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Surface-Acoustic-Wave-Enhanced Alignment of Thiolated Carbon Nanotubes on Gold Electrodes**

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One of the challenges in using carbon nanotubes (CNTs) in electronic devices is the difficulty to align and to position large amounts of them, for example, on metallic electrodes. Several techniques were employed to orientate and deposit CNTs in a controlled way, for example, by application of an ac[1,2] or dc[3,4] electric field, chemical vapor deposition on a catalyst,[5–7] or chemical functionalization in order to achieve some degree of self-assembly.[8–11]

Taking advantage of their molecular properties, chemical modification can be employed to attach functional groups to CNTs, which incorporate some desired binding properties to the CNTs. This makes it possible, for example, by attachment of thiol end groups, to selectively bind CNTs to metallic surfaces.

In this article, we report a method to deposit and to chemically attach single-walled carbon nanotubes (SWNT) perpendicularly to prepatterned gold electrodes by a combination of two techniques: First, the SWNTs are chemically treated in order to produce thiol end groups on the SWNT ends and defect sites; second, by the application of surface acoustic waves (SAWs) to a SWNT suspension, the SWNTs can be orientated with respect to the electrodes.[12] SWNTs produced by laser ablation were obtained from Tube@Rice (Rice University). The tubes were first sonicated in 3:1 H_2SO_4:HNO_3 (96:67 %) for 90 min following the procedure described by Liu et al.[8] This treatment breaks up the nanotubes and leads to the formation of carboxylic acid groups at the ends of the shortened SWNTs and at defect sites on the sidewalls, which was verified by infrared spectroscopy. The shortening of the SWNTs was verified by comparing AFM images of oxidized and untreated nanotubes. The SWNT solution was rinsed over a PTFE membrane (0.2 μm, Millipore) and resuspended in water. In the next step, the SWNTs in water were reacted with cysteamine in MES buffer (MES: 2-(*N*-morpholino)ethanesulfonic acid; 0.1 mol, Pierce) in the presence of bovine serum albumine (BSA; 5 g mL^{-1}). The amount of cysteamine was chosen to result in a 200-fold molecular excess over the SWNTs. As a reaction agent, 1-ethyl-1,3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC) was used. Cysteamine is a short chain molecule with a thiol group on one end and an amine group on the other, which forms an amide bond to the SWNTs. BSA was used to reduce nonspecific bonding of cysteamine to the SWNTs. Finally, the solution was filtered again and the SWNTs were resuspended in water and a surfactant (sodium dodecyl sulfate) was added.

In order to verify the presence of thiol groups on the SWNTs, gold nanoparticles with a diameter of 10 nm in phosphate buffered saline (10 mM, Aurion) were added to a part of the SWNT solution. After 10 min of sonication, a drop of the suspension was applied onto a Si chip and dried. The SWNTs and the gold nanoparticles can be clearly seen in the scanning electron microscopy (SEM) images (Figure 1). We estimated that at least half of the gold nanoparticles are attached to SWNTs, either to the end, to the side of a single nanotube, to or a bundle of nanotubes. The same amount of gold particles was also added to a suspension of non-functionalized SWNTs. In this case, no specific binding of gold nanoparticles to the SWNTs was seen in the SEM images (not shown).

Figure 1. SEM image of 10-nm gold nanoparticles attached to thiolated SWNTs on a SiO_2 chip.

The bonding selectivity of thiolated SWNTs to gold combined with the ability of a SAW to orientate the SWNTs was employed to align thiolated SWNTs on prepatterned gold structures. The piezoelectric field of surface acoustic waves is responsible for an alignment of SWNTs parallel to the propagation direction of the SAW.[12,13] A schematic sketch of such an alignment setup is shown in Figure 2. One drop of a SWNT suspension was placed in the capillary gap between the $LiNbO_3$ substrate (crystal orientation: rotation 128°, Y-cut, X-propagation), and a second substrate was used as a top. Interdigital transducers (IDTs) were located on the $LiNbO_3$ substrate to launch a SAW with a wavelength of 36 μm, which corresponds to a reso-

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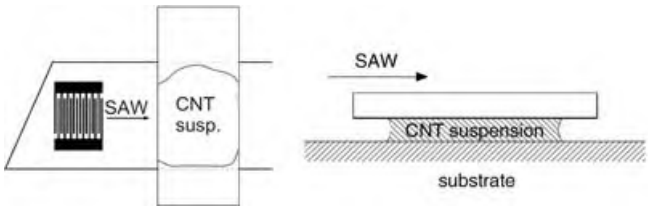

Figure 2. Sketch of the alignment setup. The SWNT suspension is placed in the capillary gap on the $LiNbO_3$ substrate, and a SAW is launched by the use of an interdigital transducer.

nance frequency of 114 MHz. The covering substrate was located above and parallel to the $LiNbO_3$ surface with a spacing of 20 μm or less. If the spacing is of the order of one SAW wavelength or less, a standing water-pressure wave arises; then the SWNTs can be aligned by the piezoelectric SAW field, and the alignment motive force parallel to the propagation direction is not masked by fluidic processes. For a time period of 10 min, a RF signal of 20 dBm power was applied to one of the IDTs in order to launch a SAW with a large amplitude. Finally, the sample was rinsed in deionized water and dried with nitrogen gas.

The setup above was used to align multi-walled carbon nanotubes (MWNTs) on $LiNbO_3$ and $LiTaO_3$ as substrate materials.[12] It was shown that on $LiNbO_3$, the MWNTs align at an angle between $\pm 25^\circ$ and $\pm 45^\circ$ with respect to the SAW propagation direction. These deviations were likely caused by a superposition of the piezoelectric SAW field and fluidic processes. It was shown that the motive force of the alignment is the piezoelectric field, which accompanies a SAW on $LiNbO_3$. At the same time the SAW-induced elliptical movements of atoms in the crystal lattice lead to fluidic processes in the CNT suspension. The superposition of both driving forces causes the CNTs to align at an angle between $\pm 25^\circ$ and $\pm 45^\circ$ to the SAW direction.

In Figure 3, two microscopic investigations of the thiolated SWNT alignment are given. Figure 3a presents an atomic force microscopy (AFM) image showing a thiolated SWNT on prepatterned gold squares on $LiNbO_3$. The SWNT is aligned at a deviation of 15° to the direction of the SAW. In Figure 3b, a SEM image with several aligned SWNTs is presented. Arrays of gold electrodes with a width of 400 nm and a pitch of 1 μm were prepared by electron beam lithography on a $LiNbO_3$ sample. After the alignment of thiolated SWNTs by the use of a SAW, the sample was covered with titanium (3 nm) and gold (3 nm) to ensure a conductive surface that would allow SEM investigations of the SWNT orientation to be performed.

Due to the superposition of the electric field, fluidic processes, and enhanced affinity caused by the thiol end groups, the SWNTs are aligned at an absolute angle between 0° and 45° with respect to the SAW propagation direction. Several arrays like the one shown in Figure 3b were prepared and the SWNT orientation was analyzed. The result is shown as a histogram in Figure 4. The orientation of around 80 thiolated SWNTs was investigated and an enhanced alignment in comparison with Ref. [12] was detected. The majority of SWNTs show an orientation with an absolute angle between 0° and 20°, in comparison with 25° to 45° reported in Ref. [12]. It is reasonable to assume that this enhancement is caused by the increased attraction of thiolated CNTs to the gold contacts. The piezoelectric motive force leads to an alignment of the SWNTs parallel to the SAW direction in the fluid. Due to the thiolation of the SWNTs, the thiol end groups attach more rapidly to the gold contacts, which leaves less time for the fluidic processes to change the alignment angle. This results in an improved alignment of the thiolated SWNTs on the gold contacts.

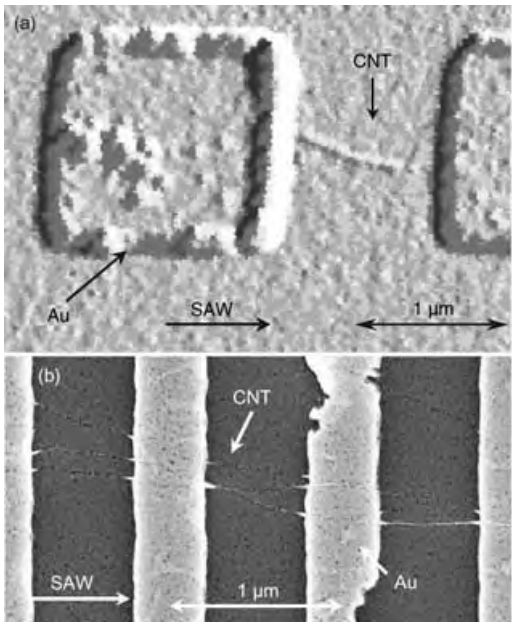

Figure 3. a) AFM image of an aligned thiolated carbon nanotube on prepatterned gold squares on $LiNbO_3$. b) SEM image of aligned SWNTs on prepatterned gold squares on $LiNbO_3$.

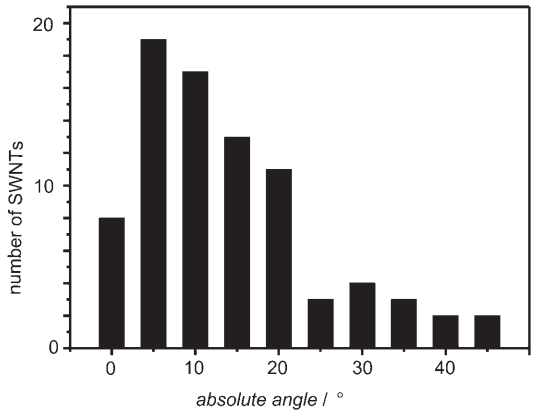

Figure 4. Orientation histogram: The number of SWNTs are counted regarding their absolute alignment angle with respect to the SAW propagation direction.

For another sample, a pair of 600-μm-long gold contacts was prepared on a $LiNbO_3$ substrate by electron beam lithography. Then, thiolated SWNTs were again aligned by the use of a SAW. As can be seen in the inset of Figure 5, this

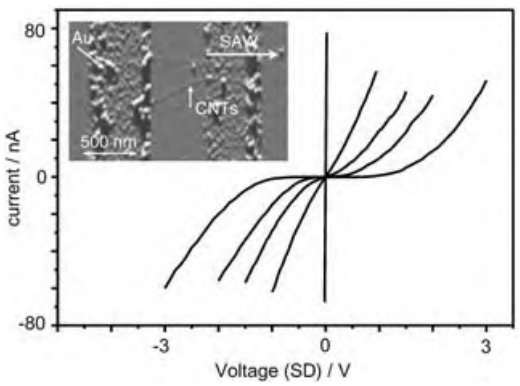

Figure 5. The current through contacted SWNTs as a function of applied source–drain bias for different temperatures. The inset shows an AFM image of part of the sample with two contacted SWNTs.

leads to one or more SWNTs bridging the 500-nm-wide gap of the finger pair. In Figure 5, the current as a function of applied source–drain voltage is presented for different temperatures. At room temperature, a linear current–voltage dependence was detected; the resistance of the two-terminal device was 250 kΩ (the almost vertical graph in Figure 5 is due to the scaling caused by the large resistance at low temperatures). With decreasing temperatures, the current–voltage characteristic becomes more and more nonlinear until, at a temperature of $T = 4.2$ K, a source–drain voltage of at least ± 2 V is required to drive a current through the SWNTs. This nonlinearity is likely to be caused by a superposition of at least two different effects. Firstly, there is a Schottky barrier between the gold contacts and the SWNTs, which becomes more prominent at lower temperatures. And secondly, it has been shown that contacted SWNTs with such lengths can be described as quantum dots of finite length.[14–19] Also, the chemical treatment of the SWNTs used to attach thiol end groups could be a source of damage to the SWNTs where short quantum dots are introduced into the SWNTs. Therefore Coulomb blockade effects, too, may lead to a suppression of current for finite source–drain voltages at low temperatures.[20] Due to the absence of any gate structure, the origin of the nonlinearity could not be identified, and further investigations are planned with implemented gate electrodes.

In summary, we produced functionalized SWNTs by chemically attaching thiol groups to site defects of the SWNTs. This was verified using gold nanoparticles, which tether to the thiolated SWNTs. Furthermore, an enhanced alignment of the thiolated SWNTs mediated by a piezoelectric SAW field on prepatterned gold structures was demonstrated.

Keywords:

carbon nanotubes · functionalization · gold · piezoelectrics · thiols

[1] K. Yamamoto, S. Akito, Y. Nakayama, *J. Phys. D* **1998**, *31*, L34.
[2] R. Krupke, F. Hennrich, H. B. Weber, M. M. Kappes, H. von Löhneysen, *Nano Lett.* **2003**, *3*, 1019.
[3] A. Nojeh, A. Ural, R. F. Pease, H. Dai, *J. Vac. Sci. Technol. B* **2004**, *22*, 3421.
[4] E. Joselevich, C. M. Lieber, *Nano Lett.* **2002**, *2*, 1137.
[5] J. Kong, A. M. Cassell, H. Dai, *Chem. Phys. Lett.* **1998**, *292*, 567.
[6] J. Hafner, M. Bronikowski, B. Azamian, P. Nikolaev, D. Colbert, R. E. Smalley, *Chem. Phys. Lett.* **1998**, *296*, 195.
[7] Y. Homma, Y. Kobayashi, T. Ogino, T. Yamashita, *Appl. Phys. Lett.* **2002**, *81*, 2261.
[8] J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253.
[9] J. K. Lim, W. S. Yun, M. Yoon, S. K. Lee, C. H. Kim, K. Kim, S. K. Kim, *Synth. Met.* **2003**, *139*, 521.
[10] N. O. V. Plank, R. Cheung, R. J. Andrews, *Appl. Phys. Lett.* **2004**, *85*, 3229.
[11] T. Smorodin, U. Beierlein, J. P. Kotthaus, *Nanotechnology* **2005**, *16*, 1123.
[12] C. J. Strobl, C. Schäflein, U. Beierlein, J. Ebbecke, A. Wixforth, *Appl. Phys. Lett.* **2004**, *85*, 1427.
[13] J. Ebbecke, C. J. Strobl, A. Wixforth, *Phys. Rev. B* **2004**, *70*, 233401.
[14] M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zettl, A. Thess, R. E. Smalley, *Science* **1997**, *275*, 1922.
[15] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, C. Dekker, *Nature* **1997**, *386*, 474.
[16] S. J. Tans, M. H. Devoret, R. J. A. Groeneveld, C. Dekker, *Nature* **1998**, *394*, 761.
[17] Z. Yao, H. W. Ch. Postma, L. Balents, C. Dekker, *Nature* **1999**, *402*, 273.
[18] T. Ida, K. Ishibashi, K. Tsukagoshi, Y. Aoyagi, B. W. Alphenaar, *Superlattices Microstruct.* **2000**, *27*, 551.
[19] J. W. Park, J. B. Choi, K.-H. Yoo, *Appl. Phys. Lett.* **2002**, *81*, 2644.
[20] P. L. McEuen, M. Bockrath, D. H. Cobden, Y.-G. Yoon, S. G. Louie, *Phys. Rev. Lett.* **1999**, *83*, 5098.