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# Nanoditches Fabricated Using a Carbon Nanotube as a Contact Mask

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## ABSTRACT

Single-walled carbon nanotubes (SWCNTs) and multiple-walled nanotubes (MWCNTs) were used as contact masks to create nanoditches within a thin layer of oxide-covered Ti. The nanotubes buried in the Ti film can be removed by ultrasonication, leaving the Ti layer with well-formed uniform ditches up to several  $\mu\text{m}$  in length and as narrow as 10 nm in width. The width of the nanoditches is determined by the diameter of the departing nanotube. The technique presented may help to build electrode-to-span molecules or may furnish a template to fabricate nanowires of various materials.

Nanotubes have been widely investigated for their intriguing structural helicity-associated electrical properties.<sup>1,2</sup> For example, single-walled carbon nanotubes (SWCNTs) have been dropped from suspension onto a set of predeposited Au fingers on Si (the Si substrate acts as a gate electrode).<sup>3</sup> In another field-effect transistor (FET) geometry, a SWCNT can be connected to source and drain electrodes at its two ends (1  $\mu\text{m}$  apart) and to a third gate electrode underneath the nanotube.<sup>4–6</sup> However, the distance between the source electrode and drain electrode is limited by lithographic resolution.<sup>7</sup> The mechanical<sup>8</sup> and chemical<sup>9</sup> properties of nanotubes are also attractive. Nanotubes can be used as AFM tips with high aspect ratios<sup>10</sup> and as nanotweezers to manipulate biological molecules.<sup>11</sup>

One of the major features of carbon nanotubes is their nanometer diameters. The diameter of nanotubes ranges from a few nanometers for single-walled nanotubes or bundles of SWNTs to a few tens of nanometers for multiple-walled nanotubes. The diameter of a single-walled nanotube is very close to the length of a molecule, which is typically a few nanometers.

A challenge in molecular electronics is to build electrodes that reside within a few nanometers apart. Two-terminal molecular electronic components have been achieved by studying a single molecule with a gold break junction,<sup>12</sup> by a STM tip or a conducting AFM tip,<sup>13</sup> or else by sandwiching a molecular monolayer between macroscopic metal electrodes, e.g., in a unimolecular rectifier.<sup>14</sup> However, none of these two-terminal device designs allow a dimension for the third gate electrode to be introduced in order to achieve a transistor effect.

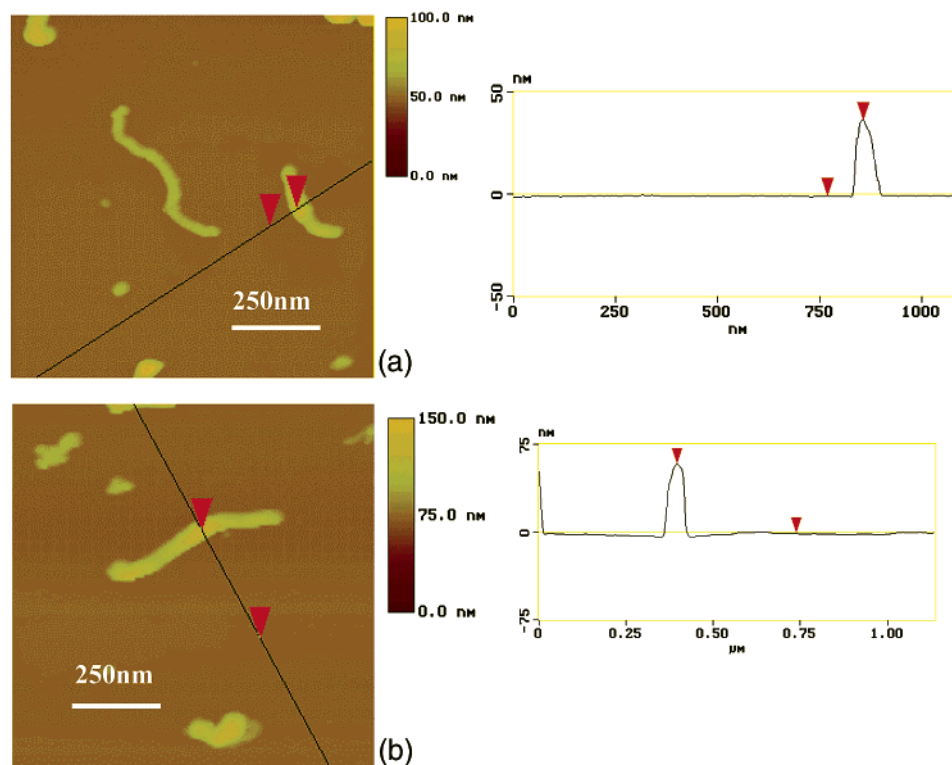
In-plane three-terminal electrodes and two-terminal electrodes, with the substrate as the gate electrode (field-effect-

transistor), both require a nanometer gap without breaking the substrate. E-beam lithography can achieve two-terminal electrodes 3–4 nm apart; the length of the gap is typically around 10 nm.<sup>15</sup> Electromigration is another powerful method to produce metallic electrodes with nanometer separation.<sup>16</sup> However, this technique requires the width of the initial metal wires to be below 200 nm, which inevitably requires e-beam lithography, and the length of the gap to be no longer than the width of the starting metal line.<sup>17</sup> A longer nanogap allows more molecules to be connected, which increases the current and the reliability of the molecular device. Another limitation is that electromigration does not apply to fabrication of planar three-terminal electrodes.

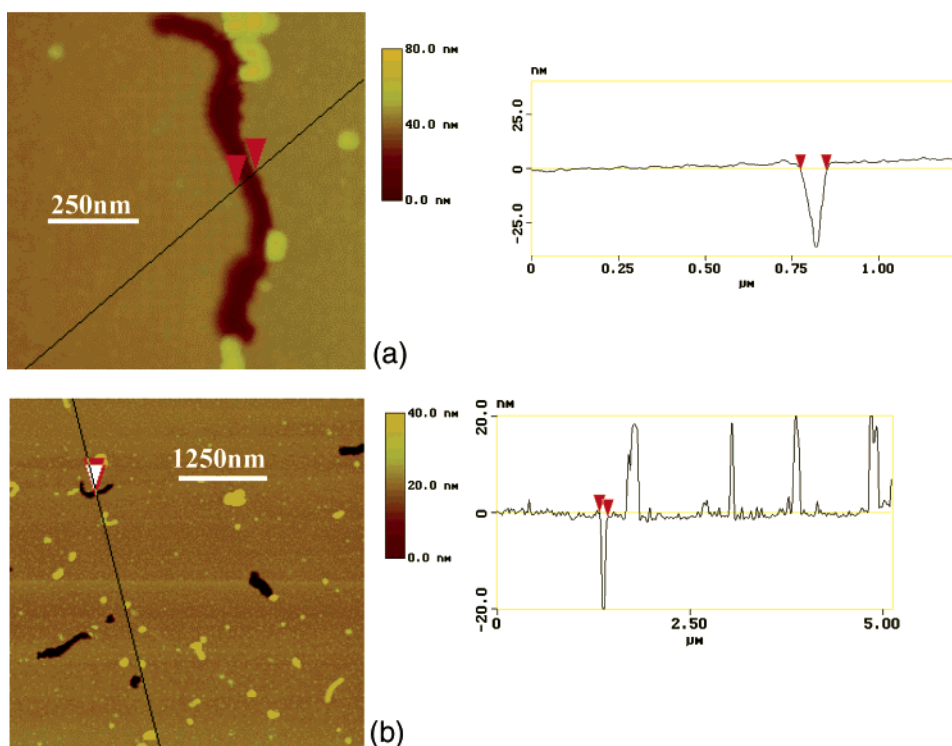
In nanosphere lithography (NSL), a nanosphere array is used as a contact mask to fabricate a periodical particle array.<sup>18</sup> Elicited by NSL, we present here a new and simple way to fabricate a reproducible 10 nm nanoditch up to a few  $\mu\text{m}$  long using a carbon nanotube as contact mask. We first deposit carbon nanotubes (SWCNTs or multiple-walled carbon nanotubes (MWCNTs)) on a suitable surface. Next, a very thin layer of Ti was evaporated onto the sample to barely bury the nanotube (5 to 30 nm, as needed). Finally, we remove only the nanotubes by ultrasonication. These steps create, after the nanotubes are removed, a reproducible set of nanoditches with well-controlled nm widths and lengths up to several  $\mu\text{m}$ .

In the experiments, Si wafers covered with thermogrown  $\text{SiO}_2$  were used as substrate. Both multiple-walled and single-walled carbon nanotubes without further treatment (NANOCS, New York,) were used as contact masks. Carbon nanotubes were dispersed onto the substrate by ultrasonication (Fisher FS5) in toluene for 30 min. Figures 1a and b show a typical AFM image (Digital Instruments Nanoscope Dimension

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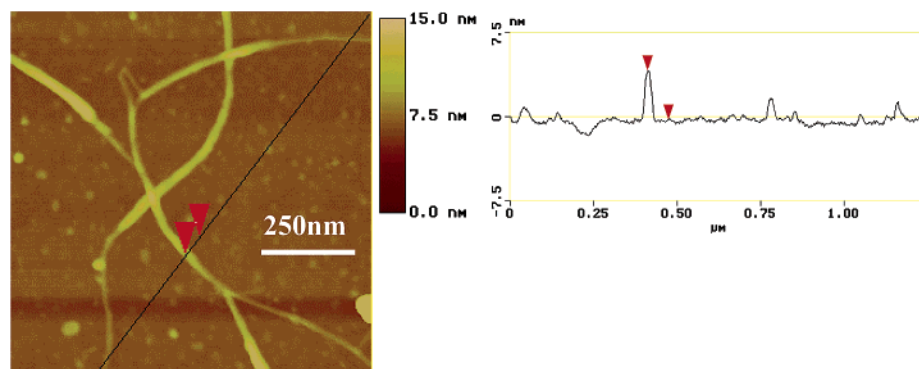
**Figure 1.** (a) Atomic force micrograph of a MWCNT on a Si/SiO<sub>2</sub> substrate, and height profile along the indicated line. Image size: 1  $\mu\text{m} \times 1 \mu\text{m}$ . The MWCNT diameter is 36 nm, as determined by the height of the nanotube. (b) Atomic force micrograph of a MWCNT on SiO<sub>2</sub>/Si substrate, and height profile along the indicated line. Image size: 1  $\mu\text{m} \times 1 \mu\text{m}$ . The MWCNT diameter is 52 nm.



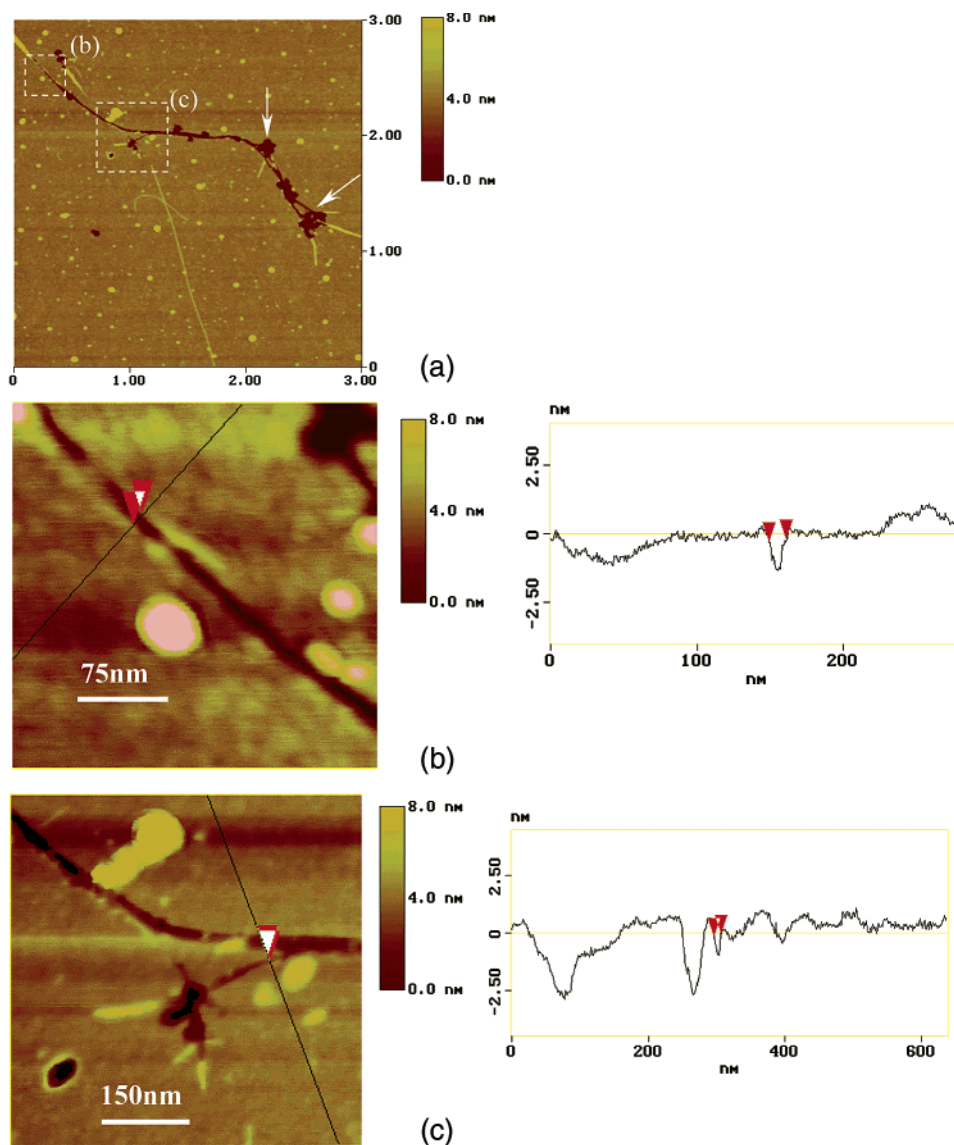
**Figure 2.** (a) Atomic force micrograph of a Ti/TiO<sub>2</sub> nanogap formed by the removal of a MWCNT by ultrasonication, and depth profile along the indicated line. The width at the top of the gap is 78 nm. (b) Atomic force micrograph of Ti/TiO<sub>2</sub> nanogap formed by the removal of a MWCNT with ultrasonication, and height profile along the indicated line. Image size: 5  $\mu\text{m} \times 5 \mu\text{m}$ . The width at the top of the gap is 97 nm.

3000, Santa Barbara) of MWCNTs on a Si/SiO<sub>2</sub> substrate. Because of the uncertainty in the radius of gyration of the AFM tip, the diameter of a MWCNT was determined by

the height of the MWCNT with respect to the substrate.<sup>19</sup> The diameters of individual MWCNTs varied between 30 and 80 nm, in agreement with the scanning electron



**Figure 3.** Atomic force micrograph of SWCNT (or thinner CNT) on Si/SiO<sub>2</sub> substrate, and height profile along the indicated line. Image size: 1  $\mu\text{m} \times 1 \mu\text{m}$ . The nanotube diameter is 4.4 nm.



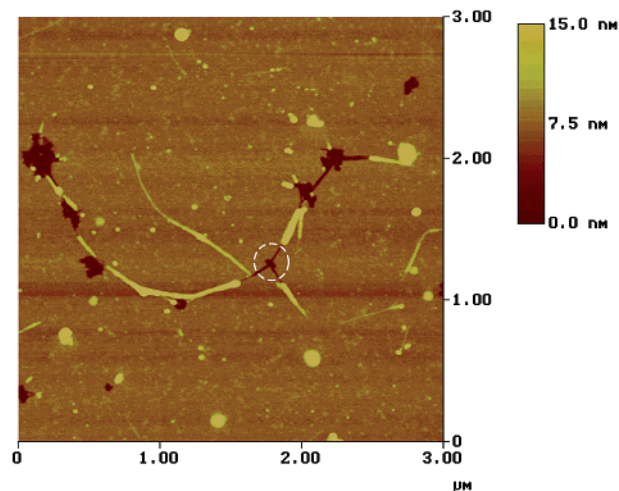
**Figure 4.** (a) Survey AFM image of the removal of “SWCNT” (or thinner CNT) from the 4.8 nm Ti/TiO<sub>2</sub> film with ultrasonication. Image size: 3  $\mu\text{m} \times 3 \mu\text{m}$ . The white arrows indicate the footprints left by a Co catalyst particle. The zoomed-in areas (b) and (c) are shown in Figure 4b and 4c, respectively. A much thinner SWCNT (probably 1.3 nm thick), covered by Ti/TiO<sub>2</sub>, is visible in the lower part of the figure; it is buried under the Ti/TiO<sub>2</sub> surface, which was too thick here to allow for its removal by ultrasonication. (b) Atomic force micrograph of Ti/TiO<sub>2</sub> nanogap formed by the removal of SWCNT (or thinner CNT) by ultrasonication, and height profile along the indicated line. Image size: 300 nm  $\times$  300 nm. The width at the top of the gap is 11 nm. (c) Atomic force micrograph of the Ti/TiO<sub>2</sub> nanogap formed by the removal of SWCNT (or thinner CNT) with ultrasonication, and height profile along the indicated line. Image size: 600 nm  $\times$  600 nm. The width at the top of the gap is 10 nm.



microscopy data furnished by the supplier. A 30 nm Ti layer was evaporated (Edwards model 306 evaporator) onto these samples, which were then ultrasonicated for 15 min. Figures 2a and b show the typical gaps formed by the removal of MWCNTs upon ultrasonication. The adhesive strength between Ti and SiO<sub>2</sub> surfaces is very intense.<sup>20</sup> The principle of ultrasonic cleaning is very complicated. Ultrasonication is believed to generate transient cavitation in fluids, with transient temperature and pressure of “5000 K and 1000 atm, [respectively], with effective residence times of <100 ns”.<sup>21</sup> Such high temperature and pressure can develop stresses between the cleaning fluid and the surface and increase the attractive forces between contaminant and cleaning fluid. The effective penetration and cracking are most likely to start where the nanotube, or the catalyst particle, meets the Ti layer.

We then applied this technique to commercial SWCNTs, having diameters ranging from 1.3 to 10 nm. Figure 3 shows typical images of these carbon nanotubes on a Si/SiO<sub>2</sub> substrate. A 4.8 nm Ti layer was evaporated onto these samples, which were then ultrasonicated for over 1 h. Figures 4a,b, and c show the typical gaps formed by the removal of these thinner carbon nanotubes with ultrasonication. The AFM images in Figures 4a–c were taken with a Supersharps Si tip (Molecular Imaging, Phoenix, AZ) in tapping mode: the typical tip radius is less than 4 nm. Figure 4a is a representative survey scan after the removal of nanotubes by ultrasonication. Figure 4a shows that the shape of the nanotubes can still be imaged even they are covered by the thin layer of Ti, because Ti atoms are very adhesive and will not fall down from the carbon nanotubes they cover. Our experiments show that SWCNTs seem to adhere better to the Si substrate than MWCNTs. Because the thickness of the Ti layer is 5 nm, most of the SWCNTs would be completely buried in the Ti film. In contrast, for MWCNTs with diameters larger than 30 nm, a 30 nm Ti layer barely covers those bigger nanotubes, and they are more likely to be removed by ultrasonication. Consequently, SWCNTs require more ultrasonication time to be shaken off the substrate. As a control experiment, Ti with the same thickness was evaporated onto a Si substrate without carbon nanotubes and was then ultrasonicated for the same time. No such nanoditches were found on those samples.

The line scans in Figure 4b and Figure 4c show that the nanoditch can be as narrow as 10 nm at the top of the gap. Due to the aspect ratio of the AFM tip, the gap width at the bottom cannot be measured accurately for a 4.8 nm deep gap. We assume that the width of the gap at the bottom is probably even narrower than that at the top because dam-like banks are more energy favorable than cliff-like banks. The edge roughness of the nanogap mainly relies on the shape and the diameter uniformity of the nanotube. The shape and the diameter of the SWCNTs we used are not perfectly uniform, as shown in Figure 3. For example, the width of the gap varies from 9 to 13 nm along the section of the gap (390 nm long) shown in Figure 4b, but most of the section is 10 to 11 nm. The catalyst particles attached to the nanotube also cause rough places along the nanogaps, as one can see



**Figure 5.** Atomic force micrograph of a pseudo three-probe electrode formed by the removal of a T-shaped nanotube (region in the white circle) from a 4.8 nm thick Ti/TiO<sub>2</sub> substrate by ultrasonication. Image size: 3  $\mu\text{m}$   $\times$  3  $\mu\text{m}$ .

in Figure 4a. The nanoditches fabricated here have lengths up to a few  $\mu\text{m}$ ; they can also be used as templates for other nanowires.

Most of the round particles are the Co catalyst used to grow the nanotubes. We observed that most of the nanotubes removed are those that had been attached to Co particles, as shown by the footprint of Co particles left after ultrasonication. It seems that the junction of the Co particle and nanotube is a weak point, from which the nanotubes can be torn off by ultrasonication.

We also observed that if a T-shaped nanotube<sup>22</sup> or two nanotubes that cross each are removed, then a pseudo-three-terminal or four-terminal electrode will be left in the Ti film. Figure 5 shows such a pseudo three-terminal electrode, formed after the removal of a T-shaped nanotube by ultrasonication.

We have successfully fabricated nanometer scale Ti gaps with length up to a few  $\mu\text{m}$  using carbon nanotubes as a contact mask. The width of the Ti nanoditch can be as narrow as 10 nm and the length of the ditch can be as long as a few  $\mu\text{m}$ . A further challenge is to introduce the nanoscopic gaps to individual macroscopic electrodes. A two-crossed nanotube junction with four ends being covered by metal<sup>23</sup> is a good starting design if the four ends of the two nanotubes can be covered by a dissolvable insulator such as Al<sub>2</sub>O<sub>3</sub>, which can be lifted off by acid to form four separated electrodes.

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## References

- (1) Odom, T. W.; Huang, J. L.; Kim, P.; Lieber, C. M. *Nature* **1998**, *391*, 62–64.

- (2) Soh, H. T.; Quate, C. F.; Morpurgo, A. F.; Marcus, C. M.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **1999**, 75, 627.
- (3) Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997**, 386, 474–478.
- (4) Postma, H.; Teepen, T.; Yao, Z.; Grifoni, M.; Dekker, C. *Science* **2001**, 293, 76.
- (5) Huang, Y.; Duan, X.; Cui, Y.; Lauhon, L.; Kim, K.; Lieber, C. M. *Science* **2001**, 294, 1317.
- (6) Derycke, V.; Martel, R.; Appenzeller, J.; Avouris, Ph. *Nano Lett.* **2001**, 1, 453.
- (7) Tan, Y. T.; Kamiya, T.; Durrani, A. A. K.; Ahmed, H. *Appl. Phys. Lett.* **2001**, 78, 1083.
- (8) Dai, H.; Franklin, N.; Han, J. *Appl. Phys. Lett.* **1998**, 73, 1508.
- (9) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, 282, 95.
- (10) Dai, H. J.; Hafner, H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, 384, 147.
- (11) Kim, P.; Lieber, C. M. *Science* **1999**, 286, 2148.
- (12) Chen J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, 286, 1550.
- (13) Cui, S. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, 294, 571.
- (14) Xu, T.; Peterson, I. R.; Lakshmikantham, M. V.; Metzger, R. M. *Angew. Chem., Intl. Ed. Engl.* **2001**, 40, 1749–1752.
- (15) Liu, K.; Avouris, Ph.; Bucchignano, J.; Martel, R.; Sun, S.; Michl, J. *Appl. Phys. Lett.* **2002**, 80, 865–867.
- (16) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruna, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, 417, 722.
- (17) Park, H.; Lim, A. K. L.; Park, J.; Alivisatos, A. P.; McEuen, P. L. *Appl. Phys. Lett.* **1999**, 75, 301.
- (18) Hulteen, J. C.; Treichel, D. A.; Smith, M. T.; Duval, M. L.; Jensen, T. R.; Van Duyne, R. P. *J. Phys. Chem. B* **1999**, 103, 3854.
- (19) Zhou, C.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **2000**, 76, 1597.
- (20) Nagata, H.; Shinriki, T.; Shima, K.; Tamai, M.; Haga, E. M. *J. Vac. Sci. Technol. A* **1999**, 17, 1018.
- (21) Suslick, K. S. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH Publishers: Weinheim, Germany, 1988; p. 130.
- (22) Li, W. Z.; Wen, J. G.; Ren, Z. F. *Appl. Phys. Lett.* **2001**, 79, 1879.
- (23) Fuhrer, M. S.; Nygard, J.; Shih, L.; Forero, M.; Yoon, Y. G.; Mazzoni, M. S. C.; Choi, H. J.; Ihm, J.; Louie, S. G.; Settl, A.; McEuen, P. L. *Science* **2000**, 288, 494.

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