NANO LETTERS

Letter

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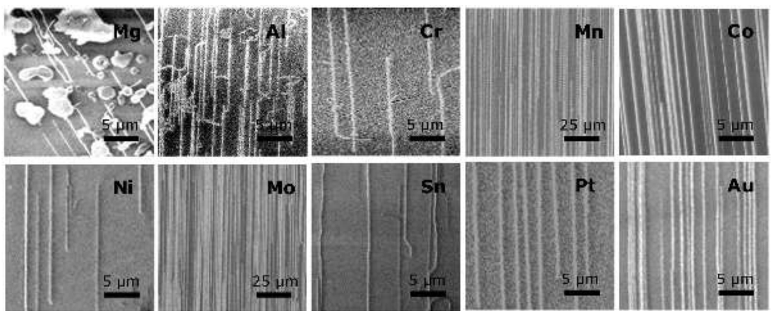
Nano Lett., **2008**, 8 (8), 2576-2579 • DOI: 10.1021/nl801007r • Publication Date (Web): 02 July 2008



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NANO LETTERS
2008
Vol. 8, No. 8
2576-2579

Horizontally Aligned Single-Walled Carbon Nanotube on Quartz from a Large Variety of Metal Catalysts

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Received April 8, 2008; Revised Manuscript Received June 5, 2008

ABSTRACT

Horizontally aligned single-walled carbon nanotubes (SWNTs) are highly desired for SWNT device applications. A large variety of metals including Fe, Co, Ni, Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, and Al successfully catalyzed the growth of such tubes on stable temperature (ST)-cut quartz by lattice guidance. In addition, Mg and Al were presented to produce random and aligned SWNTs for the first time. A hypothesis is proposed in which the precipitated carbon shell on the outer surface of the metal catalysts guides the alignment along the crystal lattice but not the catalysts themselves. By elucidating the role of the catalysts, an understanding of the aligned growth mechanism on quartz is further improved. Moreover, a simple "scratch" method by a razor blade such as the carbon steel and tungsten carbide (with 9% cobalt) is presented to pattern the "catalysts" without any complex processing steps such as lithography for the aligned SWNT growth.

Since their discovery by Iijima,[1] single-walled carbon nanotubes (SWNTs) have displayed potential in a variety of promising applications such as field effect transistors (FETs),[2] sensors,[3] light emitters,[4] logic circuits,[5] and so forth. To fulfill their potential in these applications in large scale, the location and orientation of SWNTs must be controlled; specifically, horizontally aligned organization on a flat substrate is in high demand. Post growth alignment methods such as the novel "blown bubble films"[6] are excellent for large scale and flexible substrates; however, the nanotubes used are generally short and exposed to strong acid during purification. Direct growth[7] by chemical vapor deposition (CVD) with an external force has emerged as the most attractive approach for meeting this demand. Such aligning external forces can originate from an electric field,[8] the gas flow,[9] or interactions with the substrate surface.[10–13] Among them, the surface-guided growth on single crystal substrates such as sapphire[10] or quartz[11–13] surpasses the others because of the high density and perfect alignment.[14] However, the basic alignment mechanism is still unclear. Atomic steps, nanofacets, crystallographic lattice, or a mix of these are assumed to be the guidance force without further clarification.[12,15] Moreover, the alignment driving force either from the tube−substrate or catalyst−substrate has not been distinguished because the evidence of either tip or base growth is lacking. Recently, our group has proved the crystal-lattice-guided growth on ST-cut quartz and demonstrated the tip-growth mechanism.[16] Thus, the catalysts play the major role during the crystal guided growth and will be the research focus in order to explore the full mechanism. Up to date, the catalysts have been limited to Fe[10,12–15,17,18] and Cu[16] (recently used by our group). It is important to know whether some metals could catalyze the aligned growth and some could not, and more importantly, whether different catalysts could grow nanotubes with different helicities. Narrow (n, m) distribution of SWNTs by Co−Mo has been reported, indicating that the chirality is related to the types of catalysts.[19] By exploring new catalysts for SWNT aligned growth on quartz, the guidance mechanism might be further understood; it is hoped that this will lead to type-controlled and orientation-controlled SWNTs synthesis. These goals motivate this report, in which 13 kinds of metals show horizontally lattice-aligned growth of carbon nanotubes on quartz substrates. The growth mechanism is discussed. In addition, Mg and Al are reported to grow SWNTs for the first time. Moreover, an easy blade "cut" method without any additional processing steps for the formation of patterned catalysts is demonstrated.

In this research, SWNTs were all grown by catalytic CVD using methane and hydrogen under the same growth process (see Supporting Information) to avoid any effect by the changing of growth conditions. Besides the commonly used iron-family metal catalysts such as Fe, Co, and Ni, other less common catalysts like Au, Pt, Pd, and Cu[20–22] and some rarely used metals such as Mn, Mo, Cr, and Sn were employed. Most of them have never been shown to grow horizontally lattice-aligned SWNTs on quartz. Additionally, Mg and Al were chosen because they have never been

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10.1021/nl801007r CCC: $40.75
Published on Web 07/02/2008

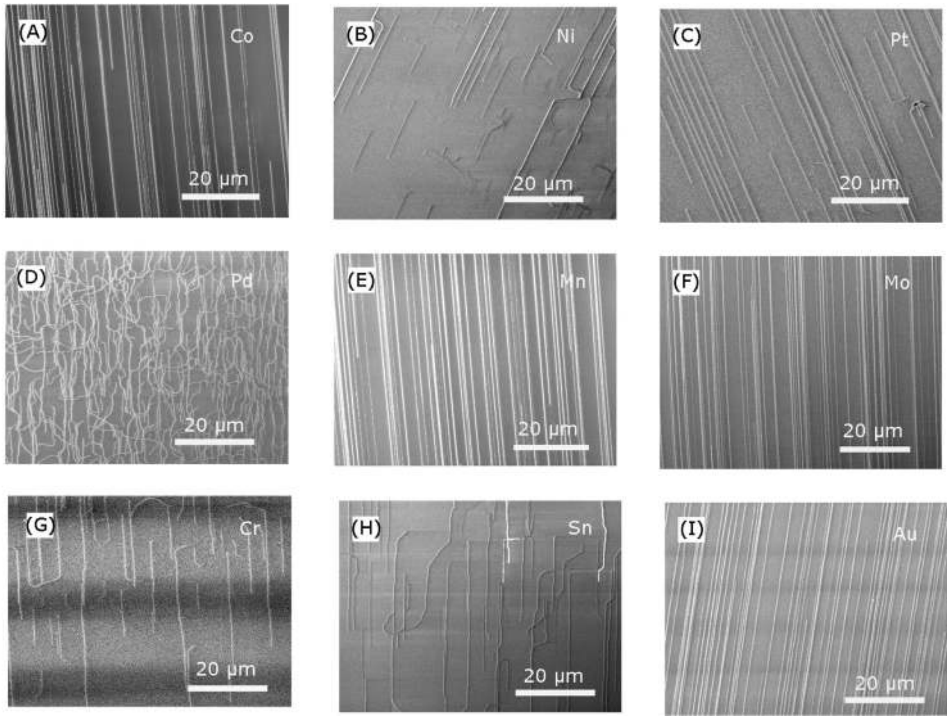

Figure 1. SEM images of horizontally aligned SWNTs growth by (A) Co, (B) Ni, (C) Pt, (D) Pd, (E) Mn, (F) Mo, (G) Cr, (H) Sn, and (I) Au. The alignment direction is the X direction on ST-cut quartz.

demonstrated as catalysts for carbon nanotubes and researchers commonly believe they are not able to grow carbon nanotubes. To our best knowledge, it is also the first time to show such a large variety of metals catalyzing SWNTs growth under the same growth conditions.

As shown in Figure 1, horizontally aligned SWNTs along the X direction of quartz surface can be seen, catalyzed by Co (Figure 1A), Ni (Figure 1B), Pt (Figure 1C), Pd (Figure 1D), Mn (Figure 1E), Mo (Figure 1F), Cr (Figure 1G), Sn (Figure 1H), and Au (Figure 1I). Fe and Cu can also produce such result under the same condition (see Supporting Information). The tubular structures grown by Cu were shown to be SWNTs according to the less than 2.8 nm diameter measured by AFM and Raman spectroscopy (see Supporting Information). The samples by Co and Au were also confirmed to be SWNTs by AFM measurement with diameter less than 2 nm and 3 nm, respectively (see Supporting Information). The degree of alignment and yield vary for different metals probably because the fixed growth conditions used here are not the optimal conditions for every metal catalyst. The gas flow rate was found not to affect the alignment direction and the surface is free of steps measurable by AFM as demonstrated previously.[16]

Additionally, Mg (Figure 2A) and Al (Figure 2B) were able to catalyze the growth of horizontally aligned SWNTs along the X direction of quartz. Highly pure salt (99.995% magnesium chloride hexahydrate and 99.999% aluminum chloride from Sigma Aldrich) and ethanol (>99.5% from Sigma Aldrich) were used to avoid any complication by possible impurity inside the salt or solvent. Furthermore, control experiments on a bare quartz wafer and another wafer with only ethanol washing were done together with the substrates which had Mg or Al catalysts. No tubes were found on these substrates. Therefore, the SWNTs are confirmed to be from the Mg and Al.

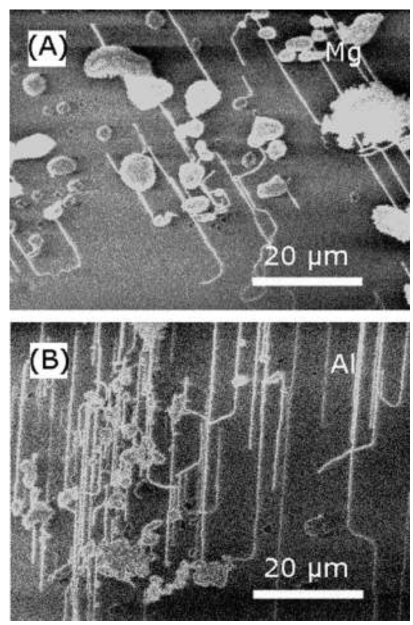

Figure 2. SEM images of horizontally aligned SWNTs growth by (A) Mg and (B) Al. The alignment direction is the X direction on ST-cut quartz.

From these results, horizontally aligned SWNTs along the X direction on ST-sut quartz can be synthesized from many metal catalysts, some of which were previously believed to be inactive for SWNT growth. Similar experiments on Si wafers with a 1 μm thermal oxide layer were also performed; they show random SWNTs networks obtained for each metal under the same treatment and growth conditions (see

Supporting Information). The only difference is that the nanotubes grown on the crystal SiO_2 surface of quartz are aligned and those grown on the amorphous thermal SiO_2 on top of Si wafer are random.

The origin of the alignment is still not well-understood. In previous publications, Rogers et al. attributed the alignment to the atomic steps formed on ST-cut quartz. In their reports, atomic steps are formed by thermal annealing of the substrates under high temperature for an extended period of time, and the steps are easily observable under AFM measurements. However, in all of the results reported here, AFM measurements showed no obvious steps; no thermal annealing was performed on the substrates. Additionally, the degrees of alignment for different growth experiments are different as shown in Figure 1. For example, tubes synthesized from Pd have relatively poor alignment under the same growth condition as other metals; however, it can be greatly improved when the growth is changed to the optimal condition. If the alignment is caused by the atomic steps, such differences are not expected since all experiments are performed on the same wafer. Another possibility is that the alignment is caused by the lattice of the substrates. The X direction on the ST-cut quartz is the direction where the motion of the metal catalyst is preferred. However, it has been reported that different metals have different interaction with the substrates.[22] But the alignment trend of the nanotubes shows no obvious preference for different metal catalysts although the alignment degrees are not exactly the same. All of the metals can provide aligned SWNTs. In order to study the movement of the catalysts, Co nanoparticles formed by diblock copolymer method[23] was deposited on quartz. AFM shows no movement of the particles when the substrate was heated to 900 °C without introducing any carbon precursor. However, after introducing the carbon precursor, the catalysts moved wildly to form aligned SWNTs. (see Supporting Information) Thus, the introduction of a carbon source seems to be an important factor for the movement of the metal catalyst and the alignment. As a result, we propose a new hypothesis to explain our experimental results. In this hypothesis, the direction of alignment is determined by the crystal lattice of the substrate. However, it is not the lattice of the metal nanoparticles that is interacting with the surface lattice to dominate the motion and the alignment. The carbon shell precipitated on the outer surface of the catalysts is more likely to be the lattice that interacts with the substrate lattice and leads the growth along the direction of alignment. The differences in the density, yield, and degree of alignment for different metal catalysts can be explained to be from the different carbon solubility in different metal under the same temperature and carbon feeding. Metal particles only provide a platform for the decomposition of the carbon precursor and dissolution of carbon. This hypothesis can explain the growth of aligned nanotubes from so many different metals. However, similar to many other hypotheses, more experimental and theoretical works are needed to confirm it.

Moreover, we also demonstrate a very simple but novel patterning method for the formation of catalyst islands used to grow these aligned SWNTs. A blade such as steel or tungsten carbide (WC, with 9% Co) can be used to scratch a line on top of the quartz. Metal particles will be generated on the surface because of the hardness of quartz. Aligned SWNTs can be grown from the scratches formed by steel (Figure 3A) and WC (Figure 3B) blades. This easy process does not require any complex patterning process such as lithography.

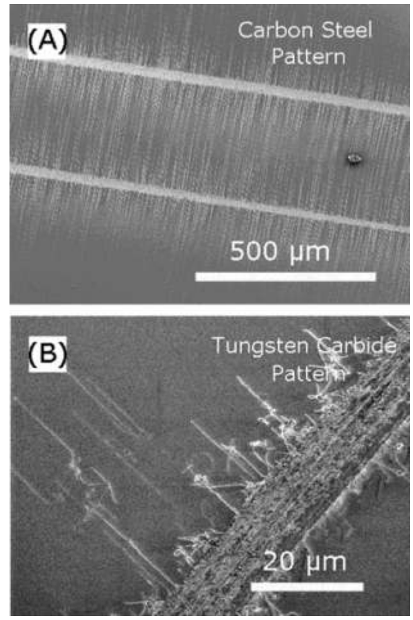

Figure 3. SEM images of horizontally aligned SWNTs growth by the blade patterning with (A) carbon steel and (B) WC (with 9% Co). The alignment direction is the X direction on ST-cut quartz.

In summary, horizontally lattice-aligned SWNTs were formed on ST-cut quartz by various metals. The hypothesis that the alignment is promoted by the carbon atoms on the outside of the metal nanoparticles is suggested. Moreover, Mg and Al are first shown to produce SWNTs. A simple pattern method is introduced. Those studies will improve our understanding of the horizontal lattice-alignment growth on quartz, provide new catalyst candidates for SWNT synthesis, and offer an easy patterning method. The SWNTs produced by different catalysts might contain different nanotube types and could lead to orientation plus property-controlled SWNTs for numerous applications.

Acknowledgment. The work is supported in part by a grant from NRL (N00173-04-1-G902), a grant from Unidym Inc., and funds from Duke University. The authors thank Dr. Cheng Qian at Xintek Inc. and Dr. Chenguang Lu at Columbia University for helpful discussion.

Supporting Information Available: SEMs and AFMs of SWNTs by various metals. AFMs of Co nanoparticles and corresponding SEMs of as-grown aligned SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Iijima, S. *Nature* **1991**, *354* (6348), 56–58.
(2) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393* (6680), 49–52.
(3) Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. J. *Science* **2000**, *287* (5453), 622–625.
(4) Misewich, J. A.; Martel, R.; Avouris, P.; Tsang, J. C.; Heinze, S.; Tersoff, J. *Science* **2003**, *300* (5620), 783–786.
(5) Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. *Science* **2001**, *294* (5545), 1317–1320.
(6) Yu, G. H.; Cao, A. Y.; Lieber, C. M. *Nat. Nanotechnol.* **2007**, *2* (6), 372–377.
(7) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. J. *Nature* **1998**, *395* (6705), 878–881.
(8) Ural, A.; Li, Y. M.; Dai, H. J. *Appl. Phys. Lett.* **2002**, *81* (18), 3464–3466.
(9) Huang, S. M.; Cai, X. Y.; Liu, J. *J. Am. Chem. Soc.* **2003**, *125* (19), 5636–5637.
(10) Han, S.; Liu, X. L.; Zhou, C. W. *J. Am. Chem. Soc.* **2005**, *127* (15), 5294–5295.
(11) Ismach, A.; Segev, L.; Wachtel, E.; Joselevich, E. *Angewandte Chemie-International Edition* **2004**, *43* (45), 6140–6143.
(12) Kocabas, C.; Hur, S. H.; Gaur, A.; Meitl, M. A.; Shim, M.; Rogers, J. A. *Small* **2005**, *1* (11), 1110–1116.
(13) Kocabas, C.; Shim, M.; Rogers, J. A. *J. Am. Chem. Soc.* **2006**, *128* (14), 4540–4541.
(14) Kang, S. J.; Kocabas, C.; Ozel, T.; Shim, M.; Pimparkar, N.; Alam, M. A.; Rotkin, S. V.; Rogers, J. A. *Nat. Nanotechnol.* **2007**, *2* (4), 230–236.
(15) Kocabas, C.; Kang, S. J.; Ozel, T.; Shim, M.; Rogers, J. A. *J. Phys. Chem. C* **2007**, *111* (48), 17879–17886.
(16) Ding, L.; Yuan, D. N.; Liu, J. *J. Am. Chem. Soc.* **2008**, *130* (16), 5428+.
(17) Kocabas, C.; Pimparkar, N.; Yesilyurt, O.; Kang, S. J.; Alam, M. A.; Rogers, J. A. *Nano Lett.* **2007**, *7* (5), 1195–1202.
(18) Liu, X. L.; Han, S.; Zhou, C. W. *Nano Lett.* **2006**, *6* (1), 34–39.
(19) Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. *J. Am. Chem. Soc.* **2003**, *125* (37), 11186–11187.
(20) Bhaviripudi, S.; Mile, E.; Steiner, S. A.; Zare, A. T.; Dresselhaus, M. S.; Belcher, A. M.; Kong, J. *J. Am. Chem. Soc.* **2007**, *129* (6), 1516+.
(21) Takagi, D.; Homma, Y.; Hibino, H.; Suzuki, S.; Kobayashi, Y. *Nano Lett.* **2006**, *6* (12), 2642–2645.
(22) Zhou, W. W.; Han, Z. Y.; Wang, J. Y.; Zhang, Y.; Jin, Z.; Sun, X.; Zhang, Y. W.; Yan, C. H.; Li, Y. *Nano Lett.* **2006**, *6* (12), 2987–2990.
(23) Lu, J.; Yi, S. S.; Kopley, T.; Qian, C.; Liu, J.; Gulari, E. *J. Phys. Chem. B* **2006**, *110* (13), 6655–6660.

NL801007R