# Temperature and Gas Pressure Effects in Vertically Aligned Carbon Nanotube Growth from Fe-Mo Catalyst

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Vertically aligned carbon nanotubes are grown from  $Al_2O_3$ -supported Fe–Mo catalyst in a hot filament chemical vapor deposition apparatus. We compare the effect of carbon nanotube growth on deposition of 0.5 and 1 nm thick Fe catalyst layers before and after deposition of 0.1 and 0.2 nm thick layers of Mo. We observe that the order of deposition plays a role in the height of the nanotube arrays, especially evident during growth at elevated reaction pressures where carbon flux is higher. We investigate the role of temperature and pressure on features of the nanotube arrays such as height, alignment, quality, volumetric density, and diameter distribution for each of the catalyst thicknesses and for each case of Fe/Mo and Mo/Fe. We compare our results to those obtained from carpets grown from pure Fe catalyst, and observe that a Mo cocatalyst can be advantageous regardless of how it is deposited. However, we find that the order of deposition plays a key role in the temperature and pressure range in which optimal single-walled carbon nanotube growth occurs.

## Introduction

The synthesis of densely populated structures of aligned carbon nanotubes,<sup>1,2</sup> and single-walled carbon nanotubes,<sup>3–6</sup> has evolved into a significant topic in carbon nanotube growth due to the direct applications available to such carbon nanotube architectures. Carbon nanotubes (CNT) already have been considered for a range of applications including field emitters,<sup>7</sup> capacitors,<sup>8,9</sup> transistors,<sup>10</sup> and even fully integrated radio devices.<sup>11,12</sup> Although aligned CNT arrays have only recently emerged, their promise in applications has already been realized in a few areas, including adhesive "Gecko" tapes,<sup>13,14</sup> as well as in membranes for use in gas transport and separation.<sup>15,16</sup>

Although there has been vast research performed on the synthesis of nanotubes, as well as vertically aligned nanotubes, there still remain fundamental questions regarding processes occurring during growth which are inherent to understanding growth mechanisms. More often than not, the rigor essential for detailed identification of parameters which are particularly important to consider in nanotube growth are neglected in the effort to achieve conditions which yield the desired diameter distribution and/or quality of nanotubes. This motivates detailed studies which account for differences in growth based on aspects, such as the order of deposition of a binary alloy catalyst, which may typically be neglected. Since growth of carbon nanotubes from a substrate involves a complicated system dominated by catalyst-substrate interactions as well as catalyst surface energy effects, even the most miniscule changes in catalyst preparation and growth conditions can lead to dramatic differences in growth. As a result, we consider one such system-where the catalyst utilized is a Fe-Mo catalyst that has been prepared by the deposition of both the Fe first, followed by the Mo, and in the reverse order as well. The Fe-Mo system has been extensively utilized in the past for carbon nanotube growth,17-29 and these studies have established that a Mo cocatalyst plays a positive role in carbon nanotube growth from Fe-based catalyst. The majority of these studies have utilized powder substrates (Al<sub>2</sub>O<sub>3</sub> or MgO) coated in solution-processed Fe-Mo catalyst particles, resulting in a low-density entangled growth of carbon nanotubes. Recently, Christen et al.<sup>29</sup> have demonstrated that the Fe-Mo catalyst can play a positive role in vertically aligned nanotube growth by utilizing a method of pulsed laser deposition to produce well-established Mo gradients along the chip utilized for growth. This allowed them to establish that a 16:1 ratio of Fe:Mo was optimum for growth with  $C_2H_2$ feedstock in a CVD apparatus, even though reasonably optimal growth was also obtained with 5 Å Fe/1 Å Mo catalyst combinations, which is a ratio utilized for our investigation.

From the standpoint of theoretical investigations, there has been limited progress on a fundamental understanding of catalysis in the growth of aligned carbon nanotubes. Recently, Puretzky<sup>30</sup> and Wood<sup>31</sup> have developed a model for the growth of vertically aligned nanotube arrays. In this model, they support how temperature and carbon flux influence the growth rates and number of walls of the nanotubes in the arrays. In particular, they emphasize the temperature-dependent competition between catalyst poisoning and increased catalytic activity due to higher C mobility as the key to understanding the relationship between growth of single-walled and multiwalled carbon nanotubes. We find this model to be particularly relevant to the work reported by the present authors, and hence explain our results in the framework of this phenomenological model.

The purpose of the study presented here is to utilize e-beam deposited Fe-Mo catalyst for growth in a hot filament CVD

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apparatus, in order to characterize the role of Mo during growth of the vertically aligned nanotube array while keeping the Fe: Mo ratio constant. Furthermore, we will present a study that varies the order of deposition of 5 Å Fe and 1 Å Mo catalyst combinations, as well as 10 Å Fe and 2 Å catalyst combinations, and uses several characterization techniques to monitor the catalyst and resulting nanotubes grown. From these measurements, we are able to characterize the state of the catalyst before and after growth, as well as monitor important aspects of the carpet such as the height, the quality, the overall alignment and order in the array, the diameter distribution of nanotubes, and the volumetric density of carbon nanotubes in the array. Finally, we seek to present a detailed picture of how temperature, pressure, catalyst thickness, and the order of binary catalyst deposition each play a role in the growth of nanotube arrays from Fe-Mo catalyst.

## **Experimental Method**

Aligned carbon nanotube arrays were synthesized in a Hot Filament Chemical Vapor Deposition (HF-CVD) apparatus utilizing C<sub>2</sub>H<sub>2</sub> decomposition over Fe-Mo catalyst having a ratio of Fe:Mo 5:1 in each case. The catalyst support consists of a 10 nm e-beam deposited Al<sub>2</sub>O<sub>3</sub> layer that is coated onto a 0.5 mm thick Si(100) wafer with a native oxide layer. The catalyst is then deposited with Fe of thickness 0.5 and 1 nm, and Mo of thickness 0.1 and 0.2 nm, respectively. Prior to growth, catalyst reduction and nucleation is achieved by exposure of the catalyst to atomic hydrogen created by a resistively heated tungsten hot filament in the presence of H<sub>2</sub>. The hot filament is situated in the middle of the quartz tube furnace, and the sample, which is placed on a quartz boat that is sitting inside a cylindrical graphite holder, is rapidly inserted into the furnace at the base of the hot filament ( $\sim 2-3 \text{ mm away}$ ) while it is on. After 30 s, the hot filament is turned off, and growth takes place for an additional 30 min. This amount of time is chosen because it allows for enough material for characterization of important properties of the carpet, such as the volumetric density. In addition, our previous studies have established that prior to the catalyst poisoning temperature, a 30 min growth period is within the range where the growth rate is invariant with the amount of growth time. The growth gases utilized in this study are H<sub>2</sub> (400 standard cubic centimeters per minute, or sccm), C<sub>2</sub>H<sub>2</sub> (2 sccm), and H<sub>2</sub>O (2 sccm), which are each brought into a 1 in. tube furnace that is otherwise held under vacuum. The H<sub>2</sub>O flow is achieved by bubbling 200 sccm of H<sub>2</sub> through nanopure water under pressure at 25 psi. The gas concentrations and flow rates are adjusted to the optimal growth conditions for single-walled carbon nanotube arrays from pure Fe catalyst of thickness 0.5 nm.<sup>30</sup> The pressure and temperature of the reaction zone during growth were varied between 1.4 and 35 Torr and 500-850 °C, respectively. To vary the pressure in the reaction zone, the velocity of gas flow was adjusted by a manual valve until a desired pressure was achieved. This produces a higher collision rate of gas molecules to the catalyst surface while preserving the relative ratios of each species. Pressures less than 35 Torr were utilized, as higher pressures started to show indications of nonuniformities in growth height due to the reduced diffusion distance of atomic hydrogen created by the hot filament. In all cases, the pressure is adjusted and allowed to settle at the desired value before the catalyst reduction takes place.

Following growth, the as-grown carpets were characterized by polarized Raman spectroscopy and scanning electron microscopy (SEM), and weighed with a precision balance with



**Figure 1.** Temperature dependence of the average height for carpets grown with Fe–Mo catalyst. Note that the order of Fe–Mo deposition is listed, accompanied by the thickness (in Å) of the catalyst layer.

accuracy to 0.1 mg. Carpet height measurements combined with weight and surface area measurements allowed us to calculate the volumetric density of the carpet.

# **Results and Discussion**

To establish the role of the Mo cocatalyst on the growth of vertically aligned carbon nanotube arrays (carpets), we performed a series of experiments with different catalyst thicknesses and a different order of cocatalyst deposition while changing reaction parameters. In recent work, we have observed that two of the most important parameters toward the control of vertically aligned SWNT synthesis are the system pressure and the reaction temperature.<sup>32</sup> As a result, we attempt to understand how a different order of cocatalyst deposition affects growth at different temperatures and pressures in comparison to that of a pure Fe catalyst. In addition, we employ polarized Raman spectroscopy to give a further understanding of the observed effects due to pressure and temperature, and explain the differences based upon the catalyst state prior to growth.

The Role of Temperature. The temperature of the reaction volume in which carbon nanotubes are grown has been found to play a key role in the features of the nanotubes. In previous studies of carbon nanotube growth from Fe-Mo catalyst, temperature has been an important parameter with growth from CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> precursor gases, as this parameter directly affects the diameter distribution of the nanotubes and the growth duration.  $^{18,24-26}$  We emphasize this role of temperature by a measure of the average carpet heights (through SEM) at several different growth temperatures and at the lowest pressure of 1.4 Torr, as shown in Figure 1. This average height measurement, shown in Figure 1, is an average of 10 or more heights taken at equally spaced points along the length of the chip with SEM measurement software. The maximum possible error in this measurement (as discussed in the Supporting Information) is  $\sim 2.4\%$ , indicating that the observed dips and peaks in carpet height graphs are real features. As is the case of growth on pure Fe catalyst<sup>32</sup> (with no Mo cocatalyst), we observe a temperature window in which growth occurs between 500 and 800 °C. For the cases with Mo deposited onto Fe/Al<sub>2</sub>O<sub>3</sub> (Figure 1, red circles and gray diamonds), we find the general carpet height and shape of the curve in Figure 1 to be similar to that of the case with no Mo cocatalyst (green triangles)-with a sharp cutoff in growth near 800 °C and the tallest carpet grown at the temperature immediately below this cutoff. This is not the case with the Fe on Mo/Al<sub>2</sub>O<sub>3</sub> (black squares and blue open circles), as the maximum growth height is shifted toward lower temperatures, resulting in a less dramatic cutoff in carpet height with respect to temperature. In addition, we observe that the 0.1 nm Mo deposited on 0.5 nm Fe gives the widest temperature range for



**Figure 2.** Temperature dependence of volumetric carpet density (in  $mg/cm^3$ ) for (a) carpets grown from catalyst of Fe thickness 0.5 nm and (b) carpets grown from catalyst of Fe thickness 1 nm.

growth. If catalyst poisoning is the reason for the sharp cutoff of growth<sup>31</sup> then we find that this combination of catalyst reduces the poisoning effect and results in the best growth prior to the cutoff.

The effect of temperature is further investigated in Figure 2, where the volumetric density of the carpet is measured as a function of temperature (with pressure of 1.4 Torr). The volumetric density is a combination of average height measurements, surface area measurements, and weight measurements of the nanotubes in the carpet. Errors in this measurement are detailed in tables in the Supporting Information, and are dominated by the error in weight measurement. One consistent trend that is observed in Figure 2 is that the volumetric density tends to decrease as the temperature is increased. In the case where 0.5 nm Fe and 0.1 nm Mo make up the catalyst layer (Figure 2a), the volumetric density decreases by more than a factor of 2 between growth at the lowest temperatures and growth at the temperature that results in the tallest carpet, as suggested in Figure 1. This can be explained by the majority of nanotubes forming more than one wall in the low temperature growth regime. As suggested by the model in refs 30 and 31, growth at low temperatures involves a carbon flux to the catalyst that exceeds the diffusion flux to the SWNT, which results in the formation of more than one wall in the nanotube. This is evident to us by Raman spectra<sup>32</sup> which indicates a significant D band (on the order of the G band intensity), which is usually indicative of the formation of disordered inner wall(s). However, as the temperature is increased, the density lowers to  $\sim$ 50 mg/ cm<sup>3</sup> and the carpets are found to be composed of mostly singlewalled carbon nanotubes, based on Raman spectra and transmission electron microscopy images. Thus, we find that the volumetric density serves as an excellent indicator of the temperature at which the carbon flux from the CVD reactor and the diffusive flux of the catalyst forming the nanotube are balanced. Since each of the carpets are grown from an identical catalyst layer, a constant volumetric density as a function of temperature near the poisoning temperature means that there is no further transition between double-walled carbon nanotubes and single-walled carbon nanotubes in the carpets as the temperature is increased. Interestingly, for the case of Fe deposited on Mo/Al<sub>2</sub>O<sub>3</sub>, we observe that the balance in these two effects occurs at lower temperatures-suggesting a difference in the diffusive properties of the catalyst responsible for nanotube growth in comparison to the case where Mo is deposited after the Fe. However, in both cases of Mo deposition order, the volumetric density prior to catalyst poisoning is nearly the same, suggesting that the SWNT density is not significantly different between the two cases. Although, at lower temperatures, the case of Fe/Mo stands out as being of lower density than the Mo/Fe, suggesting that the Mo/Fe catalyst is more prone to forming more walls when the carbon flux exceeds the diffusive flux of the catalyst. As will be discussed later, this can be due to one of two effects: either (i) the catalyst size in the Fe/Mo case is smaller or (ii) the carbon diffusivity through the catalyst is lower in the Fe/Mo case than the Mo/Fe. Since the SWNT density is observed to be the same in both cases of Fe/Mo and Mo/Fe, this enhances the argument of the latter case involving lower carbon diffusivity.

The volumetric density measurements of nanotubes grown from thicker catalyst layers, shown in Figure 2b, provide a more challenging picture to interpret. In general, since catalyst size directly affects the nanotube diameters,33 thicker catalyst layers will lead to larger catalyst islands on the surface leading to the growth of nanotubes with a larger inner diameter. As a result, there is a mixture of single-walled and multiwalled carbon nanotubes present in the carpet, which leads to a higher volumetric density in this case, although the case of Mo/Fe sustains a volumetric density of  $\sim 50 \text{ mg/cm}^3$  at temperatures above 650 °C, suggesting that this layer may either form larger particles which are more sparsely spaced on the surface, or else this catalyst layer is enriched with SWNTs, despite the thickness of the layer. One interesting comparison to make between the two different catalyst thicknesses is the total carbon activity of a catalyst layer with a specified thickness. For example, Figure 1 indicates that at 700 °C, the carpet from the Mo/Fe (1/5) layer grows  $\sim 2$  times higher than that for the Fe/Mo (2/10) layer, and the density of the Mo/Fe (1/5) layer is  $\sim$ 2.4 times greater than that of the Mo/Fe (2/10) layer. This means that the overall carbon activity for the Mo/Fe (1/5) layer is about 4.4 times that of the thicker layer. Comparing this to the Fe/Mo layers, the height of the Fe/Mo (1/5) carpet is  $\sim$ 3.7 times greater than that of the Fe/Mo (2/10) carpet at 700 °C, but the density is about 1/3 of that of the Fe/Mo (2/10) carpet, leaving an overall carbon activity of  $\sim$ 1.2, which is not significantly different between the two catalyst thicknesses. These are significant differences that result as a consequence of the way the catalyst is deposited, which will be further investigated in following sections by Raman spectroscopy.

Finally, since both the carpet density and carpet height are dependent upon the temperature at which the carpet is grown, one may consider whether there are observable qualitative differences in high magnification images of the bundles in the carpet. Presented in Figure 3 is a typical image of the sideview of a vertically aligned CNT array, grown at 700 °C (top), as well as a higher magnification side-view image at three different temperatures. One can notice an effect producing well-defined folds in the side of the carpet from looking at the top image of the carpet that is further illustrated in high magnification images of the bundles shown below in Figure 3, for different temperatures. We observe that at low temperatures (e.g., 550 °C), the vertical alignment of the carpet is good in the field of view of the image. However, as the temperature is increased to



**Figure 3.** Side-view scanning electron microscopy (SEM) image of a carpet grown from 1 Å Mo deposited on 5 Å Fe at 700 °C. Notice the ridges on the side of the carpet. Also included are high magnification images of the nanotube bundles at three temperatures (550, 700, and 800 °C), each showing the difference between low temperature and high temperature growth on the bundle structure. An arrow indicating the direction of increasing temperature is also included. The white scale bar = 500 nm.

700 °C, the carpet develops bends or folds along the vertical length of the carpet. We interpret this as being due to the mismatch in growth rates between the few wall nanotubes that are growing in the carpet and the single-walled nanotubes which are starting to become prevalent as the temperature is increased. As emphasized in Figure 2, this temperature range is not far from the temperature at which CVD flux and diffusive flux are balanced, leading to SWNT growth. However, as the temperature is increased toward 800 °C, the alignment is now retained in the field of view of the SEM and the folds no longer are present. It should be noted that these folds were also observed in the case of Fe/Mo, even though this effect happened at lower temperatures (600-650 °C), consistent with Figure 2. In addition, having such a diverse population of nanotubes leading to folds in the carpet will significantly alter the transport properties, leading to unexpectedly low transport in what appears to be an aligned nanotube array.

The Role of Reaction Pressure. One of the key features of growth of aligned nanotube arrays, particularly with  $C_2H_2$  carbon source, is the pressure of the growth gas in the reaction zone,

or equivalently, the rate of  $C_2H_2$  collisions to the catalyst. To increase the reaction pressure, the flow velocity of gases in the reactor are adjusted which means that the number of collisions between gas molecules and the catalyst surface is increased proportionally, even though the total ratio of gases ( $C_2H_2$ : $H_2O$ :  $H_2$ ) is kept fixed.  $C_2H_2$  is known for its ability to decompose in a single collision reaction-leaving it as the most reactive of all growth gases for catalytic carbon nanotube growth.<sup>5</sup> The use of gas mixtures involving  $C_2H_2$  in growth under atmospheric or high pressures near atmosphere typically results in the growth of large diameter multiwalled carbon nanotubes in the array, due to a higher number of collisions between C2H2 molecules and the catalyst. To control the carbon source so that we can grow single-walled carbon nanotube arrays from C<sub>2</sub>H<sub>2</sub>, the partial pressure of C<sub>2</sub>H<sub>2</sub> in the reaction zone is kept low with a large background pressure of a gas such as H<sub>2</sub>, while the flow rate is kept high (flow rate between 5 and 8 m/s). Therefore, it is of interest to us to understand how Fe-Mo catalyst responds to growth with  $C_2H_2$  at higher pressures than the typical 1.4 Torr. To perform this, we used a pin valve to regulate the flow



**Figure 4.** Pressure dependence of (a) height of carpets grown from Fe–Mo catalyst (in microns) at 750 °C, (b) height of carpets grown from Fe–Mo catalyst at 600 °C, (c) volumetric density (in mg/cm<sup>3</sup>) for carpets grown from Fe–Mo catalyst layers at 750 °C, and (d) areal density (in mg/cm<sup>2</sup>) for carpets grown from Fe–Mo catalyst layers at 750 °C. Catalyst layer thicknesses are labeled in units of Angstroms.

rate and hence the reaction zone pressure. The pressure was varied between 1.4 and 35 Torr, which allowed us to characterize effects of increasing pressure, and hence increasing the flux of gas to the surface. During this process, the flow rate of  $C_2H_2$ was kept at 2 sccm, which allows one to relate the increase in pressure to the increase in carbon flux due to more collisions between carbonaceous gases and the catalyst surface. As shown in Figure 4a, the carpet height for the cases of Mo deposited on Fe (at both thicknesses) is relatively linear with respect to pressure. This matches the behavior we observed for 0.5 nm of pure Fe catalyst.<sup>32</sup> However, for the case of 0.5 nm Fe on 0.1 nm Mo, the curve follows the same trend as the Mo/Fe curve until 15 Torr, where it starts to deviate toward lower growth rates than Mo/Fe. In addition, the growth rate of the thick Fe/ Mo catalyst is very low and generally invariant with increasing pressure. This raises an interesting difference between Fe/Mo and Mo/Fe that is better illustrated in Figure 4b. In this case, instead of growth at 750 °C at high pressures, the growth is carried out for Fe/Mo and Mo/Fe (both 0.1 and 0.5 nm Mo, Fe, respectively) at 600 °C instead. It is important to note that the difference between the two cases is that the CVD flux and diffusion flux are balanced at 750 °C, whereas at 600 °C, the CVD flux is already significantly higher than the diffusion flux-leading to few-wall nanotubes growing at low temperatures. In Figure 4b, it is evident that the Mo/Fe case increases in height until  $\sim 8$  Torr, where the carpet height at higher pressures stays relatively constant with increasing pressure, and hence carbon flux. In the case of Fe/Mo, the carpet height actually decreases at higher pressures until absolutely no growth is achieved at 35 Torr. As emphasized by the model in ref 31, the number of walls that a nanotube can grow is limited by the size of the catalyst particle. In the case of low temperature growth at high pressures, we are saturating the catalyst with carbon at a temperature in which diffusivity through the catalyst is already low. The Mo/Fe case stands out as being immune to the poisoning in this regime, as the growth rate is invariant with respect to pressure. However, in the case of Fe/Mo at 600 °C, the poisoning occurs at pressures above 8 Torr, suggesting that the difference between these two catalyst layers is that one is good at resisting the poisoning effect, and one is easily poisoned. Drawing back to the discussion following from Figure 2, this effect could be either due to the fact that the Fe/Mo catalyst is smaller in size—meaning that it would be easier for the particle to precipitate a carbon shell and become inactive—or else it just has a lower diffusivity of C, which allows it to supersaturate and die before sprouting a nanotube. This suggests that the best choice for a robust catalyst that can remain active in a carbonrich growth environment is the Mo/Fe.

Once again, it is interesting to consider how the volumetric density changes with respect to the increasing pressure. First of all, the carpets grown from the thick Fe/Mo catalyst were too short to estimate the average volumetric density within reasonable error. As a result, the other three cases at 750 °C are plotted in Figure 4c. One can observe that the trend in density with respect to pressure is consistent in all three cases—as we observe that the density decreases with increasing pressure. On the other hand, the areal density that can be calculated from panels a and c of Figure 4 indicates a slightly different trend, as shown in Figure 4d. In particular, there is a rapid increase in the areal density that is associated with increasing the reaction pressure, which is expected from the growth of larger diameter SWNTs and MWNTs. However, in the case of Fe/Mo (1/5), the areal density begins to decrease as the pressure is further increased, indicating the same sensitivity to a greater carbon flux than the Mo/Fe catalyst. This is characteristic of catalyst deactivation for the Fe/Mo catalyst that is consistent with the results observed in Figure 4b. This effect will be discussed in the next section in further detail in comparison to results from polarized Raman spectroscopy.

**Polarized Raman Spectroscopy.** To understand features of the nanotubes in the carpets themselves, it is important to utilize a characterization technique to better understand the properties of the nanotubes that are growing. Polarized Raman spectroscopy<sup>34,35</sup> is an important technique to understand properties of aligned nanotubes, including the quality, the alignment, and a crude estimate of the diameter distribution of a substantial amount of



**Figure 5.** D and G bands in polarized Raman spectroscopy for (A) the case where the electric field of the light is parallel to the alignment in the carpet and (B) the case where the electric field of the light is perpendicular to the alignment in the carpet. Spectra are shown for each case of Fe–Mo combinations at 1.4 Torr reaction pressure, with thicknesses labeled in units of Å.

TABLE 1: Tabulated Values from Polarized Raman Spectroscopy Data with 633 nm Laser Excitations on Carpets Grown from Each Case of Fe–Mo Catalyst Thickness and Deposition Order, at 750° C Growth Temperature and 1.4 Torr Reaction Zone Pressure<sup>a</sup>

	Fe (5 Å)	Fe/Mo (5/1)	Mo/Fe (1/5)	Fe (10 Å)	Fe/Mo (10/2)	Mo/Fe (2/10)
G/D (parallel)	6.94	15.47	4.07	3.45	4.78	5.3
G/D (perp)	6.42	12.35	4.41	4.66	5.66	6.03
G <sub>parall</sub> /G <sub>perp</sub>	2.92	2.49	1.29	2.32	3.07	3.36

<sup>*a*</sup> Listed are the G/D ratio, indicative of nanotube quality in both cases where the incident light polarization is parallel and perpendicular to the nanotube alignment, and the ratio of G band intensity between the parallel and perpendicular configurations, which is indicative of the overall nanotube alignment.

nanotubes present in the sample. We utilized both 633 and 785 nm laser excitations to further elaborate on the results presented in Figures 1-4.

Figure 5 shows the D and G bands of Raman spectra with the laser electric field polarization both (a) parallel and (b) perpendicular to the alignment of the carpet, as the laser beam was focused on the side of the carpet (laser beam direction normal to carpet side). Raman spectra were obtained for each of the carpets grown under the same conditions at 750 °C at low pressure. The results for the G/D ratios are also shown in Table 1, after subtraction of the background. As can be observed, the G/D ratio for the case of Fe/Mo catalyst (at 750 °C) at 0.5/ 0.1 nm thicknesses emphasizes this is of the highest quality (in red), followed by pure Fe at 0.5 nm (in black), and then followed by the thicker Fe/Mo (in orange). However, the caveat to this is that 750 °C is not the temperature that produces the tallest carpet for Mo/Fe, as emphasized by Figure 1. In fact, at 800 °C, the quality of the thin catalyst Mo/Fe carpet is comparable to that of Fe/Mo (G/D  $\sim$  12). In each of the cases, at temperatures below 650 °C, the G/D ratio was near or less than



**Figure 6.** D and G bands from Raman Spectroscopy for carpets grown at four different reaction zone pressures ranging from 1.4 to 25 Torr, for the cases of (a) 1 Å Mo/5 Å Fe and (b) 5 Å Fe/1 Å Mo. The growth temperature in both cases is 750 °C.

1, indicating low-quality multiwalls. That is consistent with the high average densities associated with low temperature growth in Figure 2. Also, it should be noted that the thicker catalyst layers resulted always in a lower G/D ratio, and an overall lowerquality nanotube array. One possibility for this effect is the presence of larger diameter multiwalled carbon nanotubes in the arrays. We have typically observed that multiwalls tend to be more disordered than SWNTs, leading to a low G/D when the sample does not consist primarily of SWNTs.

This further leads us to consider how the G/D ratio changes with increasing gas pressure in the reaction zone, as illustrated in Figure 6 for the two cases of Mo/Fe and Fe/Mo with the 0.5 nm Fe and 0.1 nm Mo thickness. As is evident in Figure 6, the quality of nanotubes in the arrays decreases as the pressure is increased. For the case of Mo/Fe, the decrease in G/D is gradual until 25 Torr, where the G/D ratio decreases dramatically (i.e., the D peak becomes nearly equal to the G peak). This is not the case for Fe/Mo, as the G/D ratio decreases dramatically between 1.4 and 8 Torr, indicating the sensitivity of the catalyst to the gas pressure during growth with this catalyst combination, which has already been established in Figure 4. It should also be noted that in the RBM spectra of the carpet grown at 25 Torr for the Mo/Fe, and the carpets grown above 1.4 Torr for Fe/Mo, the G band broadens, which indicates the presence of larger diameter multiwalled carbon nanotubes. To better understand the results of Raman spectroscopy, we performed high resolution transmission electron microscopy (HR-TEM) of dispersed SWNTs from each of the carpets grown at 1.4 and 25 Torr, two of which are presented in Figure 7. These images are representative of (a) a high-quality SWNT carpet and (b) a carpet grown at higher pressure (25 Torr) from a thin Fe/Mo (5/1) catalyst layer. We observe in general that the growth at low pressure involves the growth of mostly SWNTs. There are typically less few-wall nanotubes (a crude estimate of 5-10%) in the case of Mo/Fe carpets grown at 1.4 Torr (750 °C), which seems to correspond to the slightly lower G/D ratio. However, at higher pressures, there are significantly more multiwalled



Figure 7. Transmission electron microscope (TEM) images of carbon nanotubes that are representative of what is observed for (a) high-quality SWNT growth conditions at 1.4 Torr and (b) growth at higher pressure (25 Torr) for the thin Fe/Mo catalyst layer.



**Figure 8.** Radial breathing modes (RBM) from polarized Raman spectroscopy for (a) carpets grown from Fe/Mo with the incident laser polarization parallel to the nanotube alignment and (b) perpendicular to the nanotube alignment. (c) RBMs for carpets grown from Mo/Fe catalyst with incident laser polarization parallel to the nanotube alignment and (d) perpendicular to the nanotube alignment. Note that in all cases, parallel and perpendicular symbols denote cases where incident laser light polarization is parallel or perpendicular to the nanotube alignment.

carbon nanotubes, and larger diameter SWNTs. For carpets grown at high pressures (25 Torr), multiwalls with up to 10 outer walls are observed in the carpets in rare cases, even though the majority of the nanotubes ( $\sim$ 99%) have 3 or less walls. However, at the lowest pressures, we observe mostly singlewalled carbon nanotubes of a wide distribution of diametersranging between 0.7 and 8 nm, as is evident from the combination of both small diameter and larger diameter (2-4 nm) SWNTs illustrated in Figure 7a. In any case, we can relate the low G/D ratio in the high pressure carpets to the formation of larger diameter few-wall and multiwalled carbon nanotubes. Interestingly, considering this is based on volumetric densities associated with high pressure growth (as shown in Figure 4b), the density actually seems to decrease as the pressure is increased. So, to investigate this, we need to answer the following question: Why does the formation of multi-walled carbon nanotubes at high pressure lead to lower carpet densities?

We illuminate the answer to this question with radial breathing modes (RBM) from polarized Raman spectroscopy with a 633 nm laser, shown in Figure 8. The nature of RBM's in angular dependent polarized Raman spectra of carbon nanotubes is still not fully understood, and is complicated due to the imperfect alignment of the nanotubes in the arrays. Polarized Raman spectroscopy on individual nanotubes has shown that the intensity of the G band decreases to nearly zero as the electric field polarization becomes normal to the long axis of the nanotube.<sup>34</sup> Several studies have also established that RBM frequencies disappear when the polarization of the laser is aligned normal to the direction of nanotube alignment.<sup>34–36</sup> Recently, Maruyama et al.<sup>37</sup> have suggested that there are  $\Delta \mu$  $=\pm 1$  electronic excitations that result in different RBM modes present in the perpendicular configuration. On the basis of an extensive set of spectra that will be published elsewhere, we believe that the interpretation of RBM spectra in angularly

polarized Raman studies for our carpets is simply due to large bundles of nanotubes in the direction normal to the plane of the growth substrate, and individual nanotubes and smaller bundles which undergo significant interbundle wandering. Recent small angle neutron scattering experiments have also shown that two components in the spectra can be attributed to the alignment in carpets: (i) a sharp Lorentzian that describes "straight" nanotubes aligned vertically to the substrate and (ii) a broad Gaussian that describes wandering nanotubes between the straight ones.<sup>39</sup> As measured by SEM, the width of nanotube bundles range between 10 and 50 nm in our carpets, which suggests that our material is significantly different than that synthesized in refs 37 and 38. However, along with this bundling and individual tubes wandering, there is also a more complicated structure of the nanotubes in the carpets. First of all, they are ultralong compared to nanotubes grown by other methods such as HIPCO, and second, they have bends and kinks along their length, which complicates the process of Raman scattering even further. Differences in RBMs in the case of parallel and perpendicularly polarized light are shown in Figure 8. In the case where the laser light polarization is parallel to the nanotube alignment, the transitions associated with RBMs of different diameter SWNTs are broadened from that of what is expected from an individual SWNT. This is due to the fact that the SWNTs that are observed in Raman spectra are highly bundled. However, when the laser polarization is rotated by 90°, one observes that the large broad RBM peaks often split into multiple peaks with narrow line widths. In addition, at low frequencies corresponding to the RBM modes for large diameter SWNTs (between 1 and 2 nm), we see that the RBM peaks are significantly more resolved when the laser light polarization is 90° from the direction of overall nanotube alignment. We interpret this as due to individual tubes and small bundles wandering between the large bundles, which probably occur to relieve the stress between or within bundles composed of nanotubes of different diameters growing at different rates. To support our interpretation, we performed polarized Raman spectroscopy on a fiber composed of aligned HIPCO nanotubes where interbundle wandering does not occur. We observed that the intensity of the D and G bands, as well as the RBMs, decreases as the light polarization is rotated 90° from the nanotube alignment direction, similar to that reported by Fagan et al.<sup>36</sup> It should be noted here that in reference to our previous discussion of TEM images, the RBMs observed do not represent the full spectrum of nanotube diameters present in the carpets, but rather represent the minority population of SWNT diameters. This is consistent with experimentally mapped Kataura plots for similar SWNT material.<sup>40</sup> However, in cases where the catalyst size dependence could play a role in poisoning, this effect would be most apparent among the smallest diameter particles, which are being monitored through the RBMs of the smaller diameter nanotubes grown from them.

Following previous discussion, the RBMs of carpets grown at increasing reaction zone pressures (the pressure in the region where the decomposition reaction takes place to form the carpet) can explain the decrease in density of the carpet as the pressure is increased. As is evident from panels a and b of Figure 8 for Fe/Mo carpets at 750 °C, the RBM modes for the smallest nanotube diameters tend to disappear as the pressure is increased. This is especially evident in the perpendicular RBM spectra, as the spectra at 25 Torr (and 35 Torr, which is not shown) have no evident RBMs. In the parallel spectra, one breathing mode persists, which could potentially be an inner tube for a multiwalled carbon nanotube. This seems to generally



**Figure 9.** X-ray photoelectron spectroscopy (XPS) of Fe–Mo catalyst before and after growth. (a) XPS spectra for 0.1 nm Mo layer and (b) XPS spectra for 0.5 nm Fe layer both before and after growth. The dotted line in panel a is to guide the reader's eye in the core-level shift that is apparent in the two spectra.

be the case for the Mo/Fe catalyst grown carpet shown in Figure 8c,d as well, except the dramatic decrease in the smaller diameter SWNTs is not apparent until 25 Torr—which is consistent with the trend of the G and D bands presented in Figure 6 for the Mo/Fe catalyst.

On the basis of these results from Raman spectroscopy, we can establish that catalyst death is occurring for the smallest catalyst as the carbon flux is increasing. This is expected based on the fact that the smallest catalyst will have the largest surface/ volume ratio, and hence is more prone to poisoning with high carbon flux. When the flux is too high, it may not be possible for the catalyst to form an additional wall, resulting in a carbon flux that overwhelms the diffusive flux. This process probably results in the formation of an outer carbon shell or else an ironcarbide compound, which kills catalytic activity altogether. This means that only the largest catalyst can continue to grow nanotubes, leading to the growth of large diameter single-walled carbon nanotubes, as well as multiwalled carbon nanotubes (diameters less than 10 nm). Interestingly, the deposition of Mo after the Fe seems to preserve the smaller catalyst at higher pressures, leading to more SWNT RBMs present in the spectra shown in Figure 8. This emphasizes that, depending on how the catalyst is deposited, the lifetime of small diameter catalysts growing SWNTs can be enhanced. This will be discussed in the next section.

**Catalyst State before and after Growth.** In the process of understanding the observations made thus far, it is important to have a way to monitor the catalyst prior to and after growth. To do this, we performed X-ray photoelectron spectroscopy (XPS) to look at differences in the state of the catalyst before growth, and after growth. The results from XPS measurements are shown in Figure 9 for 0.5 nm Fe and 0.1 nm Mo catalyst. In each case, the spectra are relative to a charge reference of adventitious carbon with a core level binding energy of 285.0 eV. For the Mo spectra, shown in Figure 9a, the core-level peak position for the  $3d_{3/2}$  Mo peak is 235.8 and 235.6 eV for Fe/Mo and Mo/Fe, respectively. In addition, the peak position

for the 3d<sub>5/2</sub> peak corresponds to 232.6 and 232.4 eV for Fe/ Mo and Mo/Fe, respectively. A consistent splitting of the Mo peaks of  $\sim$ 3.2 eV is observed, which is in agreement with the known value of 3.15 eV. These values correspond best to a MoO<sub>3</sub> compound. Interestingly, there is a slight shift in the core level binding energy between the cases when the Mo is deposited before and after the Fe. Although a shift of 0.2 eV is not significant enough to suggest a difference in the oxide state of the Mo, similar core-level shifts have been observed in previous studies which document the core-level energies of surface atoms. In fact, it is well-known in the literature that surface states of metals will result in core-level binding energies at slightly lower energies than those of bulk-like states.<sup>41,42</sup> The typical shift is on the order of 0.1-0.4 eV. A closer inspection of a Gaussian fit to the Mo spectra for the Fe/Mo catalyst also includes a shoulder present at 232.4 and 235.6 eV, which is in general agreement with this idea. This interpretation also follows from the difference in surface energies at room temperature between Fe and Mo.43 The surface energy of Mo is 2.877 J/m<sup>2</sup> compared to 2.939 J/m<sup>2</sup> for Fe, predicting Mo that is on the surface of Fe to be stable. This idea will be further analyzed in the next section, but suggests an interesting possibility for the role of Mo based on the order of deposition.

In addition to the catalyst state before growth, Figure 9a also shows Mo spectra after the carpet has been grown and peeled from the substrate with an adhesive. The Mo core-level peaks are no longer evident, which could be due to the fact that either (i) the Mo<sub>x</sub>O<sub>y</sub> peaks have broadened due to the Mo only having an air exposure of ~15 min between the time in which the carpet was grown and the time in which the chip was placed under high vacuum in the spectrometer or (ii) the Mo no longer is on the substrate due to either being removed along with the carpet or other processes such as sublimation of the oxide prior to growth.

Figure 9b presents XPS spectra of Fe for the three cases shown in part a. The key feature of this spectra is the binding energy peak located at 707.6 eV that is too high in binding energy to correspond to metallic Fe, but too low to correspond to FeO. We suggest that this may be due to the formation of a carbide state of Fe. XPS measurements of  $Fe_3C^{44}$  indicates a peak position of 708.1 eV, which is near what is observed in this experiment. Since other carbide states of Fe exist besides  $Fe_3C$ , this could correspond to less carbon-rich Fe carbide. It is highly likely that the carbide phase forms after the sample is removed from the reactor and it cools in the presence of carbonaceous gas flow, but it highlights the possibility of carbide formation in this system as a mechanism for catalyst poisoning and eventual death.

To support our interpretation of the catalyst state before and after growth, we have performed simulations utilizing the BFS method for alloys<sup>45</sup> combined with the Metropolis Monte Carlo method to investigate the lowest energy configuration at different temperatures for a catalyst having a 1:5 ratio of Mo to Fe. A detailed analysis of these simulations will be published elsewhere.<sup>46</sup> However, we find that a Mo core that is embedded in a larger Fe particle is highly metastable—driven by the significant increase in strain energy required for a Mo atom to exchange from the core of Mo atoms through sites involving full Fe coordination and eventually to the outside of the catalyst. However, a catalyst with surface segregated Mo is always of lower energy than the same catalyst with a Mo core. This means that the order of deposition (in which case, the Fe and Mo are elemental) plays a role in putting the catalyst in a state that

will ultimately affect how the catalyst reacts to the carbon source, and hence grows carbon nanotubes.

Strengths and Weaknesses of Fe/Mo and Mo/Fe. One primary aspect of studying how the order of deposition affects the growth of carbon nanotubes is to understand which case stands out as being the best in supporting growth. However, it should be noted that "best" is a relative term and is completely defined by the carbon nanotubes which are sought. For example, a catalyst that can easily be deactivated under a high carbon flux may not be acceptable for growth under atmospheric conditions with  $C_2H_2$ .

In our observations, we find that the Mo/Fe case is the best at resisting catalyst death in the presence of a large carbon flux. In the picture emerging thus far, this can be attributed to the state of the catalyst, proposed to be Fe with surface segregated Mo atoms. If this was the case, the Mo would reside on the outer part of the catalyst and most likely form a Mo carbide. This is emphasized by  $\Delta G$  for the formation of a Mo carbide,<sup>47</sup> which is negative ( $\Delta G < -7$  kcal/mol) for each observed Mo<sub>x</sub>C<sub>y</sub> phase present in the bulk phase diagram (MoC, Mo<sub>2</sub>C, and Mo<sub>3</sub>C<sub>2</sub>). This is compared to Fe<sub>3</sub>C, whose  $\Delta G$  only becomes slightly negative near 800 °C. This means that one possible role of the Mo in this combination is to form a surface carbide that moderates the flux of carbon to the Fe itself. Mo itself is catalytic in the presence of propene,48 which also does not rule out its aid in C<sub>2</sub>H<sub>2</sub> decomposition. However, growth rates achieved with Mo/Fe are never as high as those achieved with just a 0.5 nm thick layer of Fe,<sup>32</sup> suggesting that surface bound Mo plays some role in regulating the C to the nanotube. This means that the benefit of this catalyst combination (Mo/Fe) is its resistance to catalyst death and growth termination amidst high carbon flux, and the ability of the small diameter Mo/Fe catalyst to stay active for growth at the highest pressures (hence, highest  $C_2H_2$  collision rates) studied in this work.

On the other hand, the Fe/Mo catalyst is a bit different. On the basis of the picture emerging so far, this catalyst involves the formation of Mo islands which then act as nucleation sites for Fe atoms in the next deposition step. This results in metastable Mo cores which form on the inside of the catalyst. After reduction, the Mo cores are now subject to carbide formation in the framework of a carbon bulk diffusion argument.<sup>30,31</sup> The result of this is now that the overall C solubility of neighboring Fe atoms increases and catalyst poisoning occurs at lower temperatures, according to Figures 1 and 2. Since the Fe surface is exposed to C2H2 collisions, decomposition will take place similar to that of pure Fe catalyst, except now the inner Mo core determines the C diffusion rate, and hence growth rate of carbon nanotubes. In the case where the Mo core exists in a carbide phase, it could also potentially be viewed as a nucleation site for the formation of a Fe-C phase, which would result in an overall lower poisoning temperature for carpet growth. This means that the overall strength of this catalyst combination is the growth of SWNTs at temperatures lower than those of the Mo/Fe and ultimately pure Fe, even though the primary weakness of the catalyst is its sensitivity to carbon flux-which more easily solubilizes carbon and results in catalyst death. It should be noted that this system shows some similarity to the Co-Mo system, where there has been found to be a complex interaction between the Co and Mo to form catalysts which result in size-selective SWNT growth.<sup>49,50</sup> In fact, the selectivity of this Co-Mo system is found after the MoO<sub>x</sub> converts to a MoC, breaking the interaction between the Co-Mo and the Co catalytic particle, and stabilizing the Co particle for SWNT growth.<sup>50</sup> Although

the Co-Mo catalyst is formed in a different way than the Fe-Mo catalyst presented here, it bears some similarities in the sense that mixed Co-Mo bonds are not beneficial to SWNT growth. This is compared to the case where Mo remains in the middle of the Fe cluster leaving mixed Mo-Fe bonds that result in enhanced growth termination at higher carbon flux. However, growth with a Co-Mo catalyst is most efficient when the MoC is supporting a Co catalytic center-resulting in the size-selective SWNT growth for which this catalyst combination is wellknown.

It should also be noted that an alternate explanation for the results presented here is that the MoO3 goes through sublimation prior to growth.<sup>51</sup> It is known that sublimation of bulk MoO<sub>3</sub> begins to occur at around 650 °C, which is lower than the furnace temperature utilized during optimum growth in the studies presented here. We believe that this is not the case due to two specific reasons. First of all, the hot filament CVD method ensures rapid reduction of all oxides prior to temperatures at which sublimation has been found to occur. This means that elemental Fe-Mo bonds exist which are not conducive to Mo sublimation. Second, XPS data have been taken after growth of a carpet (and peeling) at 600 °C, which indicates the same lack of identifiable Mo peaks as are observed in Figure 9a.

Finally, we emphasize that the order of catalyst deposition is an important subtlety to consider when designing catalyst and interpreting growth of carbon nanotubes from these catalyst particles. This is especially important in the case of binary and more complicated catalyst systems, as these will be most susceptible toward structural differences based upon how the catalyst is prepared. As we show in this study, the popular Fe-Mo catalyst combination is no exception-resulting in markedly different carpet growth based upon the order of catalyst deposition.

### Conclusions

We present results from the growth of vertically aligned CNT arrays from catalyst layers composed of 0.5/1 nm of Fe and 0.1/0.2 nm of Mo, respectively. We observe significant differences in measured carpet growth depending on whether Fe is deposited before or after Mo. Measurements of the average carpet height and volumetric density of the carpets suggest that growth from Mo/Fe resembles that of a pure Fe catalyst layer, whereas growth from Fe/Mo catalyst layers results in a temperature range for optimal carpet growth (in addition to highquality SWNT growth and poisoning) that is shifted toward lower temperatures. Utilizing XPS data and computer simulations, we suggest that the difference in surface energy between Mo and Fe plays a role in keeping the Mo surface segregated when it is deposited after the Fe. However, when the Mo is deposited first, it forms Mo cores which significantly alter the catalytic activity of the resulting Fe-Mo catalyst. As is shown by Raman spectroscopy, having surface segregated Mo improves the ability of the smaller catalyst particles to stay active among conditions of high carbon flux with  $C_2H_2$ , a result that we emphasize is due to the formation of a Mo carbide on the surface acting to regulate the carbon flux to the catalyst. However, having surface-bound Mo cores (Mo deposited first) results in SWNT growth at lower temperatures and a greater sensitivity of the catalyst to increased carbon flux. This work emphasizes how what may be perceived as an insignificant detail (i.e., the order of catalyst deposition) during catalyst preparation can result in being a significant factor influencing the growth of aligned nanotube arrays.

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Supporting Information Available: Error analysis of carpet height and volumetric density measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

### **References and Notes**

(1) Fan, S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M.; Dai, H. Science 1999, 283, 512

(2) Cassell, A. M.; Verma, S.; Delzeit, L.; Meyyappan, M.; Han, J. Langmuir 2001, 17, 260.

(3) Murakami, Y.; Chiashi, S.; Miyauchi, Y.; Minghui, H.; Ogura, M.; Okubo, T.; Maruyama, S. Chem. Phys. Lett. 2004, 385, 298.

(4) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. Science 2004, 19, 1362.

(5) Eres, G.; Kinkhabwala, A. A.; Cui, H.; Geohegan, D. B.; Puretzky, A. A.; Lowndes, D. H. J. Phys. Chem. B 2005, 109, 16684

(6) Xu, Y.; Flor, E.; Kim, M. J.; Hamadani, B.; Schmidt, H.; Smalley, R. E.; Hauge, R. H. J. Am. Chem. Soc. 2006, 128, 6560.

(7) Fan, S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M.; Dai, H. Science 1999, 283, 512.

(8) Li, J.; Cassell, A.; Delzeit, L.; Han, J.; Meyyappan, M. J. Phys. Chem. B 2002, 106, 9299.

(9) Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanakie, O.; Hatori, H.; Yumura, M.; Iijima, S. Nat. Mater. 2006, 5, 987.

(10) Javey, A.; Guo, J.; Farmer, D. B.; Wang, Q.; Wang, D.; Gordon, R. G.; Lundstrom, M.; Dai, H. Nano Lett. 2004, 4, 447.

(11) Rutherglen, C.; Burke, P. Nano Lett. 2007, 7, 3296.

(12) Jensen, K.; Weldon, J.; Garcia, H.; Zettl, A. Nano Lett. 2007, 7, 3508

(13) Ge, L.; Sethi, S.; Ci, L.; Ajayan, P. M.; Dhinojwala, A. Proc. Natl. Acad. Sci. 2007, 104, 10792.

(14) Qu, L.; Dai, L. Adv. Mater. 2007, 19, 3844.

(15) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. Nature 2005, 438, 44.

(16) Corry, B. J. Phys. Chem. B 2008, 112, 1427.

(17) Li, Y.; Liu, J. Chem. Mater. 2001, 13, 1008.

(18) Harutyunyan, A. R.; Pradhan, B. K.; Kim, U. J.; Chen, G.; Eklund, P. C. Nano Lett. 2002, 2, 525.

- (19) Qian, W.; Liu, T.; Wei, F.; Wang, Z.; Yu, H. Carbon 2003, 41, CO1-848
- (20) Liu, B. C.; Lyu, S. C.; Lee, T. J.; Choi, S. K.; Eum, S. J.; Yang, C. W.; Park, C. Y.; Lee, C. J. Chem. Phys. Lett. 2003, 373, 475
- (21) Lyu, S. C.; Liu, B. C.; Lee, T. J.; Liu, Z. Y.; Yang, C. W.; Park, C. Y.; Lee, C. J. Chem. Commun. 2003, 734.
- (22) Liu, B. C.; Liu, S. C.; Jung, S. I.; Kang, H. K.; Yang, C.-W.; Park, J. W.; Park, C. Y.; Lee, C. J. Chem. Phys. Lett. 2004, 383, 104.

(23) Lacerda, R. G.; Teo, K. B. K.; Teh, A. S.; Yang, M. H.; Dalal, S. H.; Jefferson, D. A.; Durrell, J. H.; Rupesinghe, N. L.; Roy, D.;

Amaratunga, G. A. J.; Milne, W. I.; Wyczisk, F.; Legagneux, P.; Chhowalla,

M. J. Appl. Phys. 2004, 96, 4456. (24) Mehn, D.; Fonseca, A.; Bister, G.; Nagy, J. B. Chem. Phys. Lett. 2004. 393. 378.

(25) Wang, W. L.; Bai, X. D.; Xu, Z.; Liu, S.; Wang, E. G. Chem. Phys. Lett. 2006, 419, 81.

(26) Hart, A. J.; Slocum, A. H.; Royer, L. Carbon 2006, 44, 348.

(27) Yu, H.; Zhang, Q.; Zhang, Q.; Wang, Q.; Ning, G.; Luo, G.; Wei, F. Carbon 2006, 44, 1706.

(28) Ago, H.; Uehara, N.; Yoshihara, N.; Tsuji, M.; Yumura, M.; Tomonaga, N.; Setoguchi, T. Carbon 2006, 44, 2912.

(29) Christen, H. M.; Puretzky, A. A.; Cui, H.; Belay, K.; Fleming, P. H.; Geohegan, D. B.; Lowndes, D. H. Nano Lett. 2004, 4, 1939.

(30) Puretzky, A. A.; Geohegan, D. B.; Jesse, S.; Ivanov, I. N.; Eres, G. Appl. Phys. A: Mater. Sci. Process. 2005, 81, 223.

(31) Wood, R. F.; Pannala, S.; Wells, J. C.; Puretzky, A. A.; Geohegan, D. B. Phys. Rev. B 2007, 75, 235446.

(32) Pint, C. L.; Pheasant, S. T.; Horton, C.; Xu, Y-Q.; Hauge, R. In preparation.

(33) Wei, Y. Y.; Eres, G.; Merkulov, V. I.; Lowndes, D. H. Appl. Phys. Lett. 2001, 78, 1394.

(34) Duesberg, G. S.; Loa, I.; Burghard, M.; Syassen, K.; Roth, S. Phys. Rev. Lett. 2000, 85, 5436.

(35) Anglaret, E.; Righi, A.; Sauvajol, J. L.; Bernier, P.; Vigolo, B.; Poulin, P. *Phys. Rev. B* **2002**, *65*, 165426.

(36) Fagan, J. A.; Simpson, J. R.; Landi, B. J.; Richter, L. J.; Mandelbaum, I.; Bajpai, V.; Ho, D. L.; Raffaelle, R.; Hight Walker, A. R.; Bauer, B. J.; Hobbie, E. K. *Phys. Rev. Lett.* **2007**, *98*, 147402.

(37) Murakami, Y.; Chiashi, S.; Einarsson, E.; Maruyama, S. *Phys. Rev.* B 2005, *71*, 85403.

(38) Einarsson, E.; Shiozawa, H.; Kramberger, C.; Rummeli, M. H.; Gruneis, A.; Pichler, T.; Maruyama, S. J. Phys. Chem. C 2007, 111, 17861.

(39) Wang, H.; Xu, Z.; Eres, G. Appl. Phys. Lett. 2006, 88, 213111.
(40) Araujo, P. T.; Doorn, S. K.; Kilina, S.; Tretiak, S.; Einarsson, E.;

Maruyama, S.; Chacham, H.; Pimenta, M. A.; Jorio, A. Phys. Rev. Lett. 2007, 98, 067401.

(41) Citrin, P. H.; Wertheim, G. K. Phys. Rev. B 1983, 27, 3160.

(42) Tanaka, A.; Takeda, Y. J. Phys. Soc. Jpn. 2004, 73, 1543.

(43) Mezey, L. Z.; Giber, J. Jpn. J. Appl. Phys. 1982, 21, 1569.

(44) Shabanova, I. N.; Trapeznikov, V. A. J. Electron Spectrosc. Relat. Phenom. 1975, 6, 297.

(45) Canzian, A.; Mosca, H. O.; Bozzolo, G. Appl. Surf. Sci. 2005, 249, 97.

(46) Pint, C. L.; Bozzolo, G.; Hauge, R. Nanotechnology, accepted.
(47) Roine, A. OutoKumpu HSC Chemistry for Windows, version 4.0,

North American Distributors: ChemSW inc. and ESM Software. (48) Ressler, T.; Wienold, J.; Jentoft, R. E.; Neisius, T. J. Catal. 2002,

210, 67.

(49) Herrera, J. E.; Resasco, D. E. J. Catal. 2004, 221, 354.

(50) Hu, M.; Murakami, Y.; Ogura, M.; Maruyama, S.; Okubo, T. J. Catal. 2004, 225, 230.

(51) Floquet, N.; Bertrand, O.; Heizmann, J. J. Oxid. Met. 1992, 37, 253.

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