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Altering the catalytic activity of thin metal catalyst films for controlled growth of chemical vapor deposited vertically aligned carbon nanotube arrays

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Abstract The growth rate and terminal length of vertically aligned carbon nanotube arrays (VANTAs) grown by chemical vapor deposition have been dramatically improved through pulsed KrF excimer laser pretreatments of multilayer metal catalyst films. Silicon wafers coated with Al, Mo, and Fe layers were laser processed in air with single laser shots of varying fluence through circular apertures, then heated to ∼750°C and exposed to acetylene and ferrocene containing gas mixtures typically used to grow vertically aligned nanotube arrays. In situ videography was used to record the growth kinetics of the nanotube arrays in both patterned and unpatterned regions to understand the changes in catalytic activity, growth rates, and termination of growth. The height of the patterned regions varied with fluence, with the most successful treatment resulting in 1.4 cm tall posts of nanotubes embedded in a 0.4 cm tall nanotube carpet. High-resolution transmission electron microscopy images from the nanotubes in the posts revealed fewer walls, smaller diameters, and a much narrower distribution of diameters compared to the nanotubes grown in the carpet. This information, along with data obtained from weighing the material from each region, suggests that pulsed laser processing can also significantly increase the areal density of VANTAs.

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While spinning of short carbon nanotubes (CNTs) into centimeter and longer fibers is readily achieved [1–3], directly synthesizing aligned, continuous nanotubes to similar lengths to explore highly electrical- and thermal-conductive composites is an active area of research. By combining process optimization, improved catalysts, and chemical vapor deposition (CVD) we have previously demonstrated *multi-millimeter* long arrays of aligned CNTs containing mixtures of single, few, and multiwall nanotubes [4]. Recent thermal conductivity measurements [5] have shown that these continuous nanotube arrays not only exhibit a higher conductivity and anisotropy than any other macroscopic assembly of CNTs to date, but they have conductivities equal to or better than published values for most contemporary thermal interface materials. The growth kinetics and terminal length of the array, as well as the number of walls of the nanotubes within the array are governed by the catalytic activity and chemistry of the metal catalyst nanoparticles which form at the base of the nanotubes in these arrays. Here, excimer laser processing of the (Mo/Fe/Al) multilayer metal film system introduced by Delzeit et al. [6] prior to nanotube growth by CVD is explored as a method to alter the catalytic activity of the films in order to further assess the effects on terminal length, wall number, and density of these arrays.

Catalyst coated silicon wafers having a diameter of 100 mm were prepared at room temperature by e-beam evaporating 10 nm of Al, followed by 1 nm of Fe, and finally 0.2 nm of Mo (all values nominal). KrF excimer laser irradiation was carried out using the apparatus shown in Fig. 1, and subsequent ferrocene-assisted CVD was performed as

discussed in Eres et al. [4]. The experimental variation was minimized by utilizing 10×25 mm^2 samples that were all cleaved from the same wafer. Under typical conditions, a single shot of laser light was directed at the sample in air to produce a well-defined laser processed zone having a diameter of 2.35 mm. In an effort to develop a processing diagnostic, simultaneous reflectivity measurements using a HeNe laser (incident at ∼45°) also were recorded. The excimer laser fluence ranged from 0.6 to 0.9 J/cm^2 at the sample, and in situ videography was used during subsequent CVD to study changes in vertically aligned carbon nanotube array (VANTA) growth rate in and around the laser processed zone.

Although a number of CVD growth conditions were explored by Eres et al., those used in the present case were fixed and matched the optimum regime identified in that work—i.e. optimized for the as-deposited Mo/Fe/Al catalyst trilayer. More specifically, the process was performed in a 580 mm long single zone tube furnace equipped with a 38 mm diameter quartz tube. The sample was placed on a glazed ceramic boat and positioned 160 mm off center towards the inlet side of the tube. The gas inlet was left open to air while ramping to 750°C, and then connected to a 100 sccm $H_2 + 250$ sccm He mix after reaching steady state. Ferrocene was then introduced, with the sublimation source reaching a steady state rate of approximately 75 μg/min after 9 minutes. Finally, acetylene was added at a rate of 9 sccm to initiate growth. A 1 mm aperture at the exhaust end of the tube resulted in a CVD growth environment that was slightly above atmospheric pressure.

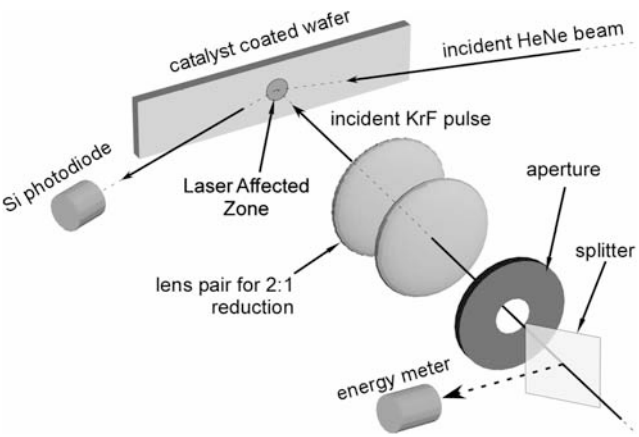

Fig. 1 Experimental setup to irradiate catalyst coated samples in a controlled manner. The change in reflectivity and incident energy are recorded simultaneously with each shot of the excimer laser. The HeNe laser spot size is much smaller than the processed area

The influence of laser fluence on the catalyst film and subsequent growth enhancement is captured in Fig. 2. A single sample was irradiated in five locations and then CVD was performed for 75 minutes as described above. This produced a sample having 6 distinct VANTA regions, namely 5 'posts' of differing height that were embedded in a uniform 1.5 mm 'carpet'. As shown in the figure, the optimum fluence for enhancement under these conditions occurred around 0.75 J/cm^2, a value that was insufficient for complete 'blowoff' of the metallic film, but more than sufficient for surface modification as evidenced by a change in HeNe reflectivity of 45.7%. Note that complete removal of the metallic stack and exposure of virgin Si would have resulted in a reflectivity change of nearly 53% in the present case.

To estimate catalytic activity under the optimum fluence identified above, a 8.5×7.5 mm^2 portion of carpet containing a single post was removed from the substrate and weighed. The post was then pulled from the carpet and weighed, and, from this, areal and volumetric densities were calculated for the post and carpet material, respectively. The irradiated area was found to process almost 900 μg/mm^2, whereas the surrounding area only processed 350 μg/mm^2. Clearly, on a *per unit substrate area* basis, the processed region was *far* more catalytically active than the unprocessed area. Most interesting, however, was the fact that the volumetric densities were very similar—89 vs. 77 μg/mm^3 for the post and carpet material, respectively—and suggested,

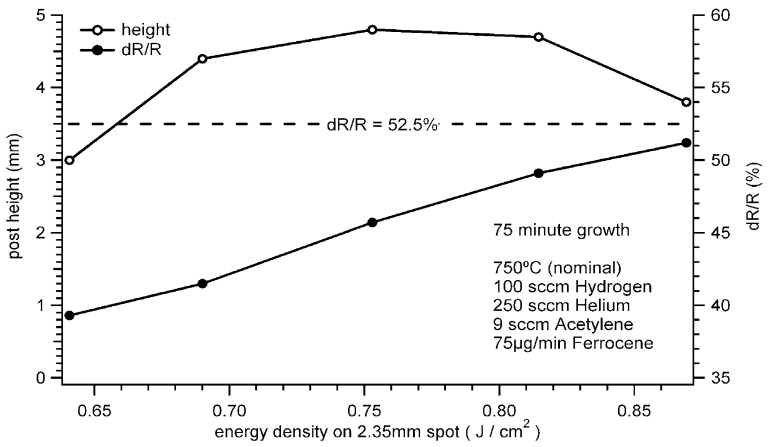

Fig. 2 Plot of resultant post height and HeNe reflectivity change as a function of fluence. Optimum enhancement under the present conditions occurs for fluences near 0.75 J/cm^2

as will become apparent later on, that laser processing produced a VANTA that was more densely packed.

To study the growth kinetics of VANTAs in and around processed regions, a second sample was produced by irradiating it in three locations using laser fluences of 0.77, 0.78, and 0.80 J/cm^2—i.e. values close to the maximum observed in Fig. 2. Surprisingly, the respective reflectivity changes in this case were only 40.6, 41.7, and 43.2%; despite our assumption that this sample was nominally the same as the first. As a processing diagnostic, the reflectivity change clearly correlated with the laser fluence, but with values that were systematically lower than on the first sample. Independent measurements on a combinatorial test sample (see Fig. 3) showed that a stack thickness reduction of approximately 2–3 nm was enough to change the reflectivity by ~6% at these fluences, underscoring both the sensitivity of this diagnostic tool and the potential importance of minute thickness variations in nanotube synthesis by this method. More interesting were the findings that resulted from performing subsequent CVD on the combinatorial sample: for a low fluence (~0.51 J/cm^2), growth was actually *stunted* in relation to the surrounding carpet. For a medium (~0.61 J/cm^2) and high (~0.78 J/cm^2) fluence, however, the growth was enhanced as expected—although notably more so in the case of a *medium* fluence. Understanding the interplay between the starting catalytic stack thickness, the initial reflectivity, the commensurate laser processing fluence, and the expected growth enhancement will be the key to reducing experimental variability, and this is the subject of ongoing research.

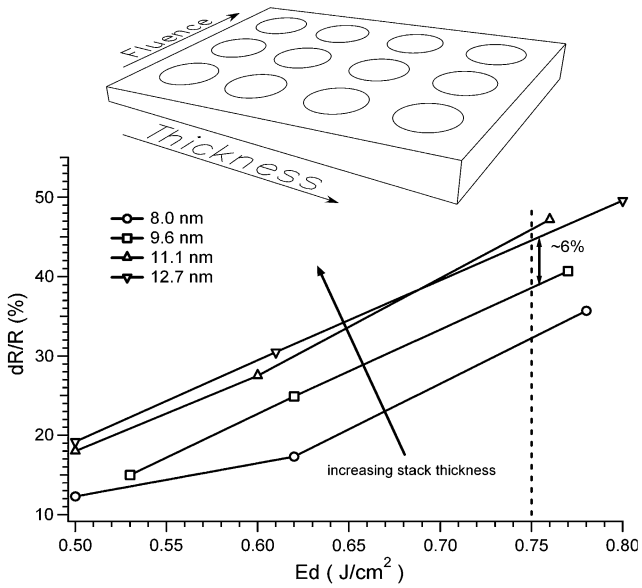

Fig. 3 Schematic of the combinatorial test sample (*top*) showing stack thickness variation in one direction, and fluence variation in the orthogonal direction. The *circles* represent the location of irradiation, and the plot (*bottom*) shows the average thickness, reflectivity change, and fluence recorded at those locations

After understanding the reflectivity discrepancy, CVD was performed for 3 hours on the sample that was irradiated in 3 locations using the procedure outlined above. Still images from time lapse videography, and data from subsequent image processing are shown in Fig. 4. Note that the posts grew out of the field of view of the camera system after 2 hours of growth. Numerical differentiation of the height vs. growth time data revealed maximum growth rates of 2.1 and 0.9 μm/sec for the posts and surrounding carpet, respectively, after 10 minutes of growth. After this, the rates slowly dropped to ~50% of their former maxima. The carpet thickness and post height at the end of the 3 hour experiment were 4 and 13.5 mm, respectively, leading to average growth

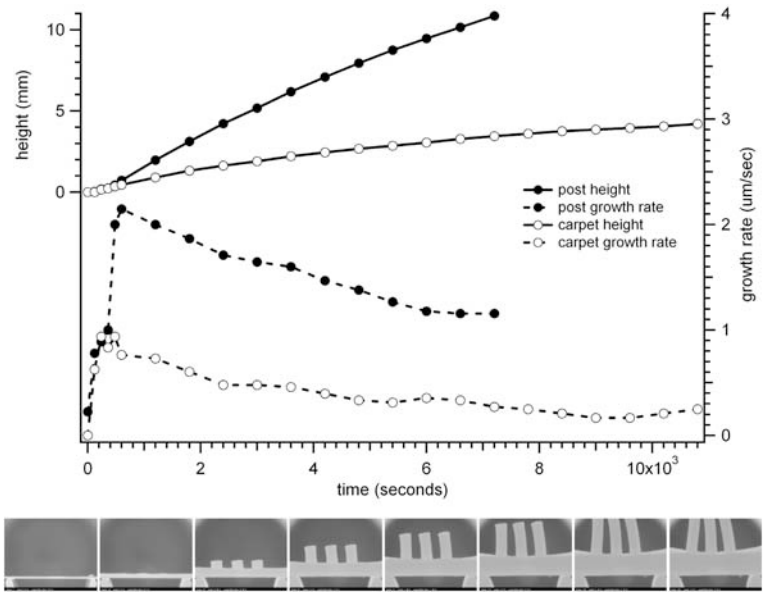

Fig. 4 CNT heights and growth rates obtained from time lapse videography image processing, and representative images of the growth of 'posts' within a 'carpet' of CNTs. Growth rates peak after 10 minutes of growth (2.1 and 0.9 μm/sec for posts and carpet, respectively), and the posts' heights exceed those of the carpet by a factor of three

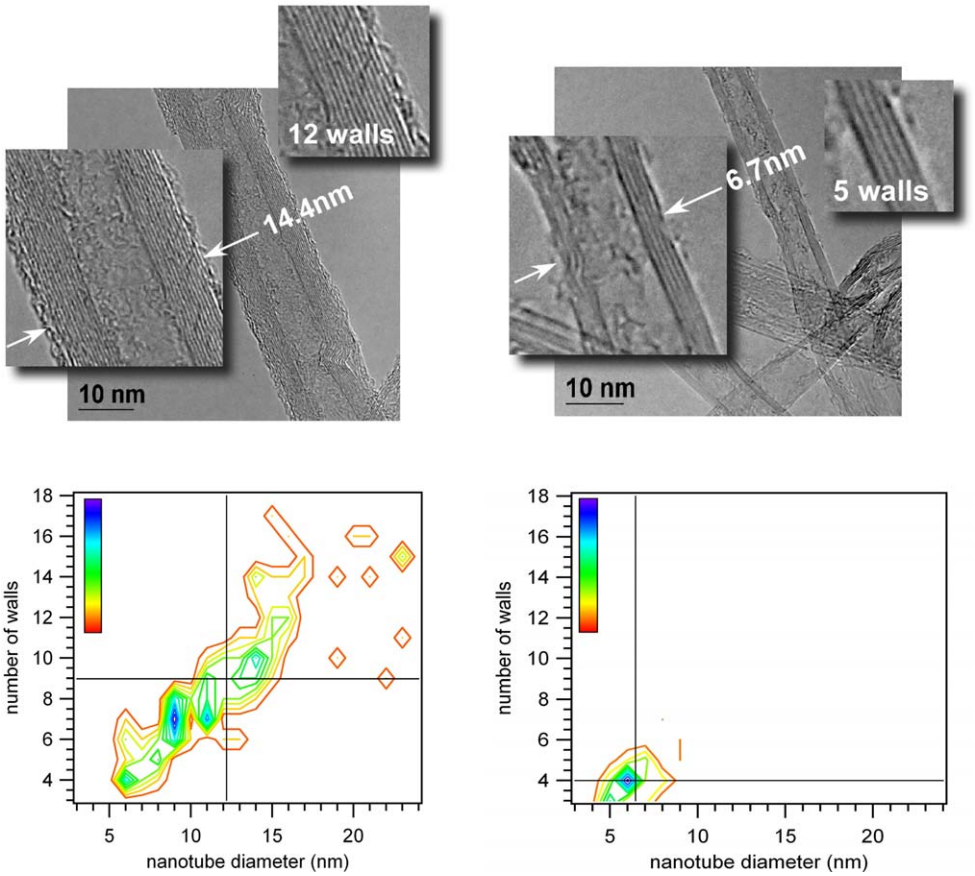

Fig. 5 Representative high resolution TEM images showing nanotube diameter and wall number for a nanotube in the post (*upper right*) and in the carpet (*upper left*). Nearly 100 nanotubes from each region were analyzed, and binned on a 2 dimensional grid to produce 2D histograms of wall number vs. diameter for nanotubes in the carpet (*lower left*) and posts (*lower right*). The *crossed lines* in each lower figure show the center of mass for that particular distribution

rates of 0.37 and 1.25 μm/sec. Although 3 hours were insufficient to observe a terminal length for the posts, the simplified analytical model proposed by Puretzky et al. [7] fits the data in the figure and predicts a terminal height of ∼28 and ∼5 mm for the posts and carpet, respectively. The model also predicts a characteristic termination time of ∼3.8 and ∼1.8 hours for the posts and carpet, respectively.

To gain an understanding of the remarkable improvement in growth rate, another sample was produced under the optimum conditions identified above, and a statistical analysis of high-resolution TEM images was performed after harvesting material from the carpet and a post. Representative images and a summary of the data from each region are shown in Fig. 5. As can be seen in the figure, the statistical spread of the number of walls and the diameters of nanotubes in the post was much narrower than that in carpet, and a simultaneous shift to fewer walls and smaller diameters occurred. Using the centers of mass to describe the distributions, one can argue that laser processing produced nanotubes that were predominantly 6 nm and 4 walled from conditions that would otherwise produce predominantly 12 nm, 9 wall nanotubes. Combining this information with the observation that the posts on this sample were 2.34 times taller than the surrounding carpet, one can argue that each nanotube in a post contains almost *half* as much carbon as a counterpart in the carpet. If this is the case, then in order to achieve equal volumetric densities as observed in the earlier weighing experiments, laser processing must promote surface conditions that result in a higher areal density of smaller nanotubes than could otherwise be produced with the thermal annealing step alone.

Scanning probe microscopy was performed to determine if there was any morphological evidence of smaller particles within the processed area, but as shown in Fig. 6, the results were essentially inconclusive. What *was* clear, however, was the 'crystallographic' nature of the surface in the processed area, which suggested that laser processing partially oxidized the catalyst prior to thermal annealing, thereby altering the nature of the feedstock available for transformation by subsequent thermal annealing. Work is currently under way to determine what constitutes an active growth region on a surface such as those shown in Fig. 6.

In summary, we have shown that pulsed KrF excimer laser processing of multilayer metal catalyst films prior to CVD can be used to effect remarkable changes in subsequent VANTA growth rates, terminal heights, nanotube diameters and wall numbers, leading to a *slim*, *fast* growth mode where feedstock is utilized more efficiently in the axial (rather than radial) direction. In addition to growth enhancement, *suppression* is also possible, suggesting that

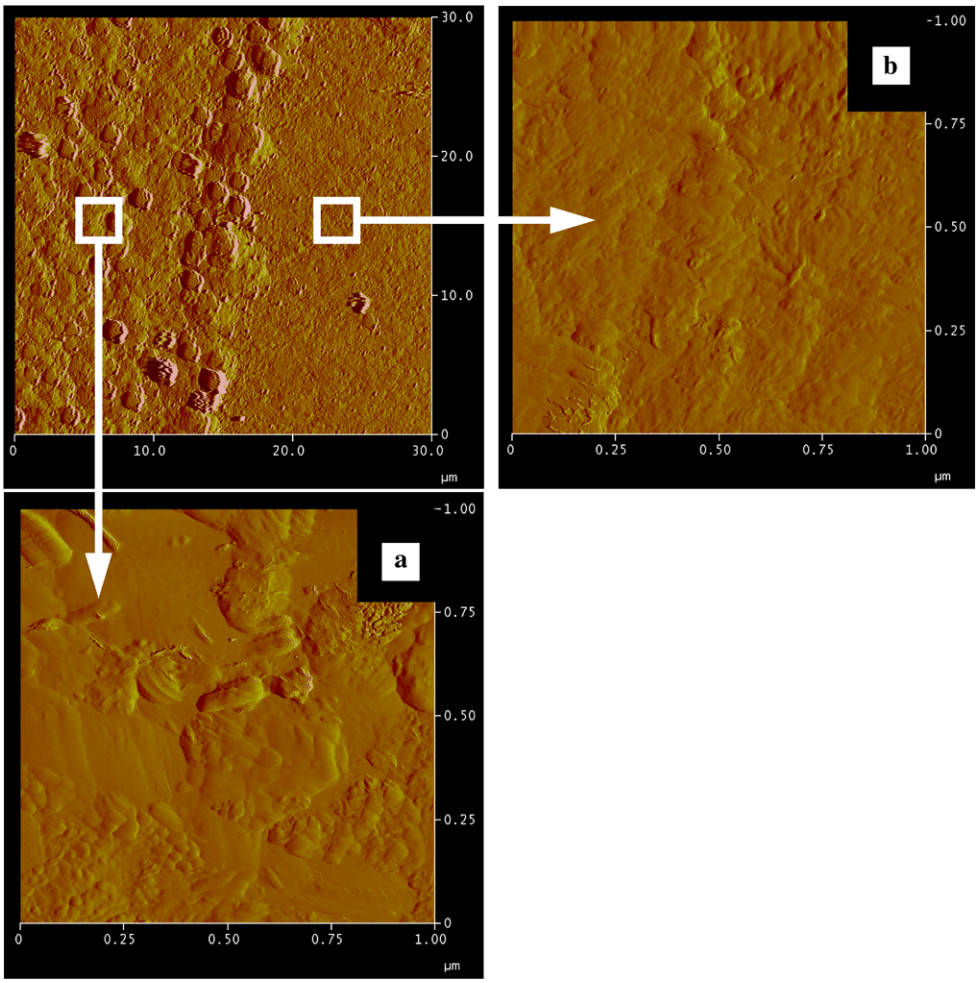

Fig. 6 Amplitude mode atomic force micrographs comparing the surface morphology of the processed region (**a**) to that of the unprocessed region (**b**). All images taken post-growth, and *after* VANTA removal. Amplitude mode was chosen to enhance morphological features

laser microprocessing of surfaces in the manner we have shown might be utilized to provide catalytic control for three dimensional 'sculpting' of VANTAs.

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