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Temperature gradient chemical vapor deposition of vertically aligned carbon nanotubes

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ABSTRACT

We present temperature gradient chemical vapor deposition (TG CVD) for producing vertically aligned (VA-) carbon nanotubes (CNTs). Independent heaters on the gas inlet and catalyst substrate sides of a cold-wall, vertical CVD reactor can modulate the gas temperature gradient to lead to controlled thermal histories of acetylene precursor. Our growth results reveal that such a precursor thermal history can play a significant role in the growth and structural features of the resultant VA-CNTs. We find several gas thermal zones particularly important to the VA-CNT growth by evaluating the precursor dwell time in different zones. Thermal treatment of the acetylene precursor at 600–700 °C is found crucial for the synthesis of VA-CNTs. When this thermal zone is conjoined in particular with a zone >700 °C, efficient growths of single-walled and double-walled VA-CNTs can be achieved. These gas thermal zones can contribute to VA-CNT growths by mixing various secondary hydrocarbons with acetylene, corroborated by the results of our reacting flow simulation. Our findings emphasize the influence of gas-phase reactions on the VA-CNT growth and suggest that our TG CVD approach can be practically utilized to modulate complex gas-phase phenomena for the controlled growth of VA-CNTs.

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Carbon

1. Introduction

Most investigations of CNT synthesis by catalytic thermal CVD have assumed that the reactions involved during the initial stages of the CNT growth occur as simple dissociative adsorption of hydrocarbon on the catalyst surface followed by surface and/or bulk diffusion of the reactants [1]. Reactions of the precursor gas, however, should be recognized as an important step in the CNT growth mechanism in case they could produce not only carbon atoms but also various carbon intermediates that can participate in the growth [2–5]. Pyrolysis of feedstock gases during the CVD process is known to generate a complex mixture of volatile organic compounds

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and polycyclic aromatic hydrocarbons [4,5]. Decoupled CVD methods with *in* situ chemical analysis have shown that various secondary hydrocarbons are generated from ethylene and hydrogen (C_2H_4/H_2), among which several alkynes have been proposed as carbon intermediates crucial for the MWCNT growths [4,6,7]. Because of the temperature change of precursor gases between gas preheating and catalytic growth zones, however, it was ambiguous whether this finding is directly applicable to typical CVD setup and conditions. On the other hand, through an interesting approach of controlling the pyrolysis duration of the carbon source (C_2H_4/H_2) in a single isothermal, atmospheric pressure CVD furnace, Yasuda et al. [8] have recently reported that extended

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precursor dwell time could drastically increase the CNT growth rate while maintaining growth lifetime and CNT quality. These findings imply the importance of gas-phase reactions in promoting the CNT growth.

Whereas these recent studies have focused on ethylene as the precursor, there has been lesser work in the study of such phenomena in the acetylene (C₂H₂)-based catalytic CVD [8,9]. Zhong et al. reported that carbon precursors such as ethylene and ethanol are eventually pyrolyzed to acetylene, suggesting the acetylene as a key precursor for CNT growth [10]. Acetylene pyrolysis, however, is known very active at elevated temperatures and can supply not only acetylene itself but also hydrogen, benzene, vinyl acetylene, methane and ethylene depending on CVD parameters such as temperature, pressure, gas dwell time, and feedstock composition [10-14]. Therefore, an influence of acetylene pyrolysis should be taken into account in understanding conventional, acetylene-based CNT growth systems. Recently, Ma et al. have reported that thermal treatment of pure acetylene at >600 °C facilitates CNT growth due to the production of unsaturated carbon chains mainly in the form of vinyl acetylene (C_4H_4) [15]. The detailed influence of acetylene pyrolysis on VA-CNT synthesis, however, remains unanswered due to complex nature and absence of practical methods for the control of multiple gas-phase reactions.

In the present study, we investigate VA-CNT growth under the different thermal rearrangement of precursors in the gas phase via a new approach we name temperature gradient CVD. TG CVD allows us to effectively boost and tailor the gas reactions for the controlled growth of VA-CNT forest. Temperature profiles in the CVD reactor were simulated and experimentally checked to recognize the thermal zones and gas dwell time in each of them responsible for growth rate and nanotube structure (diameter and wall number). Also, acetylene pyrolysis and hydrogenation reactions were calculated on such obtained, gas temperature profiles in order to estimate primary and secondary gas-phase reaction products available atop the catalyst. We present a comparative analysis of growths from various thermal gradients and provide insights into the role of gas-phase reactions in acetylene-based CVD systems.

2. Methods

2.1. Catalyst preparation

Silicon $\langle 100\rangle$ wafers were used as the substrates. Electron beam evaporation (Univex 450, Leybold) was used to prepare the under layer (20 nm Al_2O_3) and catalyst layer (10 nm Fe atop 10 nm Mo) on this substrate. Thickness of each layer is checked by use of atomic force microscopy (AFM) upon metal deposition on a silicon substrate with 20-µm-pitched, lithographic line patterns.

2.2. CVD setup and condition for VA-CNT growth

CNT forests were synthesized in a vertical, cold-wall CVD reactor (Black Magic[™], AIXTRON) (Fig. S1a in Supplementary information). A shower head manifold at the top of the

reaction chamber impinges precursor gases on a graphite sample stage 41 mm below. Dual graphite disc heaters of 10 cm in diameter, one placed at the top shower head and the other underneath the bottom sample stage, can be operated independently to offer three heating modes: bottom heating (BH), top heating (TH), and bottom-top heating (BTH). Infrared pyrommetry was used to measure in situ the substrate temperatures under different heating conditions. The infrared radiation pyrometer we employed has an accuracy of ± 6 °C and can measure the sample stage temperature using the two-wavelength ratio method. Process parameters such as chamber pressure, gas flow rates, and sample stage temperature were software controlled.

Prior to CNT growth, the CVD chamber was cleaned using oxygen plasma at 500 °C for 10 min. Then, the catalyst substrates were loaded on the sample stage, followed by chamber evacuation below 0.2 mbar. The reactor temperature was above 100 °C during loading/unloading to minimize moisture condensation. Under a shower head gas injection of hydrogen (H₂, 200 sccm) and argon (Ar, 300 sccm), the reactor temperature was raised to the growth temperature at a ramp rate of 300 °C/min and maintained for 5 min to induce metal catalyst reduction. The fast ramping is known to defer catalyst sintering, unfavorable for catalytic activity and dense nucleation [8]. In the CNT growth stage, 5 sccm of acetylene (high purity >99.6%, PanGas) was added to the shower head gas flow for 15 min. Upon completion of the growth, the reactor was cooled down in argon. The chamber pressure was maintained constant at 480 mbar throughout the entire growth process (Fig. S1b).

2.3. Characterization of as-grown VA-CNT

The structures of the as-grown CNTs were characterized by scanning electron microscopy (SEM, Zeiss ULTRA 55 at 5 keV) and transmission electron microscopy (TEM, Philips CM 12 at 100 keV). The height of each CNT forest was determined by averaging five or more height measurements taken along the cross section of the chip $(1 \times 1 \text{ cm}^2)$ using SEM. TEM samples were prepared by sonicating a piece of the as-grown CNT forest $(0.5 \times 0.5 \text{ cm}^2)$ in 20 mL of ethanol. Micro Raman spectra were recorded by Renishaw RM 1000 using a 785-nm laser line ($E_L = 1.58 \text{ eV}$) and WiTec CRM 200 using a 532-nm laser line ($E_L = 2.33 \text{ eV}$). All Raman spectra were obtained by irradiating the sample along the axis of CNT alignment through a 100× objective lens.

2.4. Reacting flow simulation of the CVD chamber

First, thermal flow modeling of the CVD chamber was performed using a commercial computational fluid dynamics software (CFD-ACE + v2010) [16] based on the finite volume method that solves the reactor heat transfer on a two-dimensional axisymmetric representation of the reactor, since the reactor has cylindrical symmetry (Fig. S1a). A gas mixture of argon and hydrogen was simulated with temperaturedependent material properties, while acetylene was ignored since the concentration was very small. Monte-Carlo ray tracing was used to calculate the thermal radiation, considering the surface-to-surface radiation heat transfer across various



Fig. 1 – (a) Schematic of three heating modes and their simulated temperature distributions between shower head gas manifold (vertical distance: 0 mm) and catalyst substrate (vertical distance: 41 mm) along the centerline of the CVD reactor. The red color marks a gas thermal zone hotter than the yellow zone, with color gradation indicating continuous temperature variation. (b) Ascending temperature gradients toward the substrate using only the bottom heater: BH. (c) Descending temperature gradients toward the substrate by single use of the top heater: TH. (d) Nearly uniform temperature distributions using both heaters: BTH. Numbers in legends (b–d) next to the heating mode symbol indicate the catalyst substrate temperatures (°C).

boundaries (transparent, semi-transparent and opaque walls). We did not treat the gas mixture as a participating medium in the thermal radiation modeling, which did not affect the obtained temperature profiles. Onset of free convection is unlikely in our geometry and flow and thermal conditions.

Secondly, the temperature profiles obtained above were used to carry out a reacting flow simulation. We employed SPIN [17] to investigate numerically the effect of the heating mode on the gas-phase chemical composition in the experimental setup, by modeling the CVD chamber as a one-dimensional system. The comprehensive reaction kinetic model for ethylene-involving reactions [18] was employed after excluding the oxygen-containing reactions to obtain a reaction mechanism with 45 species participating in 199 reversible reactions. Although SPIN can also account for surface reaction kinetics, heterogeneous reactions were not considered in this study. The code computes the thermodynamic properties, reaction rates and transport coefficients at the mixtureaveraged level using the Chemkin package [19] and transport library [20], respectively. The boundary conditions were as follows: at the shower head, the mole fractions of the reactants were fixed (acetylene: 0.0099, hydrogen: 0.3960, argon: 0.5941) and the bulk axial inlet velocity was obtained from the volumetric flow rate of the incoming mixture at the operating

temperature and pressure (480 mbar) and the flow area of the shower head; as mentioned, the substrate is assumed to be non-reactive and zero flux boundary conditions are imposed on the species.

2.5. Gas dwell time calculation

Gas dwell time, or Δt , is defined as $\Delta y/u$, where y and u are the vertical distance measured from the gas shower head manifold and the local average gas velocity in the y direction, respectively. Since the gas velocity at a location y depends on local temperature and pressure, the local time variable, t, and the gas dwell time can be obtained by:

$$\begin{split} t &= \int_{y=0}^{y} \frac{273Ap}{Q} \frac{1}{T} dy = \frac{273Ap}{Q} \int_{T(y=0)}^{T(y)} \frac{1}{T} \left(\frac{dT}{dy}\right)^{-1} dT \\ &= \frac{273Ap}{Q} \left(\frac{\overline{dT}}{\overline{dy}}\right)^{-1} \int_{T(y=0)}^{T(y)} \frac{1}{T} dT = \frac{273Ap}{Q} \left(\frac{\overline{dT}}{\overline{dy}}\right)^{-1} \ln \frac{T(Y)}{T(0)}, \end{split}$$
(1)

$$\Delta t_{T_1 - T_2} = |t(y_2; T_2) - t(y_1; T_1)| = \frac{273Ap}{Q} \left(\frac{\overline{dT}}{\overline{dy}}\right)^{-1} \ln \frac{T_2}{T_1},$$
(2)

where A is the cross sectional area of the vertical CVD chamber, Q is the total gas volume flow rate at the standard state (273 K, 1 bar), p is the chamber pressure, dT/dy is the gas



Fig. 2 – Plots of (a) average heights of CNT forests for 15-min growths in BH, TH and BTH modes and (b) I_G/I_D ratios derived from the corresponding Raman spectra, with respect to catalyst substrate temperature (T_{sm}). Growth windows for the three heating modes lie in different temperature ranges but overlap in 670–700 °C. Solid and dashed lines in (b) are guidelines for Raman I_G/I_D ratios obtained by use of 785 nm and 532 nm laser excitations, respectively.

temperature gradient, T_1 and T_2 are the bounds of a gas thermal zone of interest, and an upper bar indicates an average value. We approximated the gas temperature gradient to be constant from the linear profiles of gas temperatures obtained in Fig. 1b and c. For the BTH mode where temperature profile is nearly uniform (Fig. 1d), $dT/dy \approx 0$, and the gas dwell time was obtained from direct reading of the simulation data.

3. Results and discussion

3.1. Temperature distribution in a TG CVD chamber

Fig. 1a shows the various heating schemes of the TG CVD chamber employed in this study, and Fig. 1b-d show the simulated temperature distributions of precursor gases for these heating schemes. The substrate temperatures measured in situ by infrared pyrommetry made a good agreement with the simulated values. In the BH mode of the reactor, precursor gases could gain sufficient thermal energy for gas-phase reactions near the catalyst substrate when the set temperature of the substrate (T_{sm}) is high. In the TH mode the gases flow through thermal zones hotter than the catalyst substrate, and the substrate is indirectly heated by thermal radiation from the top heater. Given the identical catalyst temperature, it is likely that gas-phase chemical transformation of the precursors in the TH mode takes place at much higher temperatures than in the BH mode. When both top and bottom heaters are turned on (BTH) at the same temperature, the reactor temperature takes an almost uniform distribution (Fig. 1d). Thus, the gas chemical transformation in the BTH mode could occur in a nearly isothermal process at T_{sm} ,

similar to the conditions inside a conventional, hot wall tube furnace.

3.2. Growth characteristics of VA-CNT grown by TG CVD

Fig. 2 shows the variations in height (by SEM) and quality (by Raman spectroscopy) of VA-CNTs grown by our acetylenebased TG CVD with respect to T_{sm} and for each heating mode. It is clearly seen in Fig. 2a that the range of T_{sm} favorable for VA-CNT growth varies per each heating mode. Whereas the effective T_{sm} for VA-CNT growth was similarly ranged for the BH and BTH modes, agreeing also with previous results obtained by the conventional thermal CVD [1], it became wider and shifted to low $T_{\rm sm}$ for the TH mode: i.e., 670–775 °C in BH and BTH ($\Delta T_{sm} = 105 \,^{\circ}$ C) vs. 535–700 $^{\circ}$ C in TH modes (ΔT_{sm} = 165 °C). Note that we only accounted for the VA-CNT results in Fig. 2, excluding those of sparse networks of CNTs occasionally found outside these temperature windows. Such differently ranged T_{sm} growth windows imply that thermal treatment of the feedstock gases (acetylene and hydrogen) in a TG CVD chamber is likely to generate different types and/ or compositions of pyrolysis products (secondary hydrocarbons) affecting the nucleation and elongation of nanotubes. VA-CNT quality, represented by a Raman G-to-D intensity ratio $(I_G/I_D, Fig. 2b)$, is positively correlated with the height data of the BH and BTH modes whereas it increases monotonically with T_{sm} in the TH mode. Observed disparity in I_G/I_D at two different laser excitations (532 and 785 nm) can stem from the characteristic of Raman spectroscopy of a bulk CNT forest in that a Raman spectrum can mainly reflect the features of those CNTs in resonance with a given laser excitation



Fig. 3 – The enlarged RBM region of the Raman spectra collected from VA-CNT samples grown in (a) BH, (b) TH, and (c) BTH modes. Three different types of RBM distribution were identified and displayed in different colors. Type I with two RBM bands centered at around 231 and 136 cm⁻¹ emerges in high T_{sm} , BH and TH growths (green). Type II with one dominant RBM band at around 231 cm⁻¹ is exclusively obtained for intermediate T_{sm} TH growths (red). Type III with several paired bands appears in BTH growths and low T_{sm} , BH and TH growths (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[21,22]. For example, an outstanding discrepancy between solid (785 nm excitation) and dashed (532 nm excitation) red¹ lines of Fig. 2b observed in the TH mode ($T_{sm} > 550$ °C) may hint a presence of a considerable variety in the CNT structures in the forest. Relatively little difference was seen for CNTs grown in the BH and BTH modes.

Average heights of our CNT forests grown in the BH mode represented a well-known trend [23]: viz. the VA-CNT height increased, peaked and decreased with respect to $T_{\rm sm}$. At $T_{\rm sm}$ of 725 °C in the BH mode, we obtained the tallest CNT forest with the best quality (highest I_G/I_D). This condition is regarded to be an optimum at which the carbon influx to the catalyst layer from gas pyrolysis and/or catalytic dissociation is well balanced with their catalytic conversion into nanotubes. The discrepancy in growth characteristics between BH and BTH modes manifests an influence of the precursor temperature gradients. For example, BTH-mode growth at a T_{sm} of 720 °C resulted in the far lower forest height and quality $(I_{\rm C}/I_{\rm D})$ than the BH-mode growth at the similar $T_{\rm sm}$ (725 °C). We attribute this disparity to a gas thermal condition that rendered the precursor gas in the BTH mode dwell in a narrow band of temperature above 720 °C only, possibly leading to a different conversion pathway from precursors to CNT.

The VA-CNT growth results from the TH configuration showed a drastic difference from the other heating modes. One important observation is that the TH mode enabled VA-CNT growth at temperatures much lower than BH and BTH modes. The TH mode growth began as low as 535 °C and showed a 60 °C wider growth window. It also showed a quite different $T_{\rm sm}$ dependence of VA-CNT height and $I_{\rm G}/I_{\rm D}$ ratio compared to that of the BH and BTH mode: viz. juxtaposition of three domains with the two local maxima at $T_{\rm sm}$ of 565 °C and 640 °C (Fig. 2a). The I_G/I_D ratio curve (red lines of Fig. 2b) is also likely a joint of three domains. These piecewise continuous curves of the TH-mode growth could refer to the distinct aspects of catalyst evolution at different $T_{\rm sm}$ coupled with precursor pyrolysis products from gas thermal zones much hotter than $T_{\rm sm}$.

3.3. Structural features of VA-CNT

Radial breathing mode (RBM) at <300 cm⁻¹ in CNT Raman spectra is inversely proportional to the nanotube diameter and thus considered as a good indicator of structural features of CNTs. We observe three different types of RBM peak distributions (Fig. 3): type I: two primary bands centered around 231 and 136 cm $^{-1}$; type II: one dominant band around 231 cm⁻¹; and type III: several bands composed of pair peaks of which intensities weaken at higher frequencies. The highresolution TEM images (Fig. 4) reveal that VA-CNT showing a type-I RBM distribution consists of mostly single-walled CNT (SWCNT) and double-walled CNT (DWCNT) with a bimodal diameter distribution. The type-II RBM distribution represents a mixture of SWCNT and DWCNT with a negligible addition of triple-walled CNT (TWCNT). Lastly, VA-CNT showing a type-III RBM distribution dominantly contains multi-walled CNT (MWCNT).

Results of Figs. 3 and 4 are summarized as follows. (i) BTH mode growths consistently showed type III (MWCNT) RBM peak distributions except small changes in the ratio of wall number population. (ii) Albeit having the same VA-CNT growth window as BTH mode (Fig. 2), BH-mode growth

¹ For interpretation of color in Fig. 2, the reader is referred to the web version of this article.



Fig. 4 – Diameter and wall number distribution histograms with supporting TEM images of as-grown VA-CNT samples, specifying the characteristics found in RBM profiles (Fig. 3). (a) Type I: a bimodal distribution of small diameter SWCNTs and large diameter SW/DWCNTs (N = 100). (b) Type II: a mixture of SWCNTs and DWCNTs with a negligible portion of TWCNTs (N = 90). (c) Type III: a mixture of DWCNT, TWCNT and MWCNT with no SWCNTs (N = 80).

showed a transition in the Raman RBM distribution from the signature of MWCNT (type III) to that of SW/DWCNT (type I) at T_{sm} around 710–725 °C. As T_{sm} was increased, the VA-CNT composition turned toward smaller wall number and wider, bimodal diameter distribution, attributed to catalyst evolution such as surface migration and Ostwald ripening. (iii) TH-mode growth showed double transitions in RBM profiles, one from type III to type II at $T_{\rm sm}$ around 535–565 °C and the other from type II to type I at 610–640 $^{\circ}$ C. As T_{sm} was elevated beyond 610 °C, CNT diameters slightly broadened in a bimodal way. Such transitions from MWCNT to SW/DWCNT can be attributed to an action of precursor thermal rearrangement and high-T_{sm} catalyst evolution. The bimodality in the SWCNT diameter distribution in particular is related to the catalyst Ostwald ripening [24-26]. From the above observations we found an interesting trend that CNT-type transitions accompanied an appearance of local maxima in the growth height curve (Fig. 2a), which implies the interdependence among the nanotube types, their compositions in VA-CNTs, and growth rates. Mechanistic explanation behind this growth transition behavior may need further investigation.

It is known that the areal density and the degree of alignment of VA-CNTs can be interrelated through a crowding effect among adjacent CNTs [27], where large areal density of CNTs can promote the degree of alignment. Cross-sectional SEM images (Fig. S2) appear to hint that VA-CNTs having maximal density and good alignment might correspond to the tallest and best quality forest obtained at the optimum $T_{\rm sm}$ for each heating mode, although making the unambiguous conclusion should be deferred until more deterministic characterizations such as X-ray scattering [28] could be obtained.

3.4. Important gas thermal zones and gas-phase reaction products

Earlier studies have reported that the unsaturated nature of acetylene enables it to polymerize into gaseous polymers with peak activity between 600 and 700 °C. Above 800 °C, decomposition of acetylene molecules begins to surpass the polymerization until it becomes the single dominant reaction beyond 1000 °C [29–34]. In order to understand the action of precursor thermal rearrangement in light of the aforementioned growth behavior, we focus on distinct gas thermal zones with precursor dwell time, Δt , along with the precursor reaction products available atop the catalysts (Fig. 5). We selected three primary gas thermal zones of interest as: <700 °C, 700–800 °C and >800 °C based on Refs. [29–32]. In Fig. 5 we mark the temperatures at which the transitions of the CNT type took place in dashed vertical lines.

The important roles of these gas thermal zones and resulting pyrolysis/hydrogenation products can be understood by comparing VA-CNTs growth results at similar catalyst temperatures, T_{sm} , yet in different gas heating modes.

First, comparison of BH and BTH mode growths at $T_{\rm sm}$ of 720–725 °C shows that the BH mode is superior in height, quality, and selectivity towards SWCNTs. There is a clear contrast in the gas dwell time composition that $\Delta t_{<700}$ and $\Delta t_{700-800}$ is 6.2 s and 0.7 s for the BH mode and 0.1 s and 6.1 s for the BTH mode, respectively. It suggests that $\Delta t_{<700}$ is important in the VA-CNT growth particularly when $T_{\rm sm}$ or the catalytic activity is high enough: i.e., the growth becomes efficient when high catalytic activity is coupled to the precursor gas species produced in the <700 °C zone. When <700 °C zone does not exist in the gas phase as in the BTH mode



Fig. 5 – Changes of gas dwell time in the individual gas thermal zones in (a) BH, (b) TH, and (c) BTH modes. We selected three gas thermal zones of interest as: <700 °C (black), 700–800 °C (orange), and >800 °C (green). The temperatures at which transition of the CNT type occurs are marked with a black dotted line, and the corresponding types of CNT forest are noted. In (a) and (b), the <700 °C gas thermal zone is further divided into two subsets of <600 °C (line-dotted) and 600–700 °C (dashed). (d) Simulation results of the precursor gas compositions expected to exist primarily atop the catalyst surface. Production of vinyl acetylene (C₄H₄), methane and ethylene in the gas phase hints that acetylene polymerization, decomposition and hydrogenation can go on, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

growth, only short MWCNTs could grow, even at the similar catalytic activity to that of the BH mode. This is also supported by the observation that the TH mode growth at high $T_{\rm sm}$ (>700 °C) without $\Delta t_{<700}$ produced no VA-CNT. From the gas-phase reaction products point of view, excessive thermal rearrangement can generate secondary hydrocarbons too much to yield the VA-CNT growth, while moderate reactions producing byproducts and intermediate species of polymerization but minimal concentrations of decomposition products can be advantageous to the growth (Fig. 5d). Compared with the BH-mode counterpart, our simulations predicted that the BTH-mode growth ($T_{sm} = 720 \,^{\circ}C$) can produce more secondary hydrocarbons, almost equal to the levels of BHmode growth at 760 °C. Fed with plenty of pyrolysis products catalysts at 720 °C do not seem to have been evolved enough to yield SW/DWCNTs, instead of which MWCNTs (type III) can be grown (Fig. 5d).

The second comparison is made between BH and BTH mode at T_{sm} of 670 °C, a moderate catalytic activity. Both cases produced MWCNT (type III) with similar quality (I_G/I_D),

although the BTH mode grew longer VA-CNTs. Since precursor gases flow through the <700 °C zone mostly in both cases, we further decoupled the gas thermal zones into <600 °C and 600–700 °C zones. $\Delta t_{<600}$ and $\Delta t_{600-700}$ is 5.0 s and 2.2 s for the BH mode and 0 s and 6.5 s for the BTH mode. Presumably, precursor thermal treatment in the 600–700 °C zone seems to produce reactants more effective to VA-CNT growth than in the <600 °C zone. Indeed, simulated gas compositions atop the catalysts indicate polymerization goes on a bit more in the BTH mode. Decompositions in both cases were weaker by four or five orders of magnitude than polymerization.

Third, in low- $T_{\rm sm}$ (<725 °C) regime, TH mode enabled VA-CNTs to grow even at much lower $T_{\rm sm}$ of 565–640 °C and unexpectedly produced CNTs of smaller wall numbers compared to the BH- and BTH-mode growths. The major difference in the gas dwell time composition is that TH mode at this $T_{\rm sm}$ incorporates high gas thermal zones (700–800 °C and >800 °C) with the extensive <700 °C zone. The presence of high temperature (>700 °C) zones on top of the <700 °C zone for precursor thermal rearrangement seems to help CNT nucleation on relatively less active catalysts and play a positive role in the SW/DWCNT production. We emphasize that without any change in the catalyst system structural features of VA-CNTs can be altered by tailoring gas dwell time in various thermal zones, attributed to the secondary gas precursors generated during thermal rearrangement or pyrolysis.

Lastly, the stacking order between gas thermal zones with similar dwell times *per se* makes little impact on growth height and nanotube structure. For example, BH mode at $T_{\rm sm}$ of 750 °C and TH mode at 565 °C both contain $\Delta t_{<700}$ of around 5.0–5.3 s and $\Delta t_{700-800}$ of 1.3–1.5 s. Both growths successfully resulted in VA-CNT of SW/DWCNT with minor differences in height (BH > TH) and CNT type (type I for BH vs. type II for TH). The latter discrepancy in the CNT type can be attributed to an accelerated Ostwald ripening at higher $T_{\rm sm}$ (750 °C) in the BH-mode growth. It is remarkable that the impact of different catalytic activities (represented by $\Delta T_{\rm sm}$ of 185 °C) on the resulting VA-CNT structure is surprisingly small when gas dwell time composition is similar.

In general the growth and resultant structure of VA-CNTs are not only influenced by gas phase condition but also by catalyst preparation and evolution such as migration/coalescence, ripening, and subsurface diffusion. We opted for a rather thick, Fe–Mo catalyst system, as it is expected to evolve little in comparison with such a thin metallic system that often undergoes a significant catalyst loss and transformation. Acquisition of catalytic activity and thermal evolution on the substrate during the CNT growth will be presented in a different study.

3.5. Role of important gas thermal zones in the TG CVD of VA-CNT

We now discuss the roles of the identified thermal zones based on the previous findings on the high temperature thermal reactions of acetylene [29-33]. Under Egloff's categorization of pure acetylene pyrolysis, weak and vigorous polymerization of acetylene can occur in the <600 °C and 600-700 °C zones, respectively. In the 700-800 °C zone both polymerization and decomposition are significant, and decomposition becomes exclusive in the >800 °C zone. Thus, under the high pressure CVD condition employed in this study, it is plausible that depending on the thermal constitution of gas dwell time precursors approaching catalyst at a certain T_{sm} are different composition mixtures of polymerized building blocks (C3 and C4 species), decomposition fragments (C1 and C2 species), ethylene, unreacted acetylene and hydrogen, etc. Note that, in the presence of hydrogen, Egloff's acetylene pyrolysis may need to be adjusted to include thermal hydrogenation of acetylene into ethylene, etc. (Fig. 5d) [29,32,34]. Our reacting flow simulation based on the Chemkin library clearly supports the above reasoning. Other than the five species shown in Fig. 5d, more secondary hydrocarbons such as benzene, C4 species (butene, C4H8; butadiene, C4H6; butadiene radical, C4H2), C3 species (propene, C₃H₆; propadiene, C₃H₄; propyne, C₃H₄), C₂ species (ethane, C_2H_6 ; vinyl radical, C_2H_3) and atomic hydrogen (H) were also predicted at the partial pressure ranges between 10⁻¹⁰ and 10^{-6} bar (Figs. S3 and S4). The other hydrocarbons and radicals turned out to be much fewer by orders of magnitude. The results of the reacting flow simulation further points out that acetylene is still the main precursor. Albeit all existing by orders of magnitude smaller in concentration than acetylene, these minor hydrocarbon species can make a drastic contrast in the resultant VA-CNT heights and nanotube structures, which once again puts an emphasis on the role of gas thermal zones in the VA-CNT growth modulation.

According to our experimental observations, such secondary gas species allow reaction pathways for the VA-CNT growth that would otherwise be impossible. Most strikingly, in the low- T_{sm} TH-mode growth it can be inferred that the decomposition species are more reactive than the polymerized species or acetylene itself and therefore could initiate the nucleation of VA-CNT at such a low catalytic activity. We speculate that decomposition fragments could function as a direct source of surface catalytic conversion or as a conversion enhancer. On the other hand, the early growth termination occurring in the high-T_{sm} TH-mode growths, in contrast to the BH-mode growths, implies that too much of these highly reactive decomposition fragments may not be always advantageous for the VA-CNT growth particularly when the catalytic activity cannot catch up the influx of these species, possibly leading to speeded catalyst deactivation.

Finally, good quality VA-CNTs with small wall number can be obtained when a sufficiently high T_{sm} for desirable catalytic activity and heat-induced morphological evolution is combined with an optimum gas phase temperature gradient during the acetylene-based CVD process. The best gas thermal condition for supplying an optimal mixture of polymerization chains, decomposed fragments, and untransformed acetylene for VA-CNT synthesis is found with BH mode at $T_{\rm sm}$ of ca. 725 °C when the ratio between $\Delta t_{600-700}$ and $\Delta t_{>700}$ is around 6. These various carbon intermediates are considered intact at the catalyst surface during CNT nucleation and elongation, and the difference in their interaction energies with a given catalyst surface, i.e., activation energy of adsorption, dissociation and rearrangement [1,7,35,36], would significantly affect the CNT growth as often found in the volcano plots of surface catalysis. We interpret that decomposed products may easily adsorb on the surface but the energy barrier for the formation of the graphitic network would be large, while polymerized products may rather possess an energy barrier for adsorption higher than the decomposed products but instead can be readily added to the carbon chains of growing nanotubes. This interpretation explains very well the effectiveness of having decomposition products and polymerization products at low $T_{\rm sm}$ (less active catalyst) and high $T_{\rm sm}$ (active catalyst), respectively. Moreover, we expect that these polymerized and decomposed products may react in concert with acetylene molecules on the metal catalyst from our observation of a synergistic effect on the highly efficient growth of CNT forests when gas thermal zones for polymerization and decomposition are combined. Hence, the above hypothesis accounting for gas temperature distribution, gas dwell time constitution, and T_{sm}-dependent catalytic activity supports the potential of TG CVD for tailoring VA-CNT growths with controlled structural features.

4. Conclusions

Our new TG CVD approach has enabled a facile modulation of the gas precursor heating condition in a single chamber. Growth results obtained from the TG CVD process revealed that, whereas the substrate temperature primarily determines the catalyst activity and morphological evolution, the thermal history of precursor gases plays an important role in determining the growth characteristics and structural properties of the resulting VA-CNTs. We recognize that thermal treatment of acetylene-based precursor at 600-700 °C is crucial for the synthesis of VA-CNT. Combination of this gas thermal zone with a small portion of a hotter (>700 °C) zone allows for more efficient growth of VA-CNTs having small diameters and wall numbers. Also, given a constant catalytic activity, the nanotube wall number can be tailored by mixing different thermal zones. We propose that at the optimum gas temperature distribution, the acetylene-based carbon feedstock eventually transforms into a mixture of intact acetylene, polymerized and decomposed species, which eventually participate in the CNT conversion concertedly atop the catalyst. We believe that our study provides new insights on the role of thermal rearrangement of acetylene in the synthesis of VA-CNT and establishes a rational route to modulation of complex gas-phase reaction phenomena for the enhanced and controlled growth of VA-CNTs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon. 2012.11.046.

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