By controlling the timing and duration of hydrogen exposure in a fixed thermal process, we tuned the diameters of carbon nanotubes (CNTs) within a vertically aligned film by a factor of 2, and tuned the areal densities by an order of magnitude. The CNT structure is correlated with the catalyst morphology, suggesting that while chemical reduction of the catalyst layer is required for growth, prolonged H₂ exposure not only reduces the iron oxide and enables agglomeration of the Fe film, but also leads to catalyst coarsening. Control of this coarsening process allows tuning of CNT characteristics.

Because of their exceptional and anisotropic properties, layers of aligned carbon nanotubes (CNTs) have been widely investigated for electrical, thermal, and mechanical applications, such as for microelectronic interconnects, heat sinks, and structural composites. These applications require control and optimization of the diameter, wall structure, and areal density of CNTs, particularly in vertically aligned CNT “carpets” grown on and/or transplanted to other substrates.

To replace copper in interlayer vias, some studies suggest using highly packed single-wall CNTs (SWCNTs) to offer the necessary high current-carrying capacity. To match copper conductivity in vias below the 32 nm node, some models suggest a target density of SWCNTs of at least $3 \times 10^{13}$ CNTs/cm². Currently achieved maximum densities for CNTs in vias do not exceed $10^{11}$ CNTs/cm². However, other studies show that multiwall CNTs (MWCNTs) with large diameter offer higher than expected conductivity due to the participation of multiple walls to significantly increase the channels for conduction. If interlayer vias are filled with MWCNTs, the target density will be lower than that for SWCNTs, depending of the channels of conduction exhibited by the nanotubes. Furthermore, MWCNTs are usually conducting (statistically, only one third of SWCNTs are conducting).

Process control remains the main obstacle to integration of CNT growth into complex multistep fabrication processes. The CNT growth mechanism is not fully understood and many studies have shown very strong sensitivities to small variations in process parameters. CNT growth on a substrate, using thermal chemical vapor deposition (CVD) has two main stages:

(i) Formation and reduction (deoxidation) of catalyst particles.

(ii) Nucleation and growth of the CNTs on catalyst particles.

In many cases, these two stages occur in parallel under fixed processing conditions, obscuring the separate effects of these stages, and making mechanistic understanding and process optimization difficult.

A major challenge is to control the catalyst particle size, as it determines the CNT diameter. Many techniques have been employed to control the catalyst size. For example, controlling the thickness of a metal catalyst thin film has been shown to provide control over the diameter and number of walls of CNTs. Additionally, catalyst pretreatment can strongly influence CNT growth. Pretreatment of Fe/Al film in NH₃ at subatmospheric pressure causes restructuring of the catalyst into nanoclusters suitable for low-temperature growth of micron-thick carpets of SWCNTs when C₂H₂ is later introduced. Alternative techniques for catalyst formation include deposition of preformed metal...
nanoparticles, such as particles templated by block copolymer micelles, which achieve control over the diameter and areal density of CNTs. Additionally, in situ laser ablation of a catalyst target, followed by online sorting using an impactor has been demonstrated to yield catalyst densities of $10^{12}$/cm$^2$ and has yielded CNTs at a density of $10^{11}$/cm$^2$. During CNT nucleation and growth, the challenge is to balance often competing pathways leading to amorphous carbon formation rather than crystalline nanotubes. A common strategy is to add a vapor “etching” agent to the CVD atmosphere, such as H$_2$, NH$_3$, O$_2$, CO$_2$, or H$_2$O, or a combination of these agents. In addition to enabling reduction of the catalyst prior to nucleation, H$_2$ reduces gas-phase pyrolysis of hydrocarbons and also causes desorption of amorphous carbon fragments from the surfaces of catalysts. However, hydrogen radicals, which are most abundant in plasma-enhanced CVD atmospheres, can etch small-diameter (particularly small single-wall) CNTs. H$_2$ used in atmospheric pressure CVD of CNTs using C$_2$H$_4$, with a slight addition of H$_2$O vapor, yields millimeter-thick layers of aligned SWCNTs. In the latter case, it has been proposed that H$_2$O etches amorphous carbon from the catalysts, thereby increasing the catalyst lifetime. However, the specific conditions that lead to high-yield nucleation and rapid growth of CNTs in this process have not been clearly described in the literature.

In this work, we have analyzed the effects of varying the pretreatment of Fe/Al$_2$O$_3$ films in oxidizing (Ar containing parts per million of O$_2$) and reducing (H$_2$/Ar) atmospheres during the catalyst preparation stage. While using a defined thermal process, we varied only the timing of the introduction of hydrogen. We find that this leads to tunability of the diameter of CNTs by a factor of 2, and a corresponding increase of the areal density of CNTs by a factor of 10. Further, we found that introduction of H$_2$ at different times after C$_2$H$_4$ was introduced, rather than following the standard practice of simultaneously introducing the reactant and reducing gases, led to significantly enhanced CNT growth rates. We present results from detailed characterization of CNTs grown when varying the time of H$_2$ introduction relative to the time of C$_2$H$_4$ introduction, as well as a detailed analysis of the effects of H$_2$ on the formation and morphological evolution of the catalyst particles. This is done in order to explain the strong process sensitivity to, and the beneficial effects associated with, control of the sequence and timing of the introduction of reactant and reducing gases.

A film of 1.2/10 nm of Fe/Al$_2$O$_3$ was deposited on 150 mm diameter silicon wafers using electron beam evaporation, as described previously. The wafers were manually cleaved into 5 × 5 mm samples using a diamond scribe.

Catalyst pretreatment followed by CNT growth was performed in a three-zone atmospheric-pressure furnace, in a fused-silica tube with an internal diameter of 22 mm. Flows of Ar (99.9995%, Airgas), C$_2$H$_4$ (99.5%, Airgas), and H$_2$ (99.999%, Airgas) were maintained using electronic mass flow controllers (MKS, model 1179A). The substrate sample was held in the tube using a custom-made quartz fixture, and faced the flow at an inclination of 20°.

After flushing the tube with Ar for 10 min, the furnace was ramped to 770 °C over 35 min and the temperature was then held at 770 °C for 30 min, during which C$_2$H$_4$ was introduced after 15 min and H$_2$ was introduced at different times in different runs. Ar continuously flowed through the system during the heating, annealing, growth, and cooling stages. The argon flow rate was 600 standard cubic centimeters per minute (sccm) when H$_2$ was not present and 200 sccm when mixed with hydrogen. The red dots indicate experimental conditions for which CNTs were characterized using HRTEM.

The CNTs were examined using scanning electron microscopy (SEM, Philips XL-30) and high-resolution transmission electron microscopy (HRTEM, JEOL 2011). The areal density of the CNTs within a film was determined using the mass of an average CNT (based on the inner and outer diameters determined from approximately 50 CNTs measured from each sample using HRTEM), the film volume (which is estimated using SEM imaging), and the film mass, as measured using a microbalance (Sartorius ME36S). The substrate morphology was characterized using atomic force microscopy (AFM, Veeco Nanoscope IV) in tapping mode.

When we introduced hydrogen at any time between H$_2@-10$ (t = 40 min) and H$_2@+10$ (t = 60 min), we obtained vertically aligned “carpets” of multiwall CNTs with thicknesses (average tube lengths) of several hundred microns. However, changes in the timing of H$_2$ introduction relative to the time of C$_2$H$_4$ introduction led to significant
changes in the diameter and areal density of CNTs within the carpet, as well as in the average growth rate and final carpet thickness at the end of the process.

The curve in Figure 2 indicates the measured carpet height for varying times of hydrogen introduction for the process described above. This graph indicates that delaying hydrogen introduction leads to taller CNT carpets. However, not introducing hydrogen at all gives only micron-high carpets for the 15 min growth process.

The carpets that result from three specific processes (indicated by red dots in Figure 1) have been characterized in detail: H2@−5, H2@0, and H2@+10. Figure 3 shows SEM images of the carpets obtained by introducing hydrogen before, at, and after ethylene introduction for the three selected processes. Delaying introduction of H2 leads to better-aligned CNT carpets as well as taller carpets (therefore longer CNTs). HRTEM images (also shown in Figure 3) show that the CNT diameter and number of walls decreased, while the areal density increased, when hydrogen introduction was delayed. The average CNT diameter decreased from 14 nm (7 walls) for H2@−5 to only 7 nm (3 walls) for H2@+10. Concomitantly, the areal density increased by an order of magnitude from 4 × 10^9 CNTs/cm² for H2@−5 to 5 × 10^10 CNTs/cm² for H2@+10 (refer to Table 1).

While CNT growth started almost instantly when H2 and C2H4 were introduced simultaneously (approaching a steady growth rate within the first minute), exposure to C2H4 alone gave very slow growth. If we did not introduce hydrogen at all, after 15 min of exposure to C2H4 the carpet was only a few microns tall (Figure 4), from which we infer that most of the growth occurred when hydrogen is present. Although C2H4 indeed decomposes into hydrogen (in addition to multiple carbon-based compounds), at our growth temperature (770 °C) we hypothesize that the C2H4 alone does not allow sufficient coarsening of the catalyst to affect CNT properties (the C2H4 flow rate is 150 sccm compared to the H2 flow rate of 400 sccm). Furthermore, the formation of a carbide may dominate the growth phase in which only C2H4 is present (no added H2).

We will define the “apparent growth rate” as equal to the carpet height divided by the hydrogen exposure time (Figure 5). When H2 is introduced after the sample is exposed to C2H4 alone, the apparent growth rate increases rapidly. For example, introducing hydrogen 10 min after C2H4 gives an apparent growth rate of approximately 150 µm/minute, and the carpet attains a height of 0.88 mm after only five minutes of simultaneous exposure to C2H4 and H2. This apparent growth rate is approximately five times the rate achieved when C2H4 and H2 are introduced simultaneously. Furthermore, when hydrogen was introduced two minutes before the end of the process, we obtain a carpet of similar height as for H2@+10, giving an apparent growth rate exceeding 400 µm/minute (not shown).

AFM imaging of the as-deposited Fe/Al2O3 film (not shown) indicates a surface roughness below 0.25 nm, which does not change after heating to 770 °C in argon. AFM imaging of a sample without the Fe layer indicates a similar level of flatness (rms roughness below 0.25 nm), which is also retained after heating to 770 °C in argon or hydrogen (not shown).

To understand the effects of hydrogen on the catalyst, we annealed samples for increasing durations of hydrogen exposure at the growth temperature and then cooled rapidly to quench morphological evolution. This thermal process is illustrated in Figure 6. Note that these samples were cut from the same wafer we used for CNT growth and that no hydrocarbon gas was introduced during this thermal process. AFM measurements show that catalyst dots form about 5 to 10 min, and that their height subsequently increases with longer times of exposure to hydrogen at 770 °C (Figure 7).

A full understanding of the CNT growth mechanism is complicated by the fact that iron can be present in many different oxidation states. We will limit our analysis to the interpretation of the change in morphology and make selected assumptions regarding the oxidation state of the catalyst. Also, given that CNT lengths necessary for interconnect vias and for other electrical applications are in the submicron range, the thicknesses of the carpets studied here are more than sufficient for these applications.

Given the flatness of the as-deposited film, the small thickness (1.2 nm) of the deposited Fe catalyst layer and the pressure during deposition (∼2 × 10⁻¹⁰ Torr), we assume that the Fe catalyst layer is oxidized and continuous before starting the thermal process. On the basis of the Ellingham...
diagram\textsuperscript{25} and the dynamics of oxidation of bulk iron,\textsuperscript{26} we expect the starting oxide to be Fe\textsubscript{2}O\textsubscript{3}.\textsuperscript{26} Because the argon used in these experiments contains a few parts per million of oxygen impurities, we can consider it an oxidizing atmosphere that, by keeping the catalyst layer oxidized, prevents dewetting of the catalyst.\textsuperscript{18,27} Hence, a thermal process without hydrogen does not allow reduction of the iron oxide to iron, or the subsequent formation of catalyst clusters or particles. Once hydrogen is introduced, the iron oxide will be reduced and iron clusters will form. As observed by some teams using in situ XRD,\textsuperscript{28} or in situ TEM,\textsuperscript{29} or shown in molecular dynamics studies,\textsuperscript{30} it is possible that, in between the oxide and the metal transformation, intermediate metastable carbide phases may be present after C\textsubscript{2}H\textsubscript{4} is introduced.

The results shown in Figure 7 indicate that this process takes about 5–10 min at 770 °C. Using in situ XPS, Hofmann et al. observed that for Fe on SiO\textsubscript{2}\textsuperscript{31} and for Fe on Al\textsubscript{2}O\textsubscript{3},\textsuperscript{27} the catalyst is active in its metallic state. Further, in an extensive study of the morphology and oxidation state of thin film Fe on alumina, Sushumna et al.\textsuperscript{32} also observed that an Fe layer 12.5 Å thick is reduced to metallic iron when exposed to hydrogen at temperatures above 500 °C.

**Figure 3.** SEM and HRTEM images of CNT carpets after processing when H\textsubscript{2} is introduced 5 minutes before ethylene (H\textsubscript{2}@−5), at the same time as ethylene (H\textsubscript{2}@0), and 10 minutes after ethylene (H\textsubscript{2}@+10). Delaying hydrogen introduction leads to taller CNT carpets, with better aligned CNTs, and with thinner CNTs with fewer walls.

**Figure 4.** SEM image of CNTs grown for 15 min in C\textsubscript{2}H\textsubscript{4}/Ar only, without added hydrogen.

**Figure 5.** CNT apparent growth rate calculated as carpet height divided by hydrogen exposure time.
The clusters that form by film agglomeration after reduction of the iron oxide will initially be small, and consequently closely spaced. Continued annealing in the presence of H₂ allows the clusters to coarsen. This process, driven by surface energy minimization, occurs through transport of Fe among clusters, either through the vapor phase, or more likely by diffusion of Fe as adatoms on the Al₂O₃ surface. In coarsening processes, small clusters tend to shrink and disappear with their mass being redistributed to larger clusters. This process therefore results in an increase in the average cluster size as well as an increase in the average cluster spacing. These trends are consistent with the observed trends in the average CNT diameter and areal density.

The curve shown in Figure 7 can therefore be interpreted as reflecting three regimes of behavior (as schematically illustrated in Figure 8):

(i) The initial rate of change is slow as hydrogen first reduces the catalyst layer.

(ii) Once the iron oxide is reduced, mobile iron adatoms form clusters.

(iii) The iron clusters coarsen at a rate that decreases with time.

\[
\langle r \rangle = K t^n
\]

where \( \langle r \rangle \) is the average cluster size, \( K \) is a time-independent constant with a Boltzmann temperature dependence, \( t \) is time, and \( n \) is a constant \( (\approx 1) \), the magnitude of which depends on the atomic mechanism that limits the rate of coarsening (e.g., adatom attachment to clusters or adatom diffusion on the substrate surface). Evidence for catalyst coarsening after hydrogen annealing for iron deposited on SiO₂ has also been presented in an earlier study, though no analysis of the process or its consequences were discussed.

We estimated the average radius of curvature of the catalyst dots from AFM images of samples subjected to various times of hydrogen exposure with the results shown in Figure 9. To determine the radius of the catalyst particles using AFM scans, we measured the particle height \( h \) as a function of position \( x \) for multiple horizontal scans of each AFM image and determined the radius of curvature about the particle apex, \( \kappa \), using:

\[
\kappa = \frac{h''(x)}{1 + [h'(x)]^2}^{1/2}
\]

where the second and first derivatives of \( h(x) \), \( h'(x) \), and \( h''(x) \), respectively, were determined numerically. This measure of \( \langle r \rangle \), \( 1/\langle \kappa \rangle \), overestimates the true value of \( \langle r \rangle \) but provides relative values of \( \langle r \rangle \) that scale in the same way as their true values. As seen in Figure 9, we again find, as expected, that the initial coarsening rate is fast, but that the coarsening rate diminishes with time. Given that we expect the contact angle of the catalyst dots to remain the same,
independently of the time of exposure to hydrogen, the catalyst dot height and the radius of curvature should scale together.

As suggested earlier, the catalyst coarsening behavior observed without exposure of the catalysts to C\(_2\)H\(_4\) correlates with the CNT characteristics as a function of the duration of pretreatment of the catalysts in H\(_2\), indicating a mechanistic correlation. The similarity in trends can be illustrated by comparison of the average CNT diameter measured for the three process points in Figure 1 (13.6 nm for H\(_2@0\), 9.8 nm for H\(_2@0\), and 7.4 nm for H\(_2@+10\)) and the three corresponding catalyst dot heights measured with AFM. These are 2.5 nm for H\(_2@0\) (corresponding to 5 min of H\(_2\) exposure prior to the growth cycle and 15 min during the growth cycle), 0.6 nm for H\(_2@0\) (corresponding to 15 min of H\(_2\) exposure during the growth cycle), and 0.2 nm for H\(_2@+10\) (corresponding to 5 min of H\(_2\) exposure).

Owing to the accepted correlation between catalyst size and nanotube diameter, we argue that the CNT diameter increases with increasing H\(_2\) annealing time prior to introduction of C\(_2\)H\(_4\) due to the increase in the average catalyst particle size that results from particle coarsening after exposure to H\(_2\).

When H\(_2\) and C\(_2\)H\(_4\) are introduced simultaneously, the stages of reduction/coarsening and nucleation occur under the same reactant atmosphere. Here, the catalyst particles nucleate CNTs after sufficient reduction and clustering have occurred and before significant coarsening has occurred. Consequently, the CNTs have smaller diameters and are more closely spaced compared to when H\(_2\) is introduced prior to C\(_2\)H\(_4\).

When C\(_2\)H\(_4\) is introduced before H\(_2\), the catalyst experiences an extended period in which reduction and coarsening happen more slowly than when H\(_2\) is added to the flow. Thermal decomposition of C\(_2\)H\(_4\), which occurs as the gas is heated in the tube furnace and flows toward the sample, forms H\(_2\) and a variety of additional hydrocarbons (e.g., CH\(_4\), C\(_2\)H\(_2\)). Therefore, a reducing environment is present when we introduce C\(_2\)H\(_4\) without H\(_2\). The presence of even smaller CNT diameters (relative to H\(_2@0\)) suggests that the coarsening kinetics in the atmosphere of C\(_2\)H\(_4\) without added H\(_2\) are slower than with C\(_2\)H\(_4\)/H\(_2\) or H\(_2\). Figures 2 and 5 also indicate that while H\(_2\) reduction of iron oxide is required for growth, the shorter period of reduction results in the faster apparent rate of growth of CNTs. This implies that the rate of growth of CNTs from small iron clusters is much higher than rates implied for growth processes with longer H\(_2\) exposure times. This may be the result of CNT etching during prolonged periods of exposure to H\(_2\). The duration of exposure to H\(_2\) therefore not only affects the CNT diameter and spacing through effects on the catalyst size, but also affects the apparent rate of CNT growth.

In summary, we have demonstrated that by controlling the time at which hydrogen is introduced during catalyzed thermal CVD of CNTs we can control the diameter, areal density, and apparent growth rate of CNTs (all three variables are coupled together). We have also shown that once the catalyst layer, initially oxidized iron, is reduced by exposure to H\(_2\), clusters form and then coarsen over time. Introduction of hydrogen therefore leads not only to catalyst formation but also to catalyst coarsening. If CNT growth occurs immediately after reduction of the oxide, the catalysts are small and closely spaced, so that the catalyzed CNTs are also small and closely spaced. Furthermore, CNTs grown after only a brief exposure to H\(_2\) have a very high apparent growth rate. This suggests that the extended presence of H\(_2\) either leads to a slower growth rate or to etching of the CNTs after an initial rapid growth.

**Acknowledgment.** We would like to thank Nicola Abate for assistance with some of the experiments, Amanda Giermann, Dr. Ramkumar Krishnan, Dr. Reiner Moenig, Andrew Takahashi, Désirée Plata, and Dr. Kevin O’Brien (Intel), for useful discussions, and Libby Shaw for assistance with atomic force microscopy. This research was supported by the MARCO Interconnect Focus Center. G.D.N. was partially supported by an Intel Fellowship and A.J.H. was partially supported through a Fannie and John Hertz Foundation Fellowship.

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