

# Bottom-Up Growth of Carbon Nanotube Multilayers: Unprecedented Growth

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## ABSTRACT

An unusual growth phenomenon, with no precedent in vapor-phase thin film growth, is described here, for the case of the growth of stacked multiple layers of vertically aligned carbon nanotubes<sup>1–6</sup> on solid substrates. As multiple layers of ordered nanotubes are sequentially deposited from the vapor onto the substrate, each layer nucleates and grows from the original substrate surface at the bottom of the existing multiple stacks of nanotubes. In contrast to conventional understanding of thin film deposition,<sup>7</sup> the mechanism here has similarities to porous oxide film formation on surfaces.<sup>8</sup> The stacked layers of aligned nanotubes act as fully permeable membranes for the downward diffusion of growth precursor vapors, allowing growth to occur at the buried solid interface. The preexisting multiple nanotube stacks lift up to accommodate the vertical growth of fresh layers, allowing the formation of nanotube towers extending in millimeter lengths. Our results provide evidence for a new growth phenomenon, characterized by selective, interface-driven, bottom-up growth of self-assembled nanowires at buried interfaces, covered with weakly adhering thick porous membranes.

There have been many previous reports on the growth<sup>1–5</sup> and applications<sup>9–12</sup> of vertically aligned multiwalled carbon nanotube films on solid substrates. Our results here report an altogether new phenomenon, related to the growth of multiple stacks of such aligned nanotube layers, but pointing to an unprecedented growth mechanism, unforeseen in vapor-phase film growth on substrates. The remarkable features of the growth process we describe here are twofold. One, we are able to assemble multiple layers (up to an impressive eight layers; see Figure 1, which shows a series of multiply stacked nanotube towers, selectively grown on SiO<sub>2</sub>) of carbon nanotube films and organized array patterns; the vertically aligned nanotube arrays are perfectly stacked on top of each other, each grown on the substrate via chemical vapor deposition and vapor-phase catalyst delivery.<sup>5,13</sup> Second, and most fascinating, the growth occurs via a very unusual growth mechanism; we observe that during growth, each layer, consisting of uniformly aligned arrays of hundreds-of-microns-long multiwalled nanotubes, nucleates and grows from the buried original substrate plane (silicon oxide) even after the substrate gets completely covered by continuous and multiple layers of nanotubes deposited during previous growth sequences. In order for this to happen, it is imperative that the hydrocarbon and the catalyst metal precursors diffuse through several hundreds of microns of porous nanotube films and start growing on top of the buried substrate,

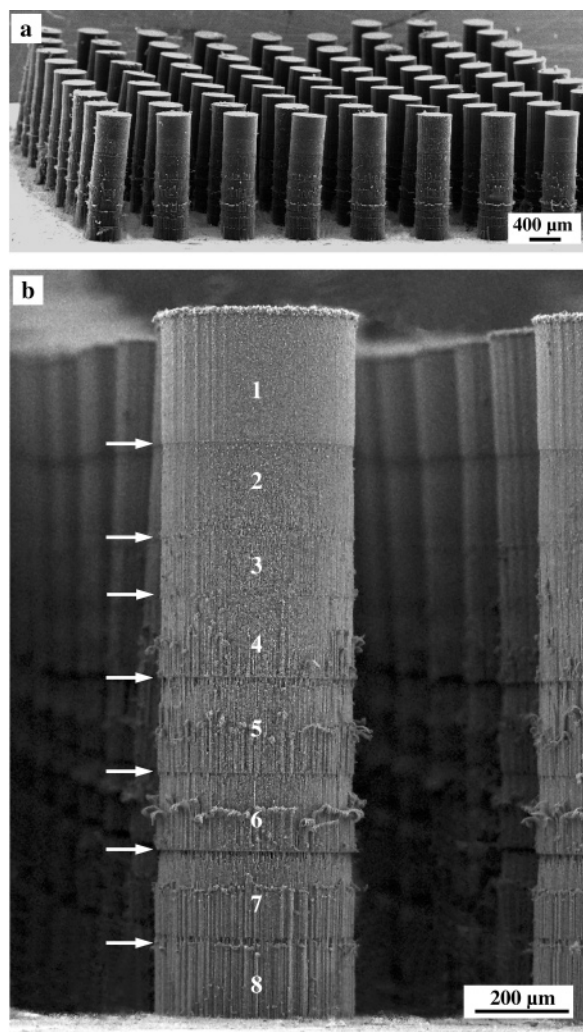
underneath the bottom of the multilayered stack of nanotubes. It also means that, every time a fresh layer is nucleated and grown from the bottom, the rest of the layers in the stack get lifted up from the substrate, moving up with the freshly growing nanotubes, from the bottom up. This unusual growth phenomenon has parallels in the growth of porous oxide films on metal surfaces.<sup>8,14</sup>

The aligned nanotube films are grown by a previously reported method,<sup>5</sup> using an injection chemical vapor deposition (CVD) method. A liquid mixture of xylene/ferrocene is evaporated and carried by Ar/H<sub>2</sub> carrier gas into a tube furnace heated to ~770 °C, and the length of the nanotubes grown is controlled by the CVD time (growth rate is typically ~10 μm/min). Figure 2 shows the evidence for the growth of multiple layers of blanket nanotube films over silicon oxide substrate, suggesting that buried growth can occur even if the layers completely cover the substrate. Figure 2a shows a completely covered two-layered film stack on the substrate. The first layer grown (marked 1), as seen, has moved to the top of the stack. A more clearly identifiable scheme is presented in Figure 2b, for a three-layered stack. Here, the first nanotube layer is grown over the entire SiO<sub>2</sub> substrate. To distinguish this layer from the subsequently produced layers, part of this layer is scratched off from the substrate. With the second CVD, a second new layer grows effectively under the existing first layer, but covering the whole substrate; the first layer gets pushed to the top. The third layer follows the same pattern. The growth rate, dimensions, orientation, and density of nanotubes are all identical for all

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**Figure 1.** (a) SEM image showing a two-dimensional array of pillars, each made of eight stacks of aligned nanotube layers. Eight separate growth sequences (CVD steps) were used to grow the eight stack pillars. The substrate made of SiO<sub>2</sub> has been patterned using Au patterns, and the nanotubes grow selectively in the SiO<sub>2</sub> exposed areas. (b) Higher-magnification SEM image showing the interfaces (position indicated by arrows) between the separate stacks of nanotubes in a single pillar. The stacks are numbered 1 to 8, corresponding to the first to the eighth stack grown sequentially. Interestingly, each subsequent stack is forming at the base, pushing the rest of the stack up, with the first stack ending at the top at the end of the growth sequence.

the layers, indicating that preexisting layers in the stack do not influence growth kinetics. Individual nanotubes are not contiguous between adjacent layers (Figure 2c), showing that preexisting nanotubes or catalyst particles are not responsible for the growth of a new layer, as reported in the case of single-walled nanotubes.<sup>15</sup>

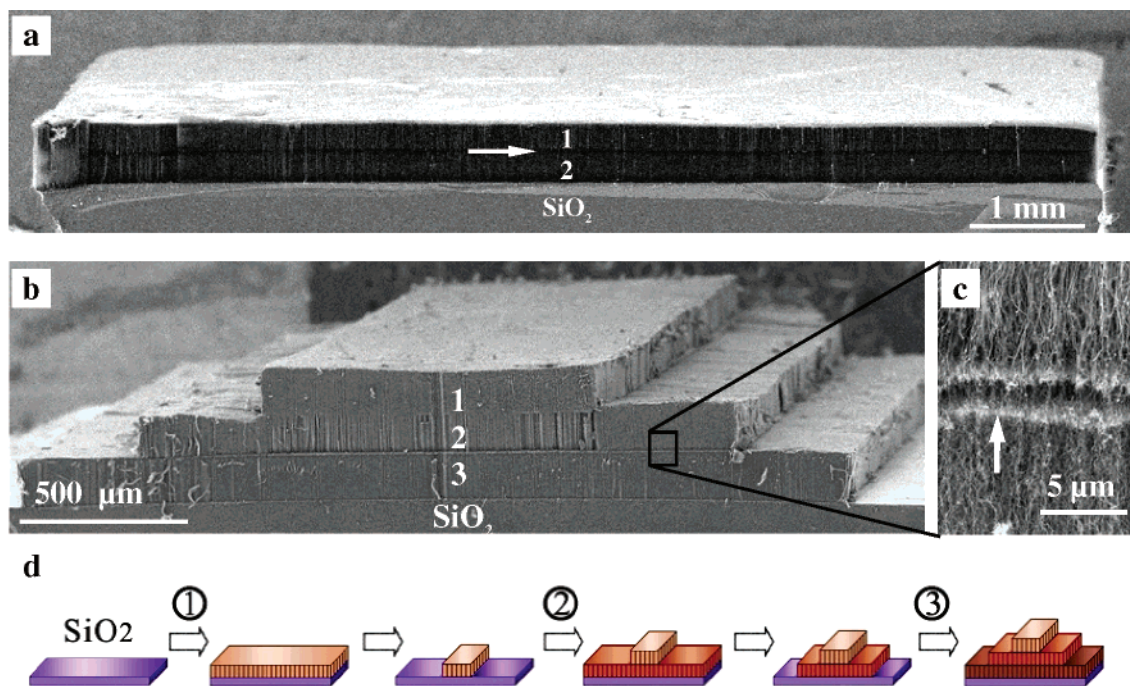
As was shown in Figure 1, growth on specified areas on the substrate can result in patterns consisting of multiple nanotube stacks. Selective growth is done by masking the SiO<sub>2</sub> substrate with Au patterns;<sup>16</sup> Figure 3 shows a four-stack pattern grown selectively on predefined areas on the substrate. The thickness of each layer in the stack is precisely controlled by the growth time (in Figure 3, the four layers have thicknesses of 300, 200, 100, and 200 μm, respectively).

Once again, the result is very clear—each fresh layer grows at the bottom of the stack, with the predeposited layers being lifted up, during each sequence of growth (see the schematic in Figure 3 for the representative growth mechanism). Stacks of various other pattern shapes can be grown in a similar fashion (for example, line patterns are shown in Figure S1, Supporting Information).

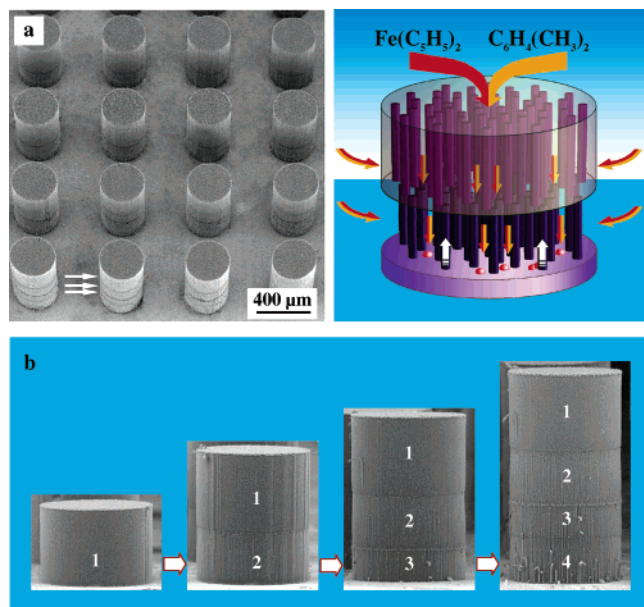
Our results suggest that vapors of the carbon source and catalyst precursor (xylene + ferrocene) diffuse through hundreds of microns of nanotube film and arrive at the bottom SiO<sub>2</sub> surface. The catalytic nucleation and growth of nanotubes by Fe particles (from ferrocene) occurs on this surface, which acts as an active catalyst support. The nanotube films grown by this technique are porous, with densities in the range ~0.1–0.2 g/cm<sup>3</sup>, suggesting that there is ample interstitial space between individual nanotubes in the film for diffusion of vapor. The average center-to-center distance between nanotubes (which have uniform diameters of ~25 nm; see Figure S2 in Supporting Information) in the film ranges between 50 and 100 nm.<sup>17</sup> The nanotube films, however, are self-supporting (and behave as a continuous film) because of the van der Waals interaction between individual nanotubes within the films. The thick layers of nanotube films formed over the substrate act as a permeable membrane that allows directed diffusion to the bottom. When only xylene is supplied (without ferrocene catalyst in the vapor) in any of the CVD sequence, no nanotube layers are formed, indicating that the growth is not catalyzed by the catalyst particles already present within prior grown layers, and each layer nucleates and grows fresh from the oxide substrate. The growth of individual nanotubes could follow either the tip growth or the base growth models<sup>18,19</sup> in this scenario.

The interaction between adjacent layers in a stack is not so strong, and each layer can be independently broken off. The stack, as a whole, can also be broken from the substrate, removed, and manipulated (Figure S3, Supporting Information), showing that the adhesion between the layers and the substrate is also not very strong. This allows for the easy vertical lift-up of the stacks as each new layer is added via the bottom of the stack, during growth. It is noted that the process of nucleating and growing new layers can be repeated several times (we have grown up to eight layers; Figure 1), without any degradation of the nanotube alignment and growth rate.

The phenomenon reported here that enables the growth of multiple stacks of nanotube films has no precedent in vapor-phase crystal film deposition.<sup>7</sup> Typical vapor-phase film growth of multilayers (by sputtering, CVD, etc.) proceed by the buildup of epitaxial layers on the top, with the fresh layer always being deposited as the top layer. The bottom-up growth of nanotube stacks, on the contrary, resembles qualitatively and at least characteristically porous oxide film growth by oxidation of metal surfaces. Many metals (e.g., Al) form impermeable thin oxide layers, which block further diffusion of oxygen to the buried metal surfaces and subsequently retard the buildup of the scales.<sup>20</sup> In cases where the oxide layer is porous, however, diffusion of oxygen



**Figure 2.** (a) SEM image of two layers of continuous vertically aligned nanotube films grown by CVD to cover the entire top surface of the substrate. As labeled, the first layer gets lifted up as the second layer grows underneath the first layer, over the buried substrate surface. (b) SEM of a pyramid structure consisting of three nanotube layers with increasing area, fabricated during three CVD runs (30 min duration each). The top layer was grown in the first run, and the bottom layer in the third run. (c) A larger-magnification image of the interface between adjacent layers, showing individual nanotubes that are aligned vertical to the interface. (d) Schematic of the assembly steps: (1) A blank SiO<sub>2</sub> substrate was used to grow the first nanotube layer by the first CVD run. To distinguish this layer from the subsequently produced layers, part of this layer is removed from the substrate. (2) A second complete layer is grown, and again, part of the layer is removed. (3) A third layer is grown which lifts up the first two layers, growing at the bottom, on the buried SiO<sub>2</sub> interface.



**Figure 3.** (a) SEM image of an array of 4-stack nanotube pillars. The interfaces between stacks are visible on each pillar (indicated by arrows on one of the pillars). (b) The sequence of growth of the pillars, shown at every step resulting in the progressive formation of more stacks. The corresponding growth times for the stacks are: first, 30 min; second, 20 min; third, 10 min; fourth, 20 min. The height of each stack corresponds to these deposition times. The schematic (top right) shows the mechanism of formation of stacks, via diffusion of precursor gases through the porous nanotube films. Only one complete stack and a growing stack are shown in the schematic. The fully grown stack gets lifted up as the new layer grows underneath, on the buried substrate.

species through the film allows continuous growth of oxide layer thickness at the bottom (buried metal surface). For example, anodic aluminum oxide grown by electrochemical oxidation of Al continues via diffusion of anionic oxygen through the porous oxide formed above, adding fresh oxide layers at the metal interface.<sup>8,14</sup> Similarly, the nanotube layers here act as fully permeable membranes that direct the diffusion of the precursor vapors of hydrocarbon and metal to the bottom substrate. The difference between the two scenarios is that, in the case of metal oxidation, the metal gets consumed during growth and the bottom plane of the oxide–metal interface travels down, where, as in the case of nanotube deposition, the substrate–nanotube interface remains at the starting position and nanotube buildup occurs above this level at all times. The phenomenon we have observed here is novel and could provide totally new approaches to multilayered porous film growth via catalytic vapor-phase deposition.

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**Supporting Information Available:** Two-layered carbon nanotube stack grown over a line pattern, TEM image of carbon nanotubes, free-standing pillars of eight-layered carbon nanotube stacks. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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