Patterned growth of single-walled carbon nanotubes on full 4-inch wafers

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Patterned growth of single-walled carbon nanotubes (SWNTs) is achieved on full 4-in. SiO_2/Si wafers. Catalytic islands with high uniformity over the entire wafer are obtained by a deep ultraviolet photolithography technique. Growth by chemical vapor deposition of methane is found to be very sensitive to the amount of H_2 co-flow. Understanding of the chemistry enables the growth of high quality SWNTs from massive arrays (10^7-10^8) of well-defined surface sites. The scale up in patterned nanotube growth shall pave the way to large-scale molecular wire devices. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1429294]

Single-walled carbon nanotubes (SWNTs) are ideal quantum systems for exploring basic science in one dimension.[1] These molecular-scale wires, derived by bottom-up chemical synthesis approaches, are also promising as core components or interconnecting wires for future electronics. Indeed, rich quantum phenomena have been revealed with SWNTs[2–5] and functional electronic devices have been built such as transistors,[3,4] chemical sensors,[6,7] and memory devices.[8] From both fundamental and practical point of views, it is desirable to assemble nanotubes into ordered structures on large surfaces for addressable and integrated devices. Not only should the assembly methods be able to place nanotubes at specific locations with desired orientations, the methods must be scalable to large areas.

Patterned growth of carbon nanotubes [e.g., by chemical vapor deposition (CVD)] represents an assembly approach to place and orient nanotubes at a stage as early as when they are synthesized.[9,10] Catalyst patterning defines the locations from which nanotubes originate,[11–14] and van der Waals self-assembly[12,15,16] or external fields[17] determine their orientations. While this approach has been effective in yielding SWNTs on small substrates for basic studies and device demonstrations, little is known about the scalability of surface catalytic patterning and the chemistry needed for growing nanotubes in large reactors.

Here we report the patterned growth of SWNTs on full 4-in. SiO_2/Si wafers. Wafer-scale catalytic patterning is achieved by deep ultraviolet (DUV) photolithography and spin casting. Catalyst islands with remarkable uniformity over the entire wafer are obtained. CVD of CH_4 (Refs. 11 and 18) at elevated temperatures is found to be ultrasensitive to the amount of H_2 co-flow, undergoing pyrolysis, growth, and inactive reaction-regimes with increased H_2 addition. Understanding of the chemistry enables the growth of high quality SWNTs from massive arrays (10^7-10^8) of well-defined surface sites on full 4-in. wafers.

A SiO_2/Si wafer was first coated with 300 nm thick of poly(methylmethacrylate) (PMMA) and exposed through a quartz mask to DUV under a Karl–Suss MA-6 photolithography system by using a home-assembled optical setup (light source: Oriel 200 W Hg Arc Lamp with Sun Lens beam diffuser by Spectral Energy). Developing the exposed regions resulted in large arrays of wells in the PMMA. A suspension of Al_2O_3 supported Fe/Mo catalyst in methanol[11] was spun onto the wafer at a low speed of 250 revolutions-per-minute followed by baking at 160 °C for 5 min. The wafer was then immersed in dichloroethane to lift off the PMMA, which afforded remarkably uniform catalyst arrays over the entire 4-in. wafer [Fig. 1(a)]. The catalyst islands vary in size down to 1 μm, limited by the mask resolution. We employed DUV and PMMA resist for catalytic patterning since PMMA was not dissolved by methanol in the catalyst suspension. Further, lift off of PMMA afforded a clean and smooth wafer surface with no PMMA residue left on the surface. With commonly used photoresists however, an undesired ''scum'' residue layer with roughness on the order of 10 nm was always left on the surface upon lift off.

CVD was carried out in at 900 °C for 7 min with the wafer placed in a 4-in.-diameter (48-in. long heating zone, Lindberg Blue) quartz tube furnace [Fig. 1(b)]. Pure CH_4 (99.999%) at a fixed flow rate of 1500 ml/min (1080 ml/min when the gas correction factor of 0.72 for methane is taken into account) was used for carbon feedstock. To investigate the growth conditions, H_2 was co-flown at a rate in the range of 50 to 150 ml/min.

Strikingly different CVD growth results are obtained

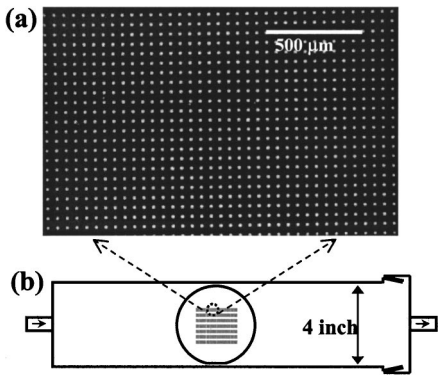

FIG. 1. (a) Optical image of an array of catalyst islands (side length 10 μm) patterned on a wafer using DUV lithography. (b) Diagram of the quartz tube reactor used for growth of nanotubes. Gases are introduced on the left-hand side and flown over the wafer placed in the center of the reactor. Exhaust leaves through the port on the right-hand side. The right-hand side cap of the tube is removable for wafer transfer.

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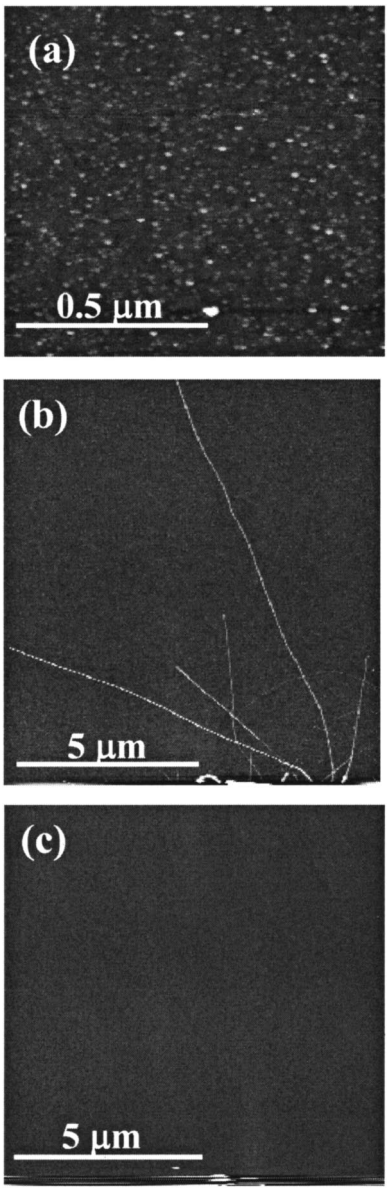

FIG. 2. AFM images of wafer surfaces near catalyst islands. (a) A rough surface with a significant amount of amorphous carbon deposits formed in the pyrolysis regime under a H_2 co-flow of 50 ml/min. (b) A clean surface and good yield of SWNTs grown from a catalyst island (at the bottom of the image, not shown) in the growth regime under a H_2 co-flow of 125 ml/min. (c) A clean surface but zero yield of SWNTs in the inactive regime with 150 ml/min H_2 co-flow.

when varying the amount of H_2 co-flow. The best condition for yielding high quality SWNT is with 125 ml/min H_2 co-flow. Figure 2(b) is an atomic force microscopy (AFM) image showing the typical results of SWNTs grown from patterned catalyst islands. Large numbers of SWNTs are observed near every island. Typically, several tubes emanate from the islands, extending to ~10 μm lengths. These long SWNTs are desired for device integrations. Growth results from catalyst islands across the entire 4-in. wafer are very consistent and uniform. Importantly, the SiO_2-wafer surface is clean without amorphous carbon deposits, indicating negligible CH_4 self-pyrolysis in the gas phase. We define the 1500 ml/min CH_4 and ~125 ml/min H_2 condition as in a desired ''growth-regime'' (Fig. 3).

A ''pyrolysis-regime'' was identified when H_2 co-flow was lowered to ~50 ml/min [Figs. 2(a) and 3]. Few SWNTs

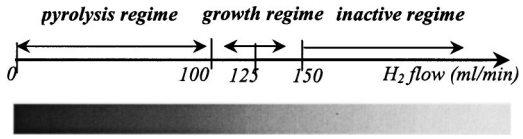

FIG. 3. Schematic presentation of three regimes of CVD growth conditions in a 4-in. system at 900 °C under a 1500 ml/min flow of CH_4. Darkness of the bar represents the amount of active carbon species in the three regimes.

were grown from catalyst islands, with AFM revealing the SiO_2-wafer surface covered by amorphous carbon deposits [Fig. 2(a)]. Worse was the observation of oily coating on the reactor wall by higher hydrocarbons generated during vigorous CH_4 pyrolysis. In contrast, an 'inactive-regime' was encountered when H_2 flow increased above ~150 ml/min [Figs. 2(c) and 3]. Clean wafer surface and reactor wall were seen but the yield of SWNTs from the catalytic islands was low (Fig. 3).

Thus, we have identified three regimes of CH_4-CVD conditions parameterized by H_2 concentration under a constant CH_4 flow in the 4-in.-CVD system (Fig. 3). The chemical reactivity of CH_4 is sensitive to H_2, a well-known phenomenon in hydrocarbon pyrolysis chemistry.[19] H_2 serves to decrease the rate of CH_4 decomposition by hydrogenating reactive carbon species.[19] Its presence slows down the CH_4 decomposition since H_2 is a product of the reaction. Nevertheless, our current finding of high sensitivity of SWNT growth to H_2 in CH_4 CVD is striking considering the small variations in H_2 concentrations that distinguish the three regimes (Fig. 3). In the pyrolysis regime ($H_2 < \sim 50$ ml/min), CH_4 decomposition is vigorous without effective H_2 inhibition. Amorphous carbon generation causes catalyst poisoning and low SWNT yield. In the inactive-regime ($H_2 > 150$ ml/min), the concentration of H_2 lowers the CH_4 reactivity below a level needed for CH_4 as an efficient carbon feedstock to the catalyst. In the growth regime ($H_2 \sim 125$ ml/min), the concentration of H_2 allows a good balance to prevent undesired amorphous carbon formation and maintain the CH_4 reactivity, leading to excellent results in catalytic SWNT growth. It should be noted that the growth conditions and results are also very sensitive to impurities in the methane gas and potential metal contaminations in the CVD quartz chamber. For consistent results, it is important to use ultrahigh purity methane as in the present work and avoid metal contamination of the system (due to deposition of vaporized metal species, e.g., Mo, onto the wall of the quartz chamber).

The aforementioned chemistry is essential to identifying highly reproducible and controllable growth conditions, and key to our patterned SWNT growth on full 4-in. wafers. More importantly, the understanding is general and applicable to predicting growth conditions for different temperatures and CH_4 flow rates, and can be extended to CVD growth for multiwalled nanotubes.[20] For instance, at 950 °C, a growth regime for SWNT is identified with 1500 ml/min CH_4 flow and 200 ml/min H_2 co-flow. This condition is found when increasing the H_2 concentration just beyond the pyrolysis regime. The reactivity of methane is higher at a more elevated temperature (950 °C vs 900 °C), thus, a higher concentration of H_2 (200 vs 125 ml/min) is required to inhibit CH_4 decomposition and bring the system into the nanotube growth regime.

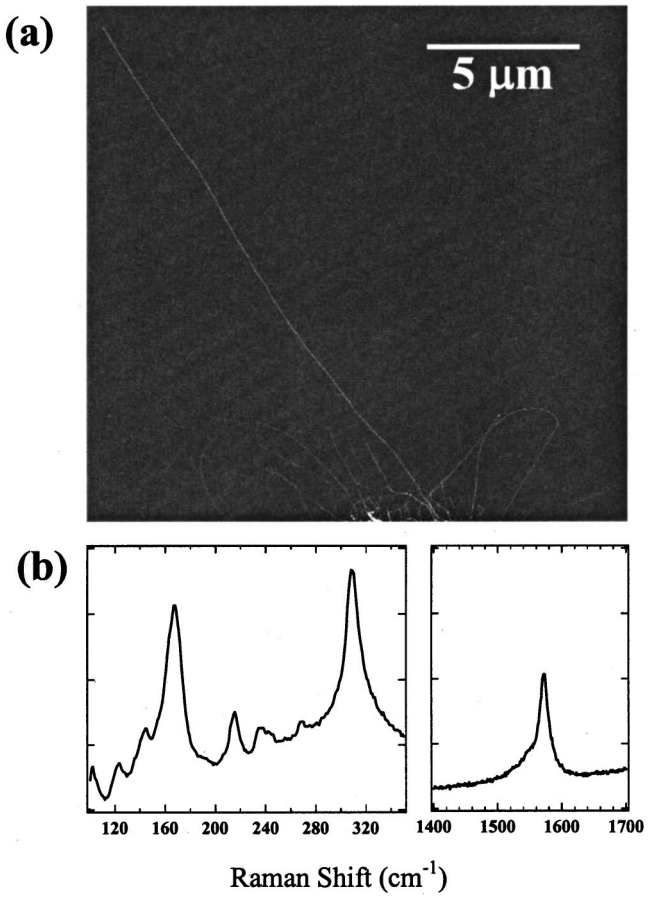

FIG. 4. (a) AFM image of nanotubes grown from a catalyst island (at the bottom of the image, not shown) on a 4-in. wafer. (b) Raman spectra of carbon nanotubes growing off of a catalyst island.

The patterned growth of SWNTs on full 4-in. wafers presented here is highly reproducible and controllable. Importantly, AFM characterization reveals no drastic variations in the yield of nanotubes from catalytic islands across the wafer surface with typically 1 to 3 long SWNTs emanating from each island [Figs. 4(a) and 2(b)]. The SWNTs are also characterized by resonant micro-Raman spectroscopy[21] (Renishaw, 785 nm laser) using a 1 μm laser beam focused a few microns away from catalyst islands. The spectra show very typical SWNT axial vibration modes around 1590 cm^{-1} and radial breathing modes (RBM) around 120–320 cm^{-1} [Fig. 4(b)], confirming that high quality SWNTs (diameters $d \sim 1$–3 nm, RBM Raman shift[21] $\sim 1/d$) are synthesized from catalytic patterns.

The scale up of patterned growth allows for high quality SWNTs readily integrated into electrical circuits at the wafer scale. This is done by carrying out a wafer-scale photolithography step for metal contacts of the nanotubes around each catalytic island after CVD synthesis. Detailed results of electrical transport properties and devices with the nanotube arrays will be presented elsewhere.

In conclusion, we have succeeded in patterned growth of massive arrays of SWNTs at the full-wafer scale. The chemistry of CH_4 CVD is found to be sensitive to the concentration of H_2, leading to three regimes of growth conditions. This very understanding has enabled our synthesis scalability. We believe that the understanding could also be useful for CVD type of synthesis of other nanomaterials. The results here shall pave the way for patterned growth at the individual catalytic nanoparticle[22] level, nanotube orientation control and device integration in a scalable fashion for future nanoelectronics.

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[1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Ekhlund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[2] C. Dekker, Phys. Today **52**, 22 (1999).
[3] P. L. McEuen, Phys. World **13**, 31 (2000).
[4] W. Liang, M. Bockrath, D. Bozovic, J. Hafner, M. Tinkham, and H. Park, Nature (London) **411**, 665 (2001).
[5] J. Kong, E. Yenilmez, T. W. Tombler, W. Kim, L. Liu, C. S. Jayanthi, S. Y. Wu, R. B. Laughlin, and H. Dai, Phys. Rev. Lett. **87**, 106801 (2001).
[6] J. Kong, N. Franklin, C. Zhou, M. Chapline, S. Peng, K. Cho, and H. Dai, Science **287**, 622 (2000).
[7] P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, Science **287**, 1801 (2000).
[8] T. Rueckes, K. Kim, E. Joselevich, G. Y. Tseng, C. L. Cheung, and C. M. Lieber, Science **289**, 94 (2000).
[9] H. Dai, Phys. World **13**, 43 (2000).
[10] H. Dai, in *Carbon Nanotubes*, edited by M. S. Dresselhaus, G. Dresselhaus, and P. Avouris (Springer, Berlin, 2001), Vol. 80, p. 29.
[11] J. Kong, H. Soh, A. Cassell, C. F. Quate, and H. Dai, Nature (London) **395**, 878 (1998).
[12] S. Fan, M. Chapline, N. Franklin, T. Tombler, A. Cassell, and H. Dai, Science **283**, 512 (1999).
[13] Y. Yang, S. Huang, H. He, A. Mau, and L. Dai, J. Am. Chem. Soc. **121**, 10832 (1999).
[14] G. Gu, G. Philipp, X. Wu, M. Burghard, A. Bittner, and S. Roth, Adv. Func. Mater. **11**, 295 (2001).
[15] A. Cassell, N. Franklin, T. Tombler, E. Chan, J. Han, and H. Dai, J. Am. Chem. Soc. **121**, 7975 (1999).
[16] N. Franklin and H. Dai, Adv. Mater. **12**, 890 (2000).
[17] Y. Zhang, A. Chan, J. Cao, Q. Wang, W. Kim, Y. Li, N. Morris, E. Yenilmez, J. Kong, and H. Dai (unpublished).
[18] M. Su, B. Zheng, and J. Liu, Chem. Phys. Lett. **322**, 321 (2000).
[19] A. Dean, J. Phys. Chem. **94**, 1432 (1990).
[20] D. Wang, P. Qi, and H. Dai (unpublished result).
[21] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. **86**, 1118 (2001).
[22] Y. Li, J. Liu, Y. Wang, and Z. L. Wang, Chem. Mater. **13**, 1008 (2001).