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Citation: Appl. Phys. Lett. **73**, 274 (1998); doi: 10.1063/1.121778
View online: http://dx.doi.org/10.1063/1.121778
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v73/i2
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Contacting carbon nanotubes selectively with low-ohmic contacts for four-probe electric measurements

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(Received 5 January 1998; accepted for publication 15 May 1998)

Contact resistances of multiwalled nanotubes deposited on gold contact fingers are very large. We show that the contact resistances decrease by orders of magnitudes when the contact areas are selectively exposed to the electron beam in a scanning electron microscope. The focused electron beam enables the selection of one particular nanotube for electrical measurement in a four-terminal configuration, even if a loose network of nanotubes is deposited on the gold electrodes. For all measured nanotubes, resistance values lie in a narrow range of 0.35–2.6 kΩ at room temperature. © *1998 American Institute of Physics.* [S0003-6951(98)04228-4]

Carbon nanotubes, discovered in 1991,[1] represent a new class of carbon-based conducting nanowires suitable for the investigation of mesoscopic electric transport phenomena. One distinguishes between multiwall nanotubes (MWNTs) consisting of a series of coaxial graphite cylinders and single-wall nanotubes (SWNTs). Graphite cylinders have predicted the remarkable property to be either metallic or semiconducting depending on how the graphite layer is wrapped into a cylinder.[2] This prediction may be verified by electrical transport measurements. Electrical resistance was first measured for bundles[3] and oriented films[4] of MWNTs yielding resistivities of 6.5×10^{-3} and 20×10^{-3} Ω cm at 300 K, respectively. In temperature dependent resistance measurements on a single MWNT, Langer *et al.* found a logarithmic increase in the two-terminal resistance at low temperatures indicative of weak localization for a disordered metal.[5] On the other hand, Ebbessen *et al.* reported four-terminal resistance measurements of different individual MWNTs with metallic as well as semiconducting temperature dependencies.[6] Since resistivities at 300 K varied by up to six orders of magnitude, from 5×10^{-6} to 6 Ω cm, this was taken as evidence that nanotubes can be metallic or semiconducting. Using the needle of a scanning-force microscope as one of the electric contact, Dai *et al.* found lower variations in resistances for MWNTs at 300 K, between 8×10^{-4} and 12×10^{-3} Ω cm.[7] Recently, resistance measurements have also been reported for SWNTs.[8] At present the origin of the large variation in measured resistances of MWNTs are under discussion. Important factors are (a) the quality of the nanotubes, (b) the fabrication technique applied to electrically address one nanotube, and (c) the quality of the electric contacts. Research on semiconductor devices has shown, that the formation of Schottky barriers may render the realization of low-ohmic contacts difficult. Good contacts, however, are a prerequisite for future research and applications of nanotubes. In this letter, a novel method is presented that allows to considerably lower contact resistances of MWNTs lying on prestructured Au-electrode fingers by many orders of magnitude at predetermined positions.

MWNTs are prepared by arc-discharge evaporation[1,9] and purified by centrifugation and sedimentation.[10] The morphology of these nanotubes was studied with transmission electron microscopy.[11] The different nanotubes have outer diameters (o.d.) between 5 and 50 nm and inner diameters (i.d.) between 1 and 7 nm. The most probable diameters are o.d.=10 nm and i.d.=2 nm. As substrate for electrical measurements a prestructured device, consisting of an electrode array each with four Au fingers, is used (Fig. 1). This electrode structure is fabricated by electron-beam lithography on a 2×2 cm^2 substrate cut from an oxidized Si wafer. The four fingers are 25 nm thick, 100 nm wide, 6 μm long, and are separated (center-to-center) by 350 nm. 1.3 mg purified nanotube powder is dispersed in 10 ml chloroform using ultrasonic agitation. A drop of this solution is then deposited on a prestructured substrate. After the evaporation of the solvent, the device is ready for inspection. The scanning-electron microscopy (SEM) image Fig. 2 shows the four Au

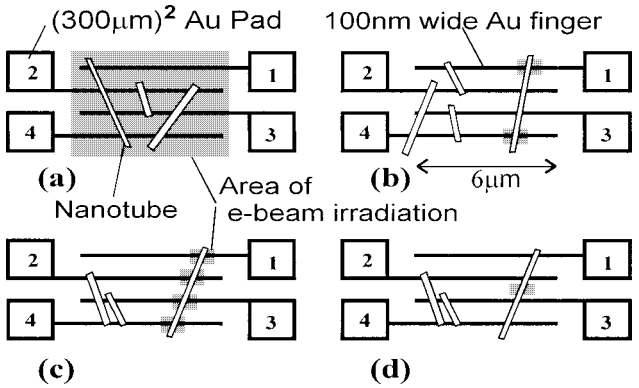

FIG. 1. Schematics of the Au structures covered by several nanotubes. The Au fingers are 25 nm thick, 100 nm wide, 6 μm long, and separated by 350 nm (center-to-center). Dashed windows indicate areas which are exposed by SEM: (a) the window covers the complete four Au-finger structure; (b) and (c) only contacts between a nanotube and the fingers are exposed; (d) the small exposure window is centered in the middle of one nanotube.

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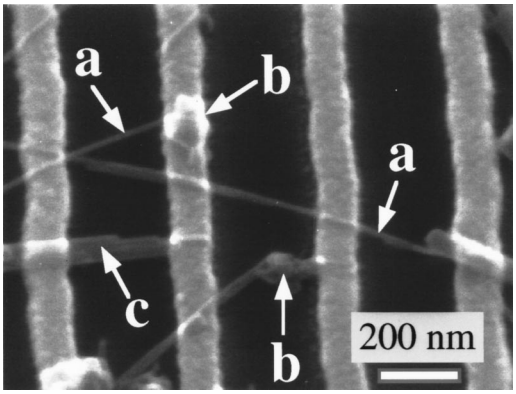

FIG. 2. Scanning-electron microscopy image of one Au-finger structure after the adsorption of nanotubes. Arrows point to (a) nanotubes, (b) nanoparticles, and (c) one bundle of nanotubes.

fingers with adsorbed (a) nanotubes, (b) nanoparticles, and (c) one (rarely observed) bundle of nanotubes. By adjusting the dimensions of the fingers and the concentration of the solution, the number of nanotubes lying over contact fingers can be modified. For the experiments reported here, only devices were used on which less than five nanotubes bridged electrode fingers. Typical configurations of nanotubes are schematically shown in Figs. 1(a)–1(c).

We first demonstrate by two-terminal ($2t$-) measurements that the electrical resistance is very sensitive to electron exposure. The exposure is realized by imaging a particular sample area by scanning-electron microscopy (SEM) operating at 20 keV during a predetermined time. A representative device is schematically shown in Fig. 1(a). The viewing window of the electron microscope is selected to cover the complete four-finger electrode structure. This window is successively exposed with increasing exposure dose. Between exposures, all six possible combinations of two-terminal ($2t$-) resistances have been measured. Figure 3 shows the dependence of the resistance as a function of electron dose for a representative pair of electrodes. The $2t$-resistance R_{2t} decreases substantially by four orders of magnitude from an initial value >100 MΩ to ≈ 30 kΩ for a total exposure dose of 0.7 C/cm^2. The fact that R_{2t} in Fig. 3

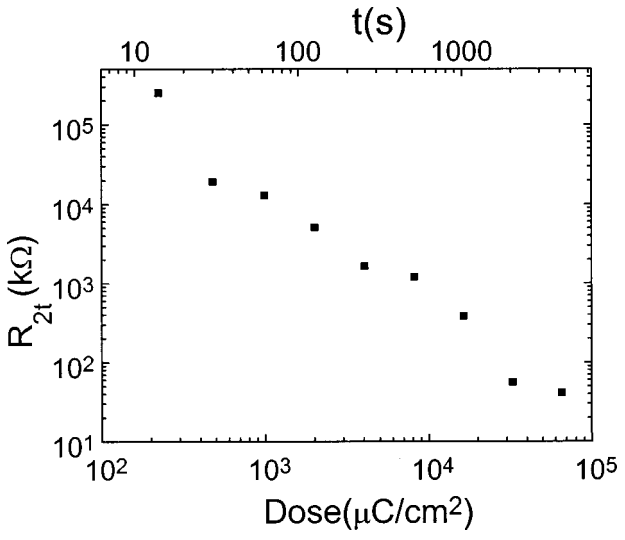

FIG. 3. Two-terminal resistance R_{2t} as a function of electron exposure dose in SEM. The illuminated area is shown in Fig. 1(a).

does not (yet) saturate for the largest dose indicates that a further decrease is possible. Due to the large area, however, the exposure times are already large (1 h or more). In order to increase the total dose further, a smaller window (containing at least two nanotube-Au contacts) was selected on other samples; now, R_{2t} saturated between 4 and 30 kΩ.

The remarkable large decrease of the two-terminal resistance can have three origins. First, a contamination film of amorphous carbon deposited during the exposure may reduce the measured resistance. Second, the electrical contacts between the nanotube and the Au fingers may improve considerably. Finally, the nanotubes may be modified by exposure with a resulting resistance decrease. The first hypothesis is tested with a similar prestructured device without nanotubes bridging the Au fingers. This sample is exposed in the SEM to a similarly large dose of 1 C/cm^2 under identical conditions. All two-terminal resistances remain larger than 1 GΩ proving that an amorphous contamination layer (if present at all) cannot be the cause of the observed resistance drop. To test the other two possibilities, selected areas are exposed instead of illuminating the whole device. These areas are 150×150 nm^2 large and are centered on places where a nanotube crosses a gold electrode. This is done on nanotubes lying over all four electrode fingers. A sufficient large exposure dose of 4 C/cm^2 is selected here. This scheme is schematically shown for two (four) different exposures on one nanotube in Fig. 1(b) [Fig. 1(c)]. Before exposure all possible $2t$ resistances are large, in the range of >1 MΩ–1 GΩ. To enable the selection of a specific exposure area on a suitable nanotube, a SEM image of the whole structure must be previously obtained. Fortunately, this is possible with a dose as small as 15 μC/cm^2. In the specific device, schematically shown in Fig. 1(b), the two-terminal resistance R_{2t} between the exposed contacts 1 and 4 decreases down to 25 kΩ, while R_{2t} between the inner contacts 2 and 3 does not change. This experimental finding implies that exposing a nanotube-Au contact locally lowers the electric-contact resistance substantially. In order to demonstrate that the nanotube itself is left unaltered by the exposure, the intrinsic resistance of the nanotube is measured using four contacts on one nanotube. These are selected by local exposure as described above [scheme shown in Fig. 1(c)]. Since the exposure considerably reduces the contact resistances, the major part of the electric current applied between leads 1 and 4 flows through the selected nanotube. The device is now reexposed using another small exposure window with a large dose of ≈ 4 C/cm^2. This time, however, the window is centered in the middle of the tube [see Fig. 1(d)], just between the inner contacts 2 and 3 which serve as voltage probes. The measured four-terminal resistance barely changes. It passes from 1.32 kΩ before, to 1.23 kΩ after exposure. We therefore have demonstrated that electron-beam exposure considerably reduces the contact resistance, and in addition, that the primary 20 keV electrons do not affect the nanotube itself. However, we cannot exclude a possible modification induced by secondary low-energy electrons, which are generated during the formation of the low-ohmic contacts. From the point of view of possible damage, our fabrication method is rather mild when compared to ion milling[5] and wet etching[7] previously used. Finally, we mention that after local modification

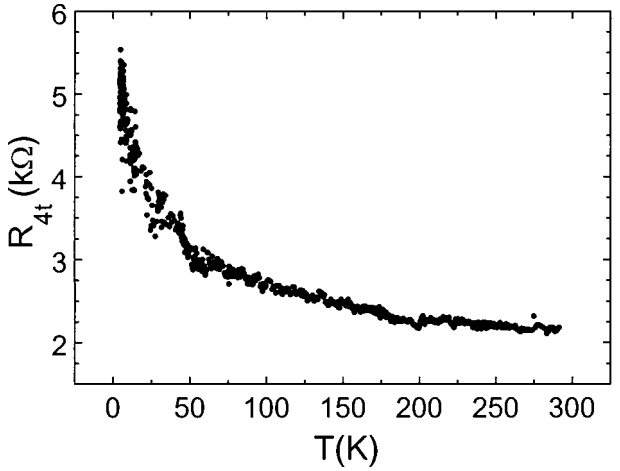

FIG. 4. Four-terminal resistance R_{4t} as a function of temperature for a single multiwall nanotube selected by the local electron exposure method [see scheme Fig. 1(c)]. A dc current of 400 nA was applied.

the contact resistances can increase to large values in the MΩ range again after one week at room temperature. A second exposure brings the resistances back to small values.

This technique of selecting one single MWNT for four-terminal measurement by local electron exposure was investigated on more than 15 samples. Of these samples, nine were successfully modified in the sense that all two-terminal resistances dropped considerably to values in the range of 4–30 kΩ. Measured four-terminal resistances do not support the data of Ebbesen *et al.*, who have found variations of up to six orders of magnitude.[6] Our nine samples give consistent values between 0.35 and 2.6 kΩ at room temperature. Unfortunately, the SEM does not allow to investigate the nanotube diameter with precision. A resistivity of $\approx 3 \times 10^{-5}$ Ω cm is deduced when we choose 1 kΩ for the four-terminal resistance, a 10 nm diameter for the nanotube cross section, and 250 nm for the gap between adjacent electrodes.

Figure 4 shows the temperature dependence of the resistance in four-terminal measurements with electric contacts obtained by the local electron exposure method. R_{4t} shows a logarithmic increase with decreasing temperature though a systematic investigation is left open for further work. With regard to the temperature dependence of the contact resistance, all two-terminal resistances increase with decreasing temperature, but stay below 60 kΩ.

In conclusion, we have developed a novel technique of ''soldering'' nanotubes to gold contacts. The technique allows to selectively contact a single nanotube out of several others by locally exposing the area where the nanotube crosses the contact finger. All experiments point to the conclusion that the electric contact between the Au electrode and the nanotube is modified but not the nanotube itself. This technique enables the study of temperature dependent electrical transport properties of carbon nanotubes.

The authors acknowledge the fruitful contributions of H. Birk, H.-W. Fink, A. Genkinger, R. Huber, and M. Krüger. This work was supported by the Swiss National Science Foundation.

[1] S. Ijima, Nature (London) **354**, 56 (1991).
[2] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992); J. W. Mintmire, B. I. Dunlap, and C. T. White, *ibid.* **68**, 631 (1992); R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).
[3] S. N. Song, X. K. Wang, R. P. H. Chang, and J. B. Ketterson, Phys. Rev. Lett. **72**, 697 (1994).
[4] W. A. de Heer, W. S. Bacsa, A. Châtelin, T. Gerfin, R. Humphrey-Baker, L. Forró, and D. Urgate, Science **268**, 845 (1995); G. Baumgartner, M. Carrard, L. Zuppiroli, W. Bacsa, W. A. de Heer, and L. Forró, Phys. Rev. B **55**, 6704 (1997).
[5] L. Langer, V. Bayot, E. Grivei, J. P. Issi, J. P. Heremans, C. H. Olk, L. Stockman, C. Van Haesendonck, and Y. Bruynseraede, Phys. Rev. Lett. **76**, 479 (1996).
[6] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, Nature (London) **382**, 54 (1996).
[7] H. Dai, E. W. Wong, and C. M. Lieber, Science **272**, 523 (1996).
[8] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, and C. Dekker, Nature (London) **386**, 379 (1997); M. Bockrath, D. H. Cobden, P. L. McEuen, N. G. Chopra, A. Zettl, A. Thess, and R. E. Smalley, Science **275**, 1922 (1997); J. E. Fischer, H. Dai, A. Thess, R. Lee, N. M. Hanjani, D. L. Dehaas, and R. E. Smalley, Phys. Rev. B **55**, R4921 (1997).
[9] T. W. Ebbesen and P. M. Ajayan, Nature (London) **358**, 220 (1992).
[10] J. M. Bonard, T. Stora, J-P. Salvetat, F. Maier, T. Stöckli, C. Duschl, L. Forró, W. A. de Heer, and A. Châtelin, Adv. Mater. **9**, 827 (1997).
[11] W. S. Bacsa, R. LaDuca, J. Hoerter, F. Chibante, S. Subramoney, J. G. Lavin, K. Parvin and R. S. Ruoff, in *Fullerenes*, edited by K. M. Kadish and R. S. Ruoff (Electrochemical Society, Pennington, NJ, 1996), Vol. 3, p. 758.