pyrolysis is the total gas dwell time. As the distance between gas inlet and catalyst substrate is relatively short compared with conventional tube furnaces, our total gas residence time is as short as around 6-7 seconds. Such short gas dwell time makes it sensible that precursors may not have enough time to complete the pyrolysis and hydrogenation reactions before reaching catalyst substrates. Hence, it is plausible that thermally rearranged precursors available at the catalyst surface constitute acetylene, hydrogen, ethylene, and various minor products of acetylene polymerization and decomposition.



**Figure 1**. Height and Raman G-to-D ratio of VA-CNT with respect to catalyst temperature. The VA-CNT height is shown by a bar, and the Raman G-to-D ratio by square symbols with a guidance line. Inset: scanning electron micrograph images demonstrating vertical alignment of dense arrays of CNT (scale bar:  $5 \mu m$ ).

The window for VA-CNT growth in terms of the catalyst temperature ranges between 670 and 775 °C agreeing with acetylene-based CVD by other researchers. [5] The height and Raman G-to-D ratio of VA-CNT are shown in Figure 1 as functions of catalyst substrate temperature. The height of VA-CNT shows a bell shape with the largest value at the substrate temperature of 725 °C. The Raman G-to-D ratio is rather constant below 725 °C, jumps to 6.0 at 725 °C and decreases monotonically above 725 °C. The Raman spectra shown in Figure 2 clearly indicate that our VA-CNT have high quality in that the G-to-D ratio is much larger than unity. An interesting finding is an appearance of the Raman radial breathing mode (RBM) at the catalyst temperatures equal to and above 725 °C. The Raman spectroscopic pattern corresponding to these temperatures and marked in blue in Figure 2 shows a list of unique features: a very small D peak; a G<sup>-</sup> shoulder; a sharp G' peak; secondary peaks (iTOLA and M);

and a multiple of RBM peaks. All of these features imply that the nanotubes grown at these temperatures are high-purify CNTs with very small wall numbers. Indeed, transmission electron micrograph (TEM) images confirmed the prediction (Figure 2). In particular, nanotubes grown at these temperatures were a mixture of single-walled and double-walled CNTs. On the other hand, VA-CNT grown at catalyst temperatures lower than 725 °C exhibited a significant Raman D peak, a blunt G' peak, no G<sup>-</sup> shoulder or secondary peaks, and negligible RBM peaks. TEM analysis revealed that nanotubes having these Raman spectroscopic features have wall numbers between 2 and 4. When we compare the VA-CNT growth via substrate heating mode with that from isothermal heating by turning on both substrate and gas-manifold heaters (results not shown), we could only observe few-walled CNTs without a shift of the nanotube pattern.

The discrepancy in VA-CNT growths under the ascending gradient of precursor gas temperature and at the isothermal condition (data not shown) clearly indicates that thermal rearrangement of acetylene-based precursors plays an important role in the VA-CNT synthesis, although the detailed mechanism and the effect of catalyst evolution remain to be elucidated.



**Figure 2**. Raman spectra of VA-CNT grown at various substrate temperatures: (a) 775  $^{\circ}$ C; (b) 750  $^{\circ}$ C; (c) 725  $^{\circ}$ C; (d) 710  $^{\circ}$ C; (e) 670  $^{\circ}$ C. Patterns of (a-c) and (d-e) are distinguished, attributed to the difference in wall number of individual nanotubes verified by TEM analysis. (f, g): TEM images of CNTs of the (a-c) and (d-e) Raman patterns, respectively (scale bar: 10 nm).

The observation of VA-CNT explained above teaches us that an ascending gradient in the acetylene-based, precursor gas temperature can result in a highly efficient growth of VA-SWNT as long as high enough catalyst temperatures are balanced with a certain gas temperature distribution. When we applied the best growth conditions to a thin catalyst of iron (0.2 nm as a crystal monitor value), prone to effective production of SWNT, we obtained much faster growth rate and elongated catalyst lifetime. As a result, a VA-SWNT array grew up to one millimeter from the thin, iron catalyst layer for an hour, as shown in Figure 3. The estimated value of the

initial growth rate exceeded 120 µm/min. The growth kinetics, not shown, was almost linear with respect to the growth time, meaning that a growth of even longer VA-SWNT can be possible. The quality and diameter distribution of as-grown VA-SWNT, shown in Figure 4, supports that our nanotubes are primarily SWNT retaining small diameters between 0.6 nm and 2.0 nm. The result of our moisture-free ultragrowth of VA-SWNT is comparable with other researchers, [5,6] but unique in that it prolongs catalyst lifetime at moderate growth rates via the control of both catalyst temperature and gas thermal gradients. Our successful result producing a long VA-SWNT manifests the impact of thermal rearrangement of the acetylene-based precursor in the entire picture of growth mechanisms.



Figure 3. An SEM image of a millimeter-long VA-SWNT obtained by the ascending, gas thermal gradient CVD applied to a thin, monometallic iron catalyst layer.



**Figure 4**. Diameter distribution and Raman spectrum of the millimeter-long VA-SWNT. The Raman spectrum agrees with the small-wall-number CNT pattern of Figure 2(a-c; f). The SWNT diameter distribution obtained by TEM analysis lies between 1.0 nm and 2.4 nm.

Based on our VA-CNT growth results, we present our speculation on the CNT growth under the ascending gas thermal gradient. Under the ascending gradient, gas temperatures are always lower than the substrate temperature. As mentioned in the previous section, it is likely that the gas components available atop the catalyst surface could be acetylene, hydrogen, ethylene, and various minor products of acetylene polymerization and decomposition. Since no information has existed about any singular behavior of acetylene hydrogenation between 470 °C and 775 °C, we rule out the possibility that the thermal hydrogenation is responsible for the shift in nanotube structure from a few walls to the single wall dominance. Regarding acetylene pyrolysis, Egloff's characterization [1] can be useful. At temperatures lower than 600 °C, polymerization prevails in the acetylene pyrolysis. Decomposition reaction gradually comes into play between 600 °C and 700 °C and become a main reaction above 700 °C. This categorization could in part explain our growth results because <700 °C growths, supposed to contain polymerized pyrolysis product only, resulted in no SWNT whereas >700 °C growths, likely to incorporate decomposed pyrolysis product, led to a shift to the SWNT growth with high growth efficiency. The large amount of decomposed species does not seem to help maintaining the growth efficiency, though. In our growth conditions, gas dwell time is not very long, and so pyrolysis reactions are not likely complete. It is surprising that only a small change in the gas species could produce a distinguished growth results. Therefore, kinetics of carbon supply could be a key factor of efficient growth of VA-SWNT. [5]

#### CONCLUSIONS

We studied the effect of gas thermal gradient in the acetylene-based precursor on the growth of VA-CNT. A shift in the nanotube wall number was observed for thick bimetallic catalyst of iron and molybdenum, at temperatures where gas thermal rearrangement is speculated to involve acetylene decomposition. The moisture-free, ultragrowth of VA-SWNT by applying this finding manifests the important role of thermal rearrangements of precursors in an efficient growth of SWNTs. Further study is necessary to characterize the effect of gas thermal zones and precursor constituents in association with gas dwell time in order to elucidate the impact of kinetics of carbon supply. The approach of controlling gas thermal gradients can be one promising option for the efficient growth of VA-CNT with the nanotube structural control.

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