

Formation of Single-Walled Carbon Nanotubes via Reduced-Pressure Thermal Chemical Vapor Deposition

Ruth Zhang,* Raymond K. Tsui, John Tresek, Adam M. Rawlett, Islamshah Amlani, and Theresa Hopson

Physical Sciences Research Laboratories, Motorola Labs, 7700 South River Parkway, Tempe, Arizona 85284

Peter Fejes

Digital DNA Lab, Semiconductor Product Sector, Motorola, 2100 East Elliot Road, Tempe, Arizona 85284

Received: August 21, 2002

We report the growth of carbon nanotubes (CNTs) via reduced-pressure chemical vapor deposition (CVD), using a gas mixture of methane/hydrogen and iron/molybdenum catalyst supported by alumina nanoparticles. The CNTs are either single-walled or double-walled as characterized by transmission electron microscopy. Investigation of various growth parameters indicates that CNT growth is limited by the gas supply when CVD is performed in the temperature range of 750–900 °C, whereas the limiting factor for growth at 700 °C is the rate of carbon diffusion through the catalyst particles. The density of CNTs changes with CVD pressure as well as gas flow rates when growth is limited by gas supply. We also use a single-step lithographic approach to form catalyst islands on top of patterned electrodes and to selectively grow CNTs bridging neighboring electrodes. The process yields both semiconducting and metallic CNTs as characterized by current–voltage measurements.

Introduction

Carbon nanotubes (CNTs) are potential building blocks for future nanoelectronic devices because of their unique structural, physical, and chemical properties.^{1,2} Single-walled carbon nanotubes (SWNTs) can behave as one-dimensional semiconductors or metals depending upon their diameter and chirality. Recently, prototype devices such as single-electron transistors,^{3–8} field-effect transistors,^{9–12} and sensors^{13,14} have been demonstrated using SWNTs as active components. To realize the full potential of SWNTs, the controlled growth of high quality material is essential. SWNTs are traditionally synthesized by laser ablation of carbon rods or direct current arc discharge between carbon electrodes in an inert gas environment. The common drawbacks of these two methods are that the tubes are formed under extremely high temperatures and are usually produced as bundles covered with amorphous carbon. Although various approaches have been developed to purify and debundle the tubes, it is still a very inefficient process to fabricate a device using those tubes.

Recently, Kong et al. used a catalyst-assisted chemical vapor deposition (CVD) approach to synthesize high quality SWNTs at relatively low temperatures.¹⁵ They demonstrated the selective growth of SWNTs by performing CVD on substrates with catalyst islands patterned using electron beam lithography.¹⁶ Furthermore, they fabricated transistor-like devices by performing a second lithography step to form electrodes.¹⁷ The advantage of this approach is that it allows the integration of SWNT synthesis with conventional semiconductor processes. However, this CVD method grows CNTs under atmospheric pressure with high gas flow rate through a quartz tube one inch

in diameter.^{15,16} The high reaction pressure and gas flow rate may raise environment and safety concerns when the process is to be scaled up for a full wafer process using large diameter quartz tubes. Therefore, one needs to explore SWNT growth using different CVD conditions. In addition, the reported approach for making electrical contact to SWNTs is cumbersome and may cause damage and contamination during the post-growth patterning process.

In this paper, we report the growth of CNTs by CVD at reduced pressures using relatively low gas flow rates. This modified CVD approach is environmentally benign and reduces safety concerns due to greatly reduced usage of hydrocarbon gas. It also allows us to investigate the effect of growth conditions on the formation mechanism of CNTs. In addition, we describe a pre-growth lithographic approach for selective growth of CNTs from patterned catalyst to bridge predefined electrodes using the CVD process. This new approach consists of first patterning metallic contact pads (electrodes), followed by patterning catalysts on top of the electrodes. CVD is then performed to form CNTs that bridge neighboring electrodes. These structures are ready for electrical testing immediately after the CVD process. Thus, contamination and/or damage to the CNTs are minimized, and yield of CNT devices is improved.

Experimental Section

The catalyst was prepared as reported by Cassell et al.¹⁸ Alumina nanoparticles were impregnated into a mixed salt solution of $\text{Fe}(\text{SO}_4)_3/(\text{NH}_4)_4\text{Mo}_7\text{O}_{24}/\text{H}_2\text{O}$ with a molar composition of $\text{Fe}:\text{Mo}:\text{Al}_2\text{O}_3 = 1:0.17:16$. The catalyst was then either spun or sprayed onto an oxidized Si wafer and dried in a vacuum oven at 80 °C for 10 min. For selective growth, the substrate was first patterned by optical lithography. Ti (10 nm) and Au (300 nm) were deposited as material for the electrodes. After

* To whom correspondence should be addressed. E mail: A783AA@motorola.com.

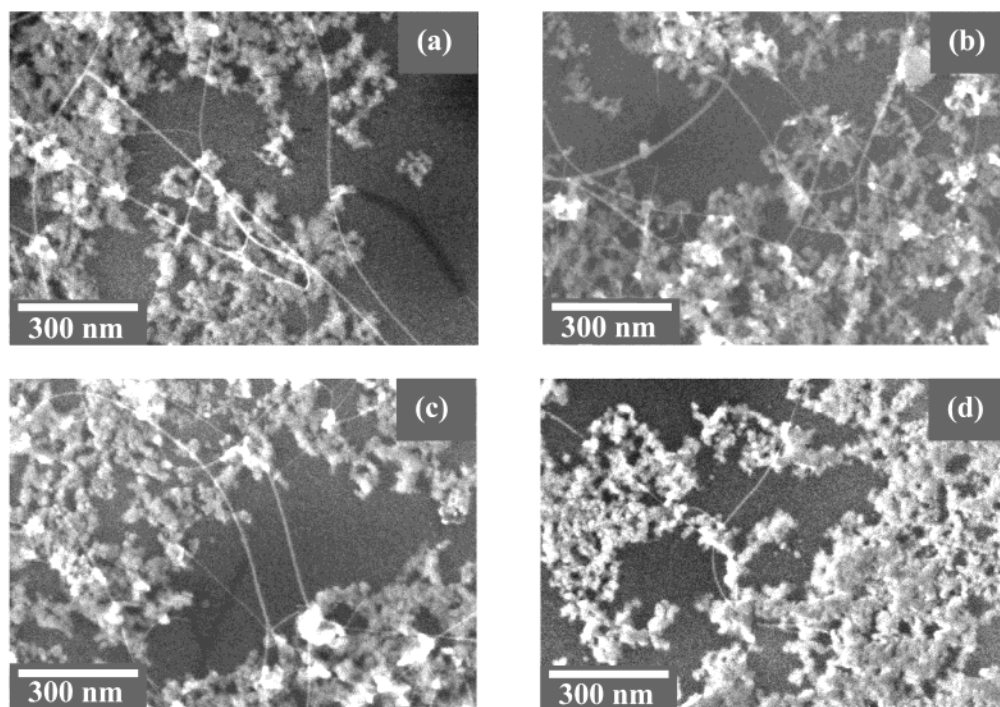


Figure 1. SEM images of CNTs grown at a pressure of 100 Torr, with methane and hydrogen flow rates of 60 and 40 sccm, respectively, and at various temperatures: (a) 900 °C; (b) 800 °C; (c) 750 °C; (d) 700 °C. The growth duration was 15 min in all cases.

metallization, the catalyst was sprayed on the metal-coated substrate which was then subjected to a conventional metal lift-off process. The finished substrate thus had catalyst only on the desired metal pads.

CNT growth was performed in a hot wall reactor fitted with a 3-in. diameter quartz tube (Tek-Vac Model CVD-300-M). After loading the substrate into the furnace, the reactor was evacuated to a base pressure of 1×10^{-6} Torr with a turbo molecular pump. Gas flow rates were controlled using mass flow controllers, and reaction pressure was regulated by a capacitance manometer that had feedback control to the pump inlet valve. The tube was first heated to 200 °C under vacuum and maintained at this temperature for 30 min. Hydrogen (H_2) was then introduced while the tube is gradually heated to the growth temperature. Growth was initiated at the reaction temperature by adding methane (CH_4) to the gas flow. Growth duration was 15 min, and the flow ratio of CH_4 to H_2 was fixed at 3 to 2. Samples were characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). The yield (i.e., density) of CNTs was estimated by examining the number of tubes grown in a given area of the substrate.

Results and Discussion

First we studied the formation of CNTs at different temperatures under a constant reaction pressure of 100 Torr, with flow rates of CH_4 and H_2 at 60 and 40 sccm, respectively. Figure 1 shows SEM images for CNTs grown at temperatures ranging from 700–900 °C. Nanotubes with uniform diameters are distributed over the catalyst-coated substrate. The fact that we did not observe any significant change in the density of CNTs in the temperature range of 750–900 °C (Figure 1a–c) indicates that the CNT growth is not limited by the temperature driven diffusion of carbon atoms through catalyst particles. However, when the temperature was reduced to 700 °C, a significant decrease in CNT density was observed (Figure 1d). We believe the diffusion rate of carbon atoms through the catalyst particles

is slower than the gas supply rate in this case, so the CNT growth process has turned into a diffusion-limited one.

Detailed structures of the CNTs were analyzed using TEM. The results indicate that the CNTs are either single-walled, with diameters of 1.4 or 2.6 nm, or double walled, with diameters of 2.8 or 3.9 nm. Typical TEM images are shown in Figure 2. The lengths of the CNTs range from a few hundred nm to several tens of microns as measured by AFM (data not shown).

Figure 3, parts a and b, show SEM images for CNTs grown at a constant temperature of 800 °C using a CH_4 flow rate of 60 sccm along with 40 sccm of H_2 at a reaction pressure of 50 and 10 Torr, respectively. Comparing with the results shown in Figure 1b, we notice that the density of the CNTs decreases as the pressure is reduced. When the reaction pressure decreases, the density of CH_4 molecules decreases, which reduces the probability of their reaction with the catalyst particles. Consequently, fewer CNTs are grown at a lower reaction pressure. This pressure dependence indicates that the number of carbon atoms supplied to the substrate limits the growth process. We did not observe any density change with pressure for growth performed at 700 °C (data not shown), which further supports the argument that CNT growth at this lower temperature is limited by the diffusion rate of carbon molecules through catalyst particles.

Additionally, we investigated the effect of gas supply rates on the growth of CNTs. As shown in Figures 3, parts b and c, we did not observe any significant changes in CNT density when we reduced the gas supply rates by a factor of 10 for growth at a pressure of 10 Torr. However, if we compare growths performed at 100 Torr with different gas flow rates, i.e., Figure 1b with Figure 3d, we notice that the number of CNTs reduces dramatically as the gas supply rate decreases. This suggests that there is a correlation between the gas supply rate and the gas consumption rate during a catalyzed CVD process. As we mentioned earlier, for a fixed catalyst density, the number of catalyst particles activated for CNT formation is determined by the density of CH_4 molecules, i.e., the reaction pressure. At

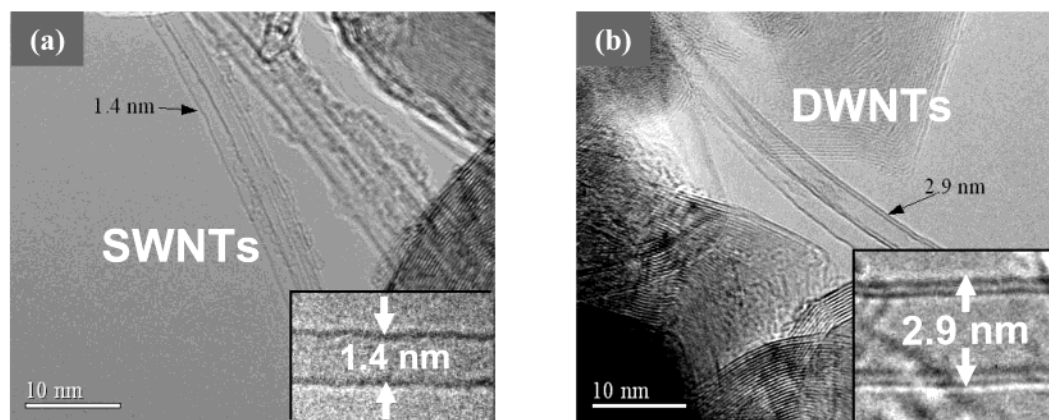


Figure 2. TEM images showing (a) single-walled nanotubes and (b) double walled nanotubes. The insets are magnified views.

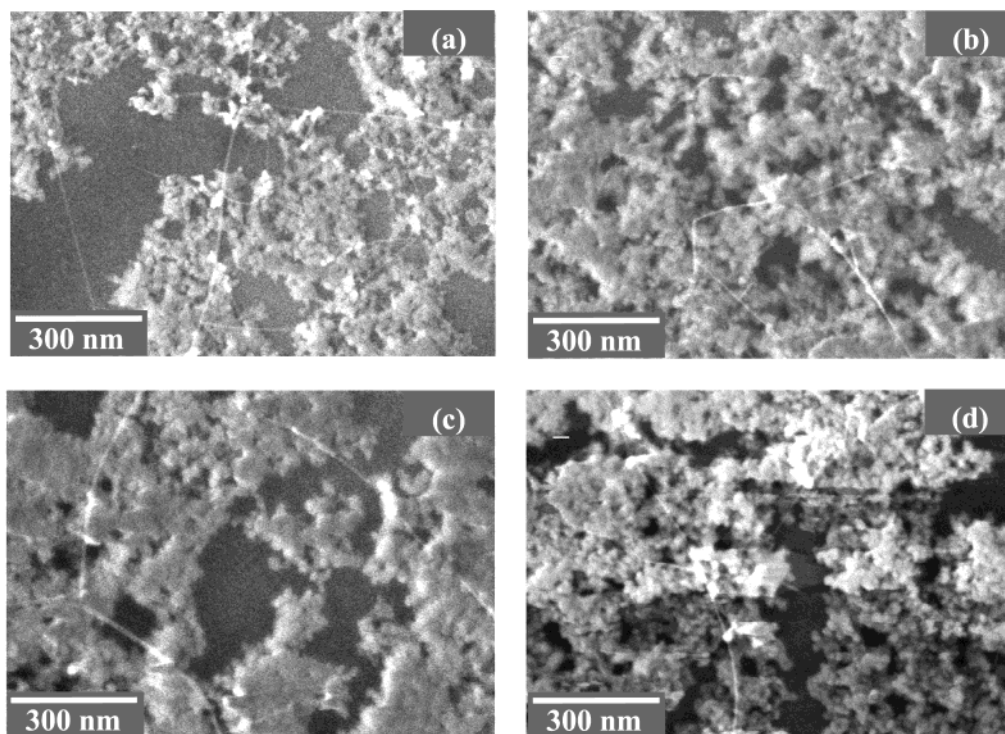


Figure 3. SEM images of CNTs grown at 800 °C with CH₄/H₂ flow rates of (a) 60 sccm/40 sccm at a reaction pressure of 50 Torr; (b) 60 sccm/40 sccm at a reaction pressure of 10 Torr; (c) 6 sccm/4 sccm at a reaction pressure of 10 Torr; (d) 6 sccm/4 sccm at a reaction pressure of 100 Torr. The growth duration was 15 min in all cases.

lower pressures, fewer CH₄ molecules interact with the catalyst particles. As a result, fewer catalyst particles get activated for CNTs growth, and the gas consumption rate is thus slower. When the gas flow rate is greater than the gas consumption rate, further increases in gas flow rate will not increase the CNT density but will only result in additional undecomposed gas molecules in the exhaust. On the other hand, when the CVD process is carried out at higher pressures, more catalyst particles are bombarded by the CH₄ molecules and become active sites for CNT growth. As a result, more CH₄ molecules will be consumed at higher reaction pressures. However, if the gas flow rate is smaller than the gas consumption rate, the growth is limited by the gas supply, and a decrease in CNT density is expected. We believe these observations provide useful information in designing CVD processes for the growth of CNTs and fabrication of CNT devices. For example, one can use the growth condition to control the number of CNTs bridging the neighboring electrodes patterned with a given amount of catalyst.

We also measured the transport properties of CNTs grown out of catalyst islands patterned on top of Au electrodes. Figure 4a shows the SEM image of a CNT bridging two electrodes separated by about 1 μm as grown by this selective CVD process. This approach allows a rapid turn-around in the electrical characterization of the CNTs after growth. Current–voltage (*I*–*V*) measurements were carried out at room temperature on a probe station using the Au electrodes as source and drain contacts and the substrate as a backside gate. The contact between the CNT and the Au electrode is mechanically stable, and two-point resistances (with gate voltage at 0 V) range from a few hundred k Ω to a few tens of M Ω . We observed that when both ends of a SWNT makes direct contact to the top of a Au electrodes, and the contact resistance is low and comparable to the results obtained using the post CVD growth contact approach.¹⁷ On the other hand, if a CNT makes contact through the catalyst materials, high contact resistance of a few tens of M Ω is usually observed. The *I*–*V* data indicate that both

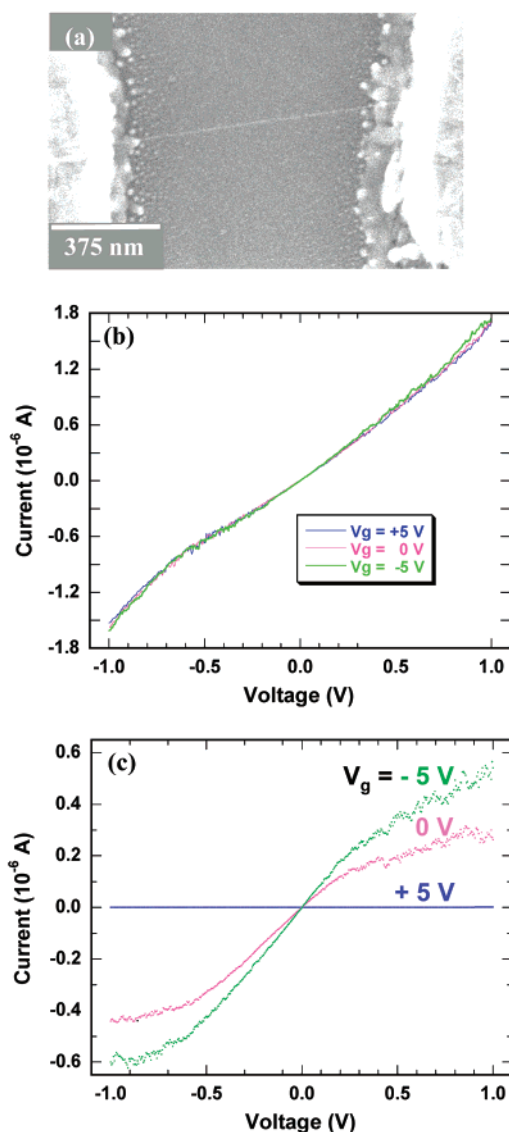


Figure 4. (a) SEM image showing two pre-patterned Au electrodes bridged by a CNT grown selectively by CVD. (b) Room-temperature I–V curves of a metallic tube under different gate bias V_g . (c) Room-temperature I–V curves of a semiconducting tube for different gate bias V_g .

semiconducting and metallic tubes can be obtained in this CVD process. Figure 4, parts b and c, show typical I–V curves measured for samples grown on patterned wafers. The CNT in Figure 4b is metallic because the curves are essentially linear and do not show any dependence on gate voltage. Figure 4c shows the growth of semiconducting CNTs in our CVD process. The sample in Figure 4c is p-type as current flow can be turned off by applying a sufficiently large positive gate voltage.

Summary

In summary, the growth of CNTs using Fe/Mo catalysts supported by alumina nanoparticles under reduced pressure CVD conditions is reported. The CNTs are either single-walled or doubled-walled and can be semiconducting or metallic in their transport behavior. We have studied the effect of various CVD parameters such as temperature, pressure, and gas flow rates on the growth of CNTs. The results provide a better understanding for the formation mechanism of CNTs in a CVD process. Furthermore, we report the use of a single-step lithographic approach to define catalysts on metallic electrodes for the subsequent CVD of CNTs. This simplifies the patterning process for the fabrication of CNT-based devices and eliminates damage and contamination that may occur during post-CVD patterning. It also allows one to carry out CNT growth under the influence of an electric field for CNT alignment using conventional Au electrodes.¹⁹

Acknowledgment. The authors would like to thank Dr. Herb Goronkin for support of this work and the Motorola APCL for assistance in processing and characterization.

References and Notes

- (1) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.
- (2) Dekker: C. *Physics Today* 1999, 52 (5), 22–28.
- (3) Collins, P. G.; Avouris, Ph. *Sci. Am.* **2000**, 62–69.
- (4) Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997**, 386, 474–477.
- (5) Kong, J.; Zhou, C.; Yenilmez, E.; Dai, H. *Appl. Phys. Lett.* **2000**, 77, 3977–3979.
- (6) Park, J.; McEuen, P. L. *Appl. Phys. Lett.* **2001**, 79, 1361–1363.
- (7) Postma, H. W. Ch.; Teepen, T.; Yao, Z.; Grifoni, M.; Dekker, C. *Science* **2001**, 293, 76–79.
- (8) Kong, J.; Cao, J.; Dai, H.; Anderson, E. *Appl. Phys. Lett.* **2002**, 80, 73–75.
- (9) Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, Ph. *Appl. Phys. Lett.* **1998**, 73, 2447–2449.
- (10) Liu, Y.; Lee, C.; Zhou, C. *Appl. Phys. Lett.* **2001**, 79, 3329–3331.
- (11) Derycke, V.; Martel, R.; Appenzeller, J.; Avouris, Ph. *Nano Lett.* **2001**, 1, 453–456.
- (12) Bachtold, A.; Hadley P.; Nakanishi, T.; Dekker: C. *Science* **2001**, 294, 1317–1320.
- (13) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, 287, 622–625.
- (14) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, 123, 3838–3839.
- (15) Kong, J.; Cassell, A. M.; Dai, H. *Chem. Phys. Lett.* **1998**, 292, 567–574.
- (16) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. *Nature* **1998**, 395, 878–881.
- (17) Soh, H. T.; Quate, C. F.; Morpurgo, A. F.; Marcus, C. M.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **1999**, 75, 627–629.
- (18) Cassell, A. M.; Raymakers, J. A.; Kong, J.; Dai, H. *J. Phys. Chem. B* **1999**, 103, 6484–6492.
- (19) Zhang, Y.; Chang, A.; Cao, J.; Wang, Q.; Kim, W.; Dai, H. *Appl. Phys. Lett.* **2002**, 79, 3155–3157.