6 August 2002

Chemical Physics Letters 361 (2002) 525–529

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

# The electrodeposition of metal at metal/carbon nanotube junctions

Derek W. Austin [a], Alex A. Puretzky [b], David B. Geohegan [c], Phillip F. Britt [d], Michael A. Guillorn [a,b,e], Michael L. Simpson [a,b,e,*]

[a] *Electrical and Computer Engineering Department, University of Tennessee, Knoxville, TN 37996, USA*
[b] *Material Science and Engineering Department, University of Tennessee, Knoxville, TN 37996, USA*
[c] *Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6006, USA*
[d] *Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6006, USA*
[e] *Molecular-Scale Engineering and Nanoscale Technologies Group, Oak Ridge National Laboratory, P.O. Box 2008, MS 6006, Oak Ridge, TN, USA*

Received 10 April 2002; in final form 19 June 2002

**Abstract**

We deposited a semiconducting single-walled carbon nanotube on Pd electrodes, and the initial charge transport measurements showed the usual large contact resistance between the electrodes and the nanotube. We electroplated Au over the electrodes with no obvious deposition of Au along the sidewalls of the nanotube between the electrodes. Post deposition charge transport measurements indicated more than a factor of six decrease in the electrode/nanotube contact resistance, yet the semiconducting behavior of the nanotube was maintained. A significant difference in the post deposition *I–V* characteristics may be explained by an electronic or mechanical modification of the nanotube/electrode junction. 

Single-walled carbon nanotubes (SWNTs) offer great promise for use in functional molecular-scale devices because of their remarkable mechanical and electrical properties [1]. These quasi one-dimensional molecules can be used as nanoscale wires [2,3] and as the channels of carbon nanotube field-effect transistors (CNTFETs) [4,5], which have been used as the active elements in inverting logic gates [6]. In many of these previous CNTFETs, the nanotube was deposited across prefabricated metal electrodes, resulting in a large contact resistance between the electrodes and the sidewalls of the nanotube. This high contact resistance is undesirable for applications in fast, low-power, electronic devices. Here we present a practical, low-cost, and scalable technique that significantly reduces the electrode/nanotube contact resistance while maintaining the semiconducting behavior of the nanotube. This process changes the nature of the metal/nanotube junction, thereby altering the *I–V* characteristics of the CNTFET. We propose two possible explanations for this change in *I–V* characteristics.

* Corresponding author. Fax: +1-865-576-2813.
*E-mail address:* simpsonml1@ornl.gov (M.L. Simpson).

0009-2614/02/$ - see front matter 
PII: S0009-2614(02)00992-2

The lowest reported values for electrode/nanotube contact resistance were obtained by patterning metal electrodes over SWNTs (see [7] for example). However, such methods require a post SWNT deposition imaging and mapping processes followed by lithographic definition of the electrodes [7]. We have applied the electrodeposition of Au to reduce the contact resistance between metal electrodes and the sidewalls of carbon nanotubes on prefabricated electrode structures. This allows the definition of many elements of the device before nanotube placement is known. Furthermore, this process can be selectively carried out for individual electrodes, and electrode pairs can be selected for metal deposition through the examination of $I$–$V$ characteristics instead of a tedious process of imaging and mapping nanotube position.

We produced our nanotubes using pulsed laser vaporization (PLV) as previously described [8]. SWNTs taken directly from the PLV reactor (i.e. no purification or processing) were ultrasonically dispersed in high purity 1,2-dichloroethane and spin-deposited onto prefabricated electrodes. The Pd electrodes on a Ti adhesion layer were patterned on an oxidized Si wafer (200 nm of silicon dioxide) using electron beam lithography. These electrodes extended 36 nm above the substrate. An individual 1.3 nm diameter SWNT was deposited across two electrodes (Fig. 1a). The silicon substrate was contacted by scribing through the native oxide on the edge of the sample and then dipping it in silver paint. This structure formed a CNTFET as has been previously described [4,5].

Initial charge transport measurements for this sample are plotted in Fig. 2. All measurements were made in air under the same ambient room conditions. These $I$–$V$ curves are indicative of a semiconducting SWNT and this CNTFET was p-channel in agreement with previously reported devices [4,5]. The two-probe resistance measured across the device is composed of the SWNT resistance and the contact resistance between the nanotube and each electrode, and at large negative gate voltages the contact resistance dominates the total resistance. The initial two-probe resistance of our device with a gate voltage of −10 V was

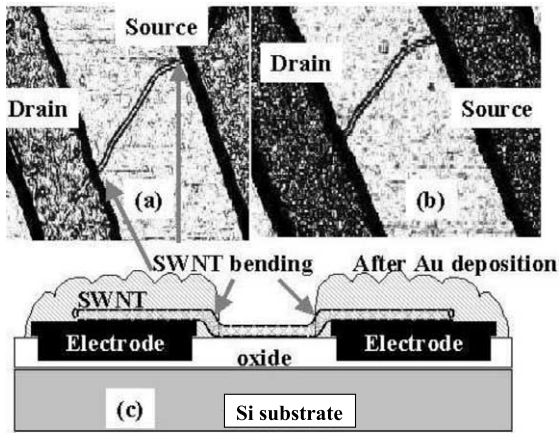


Fig. 1. SWNT deposited across electrodes. (a) AFM image of a 1.3-nm-diameter semiconducting SWNT deposited on two Pd electrodes. The prefabricated electrodes, which are 400 nm apart, extend 36 nm above the substrate and are labeled as drain and source, respectively, indicating the configuration used for the charge transport measurements. (b) AFM image after electroplating Au onto the drain and source electrodes. The two center electrodes now extend 42 nm above the substrate, and the SWNT is buried under the electrodeposited layer of Au on the electrode. The regions of the nanotube between the electrodes show no obvious Au deposits. (c) Schematic representation of SWNTs on the electrodes indicating the bending in the nanotube as it transitions from the electrode to the substrate. After electroplating, the bends in the SWNT are encased in Au.

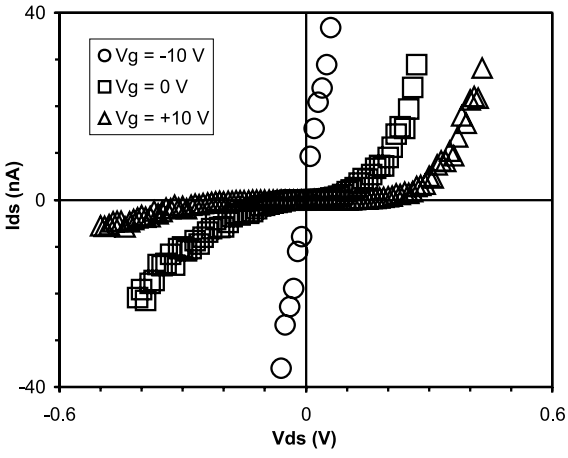


Fig. 2. Initial charge transport measurements showing the p-channel CNTFET characteristic. A back gate voltage was applied to the silicon substrate. The contact resistance was 1.7 MΩ.

1.7 MΩ, in rough agreement with other devices similarly fabricated and characterized [4–6,9].

By carefully controlling the deposition current, Au was electroplated on the two electrodes bridged by the nanotube. Both electrodes were electrically connected together and acted as the cathodes for reducing Au from a 10-μl droplet of electroplating solution (Orotherm HT, Technic). A platinum wire served as the counter electrode, and a deposition current of 20 nA was maintained for 12 min. The sample was rinsed in deionized water, dried with nitrogen, and baked in air at 150 °C for 5 min.

As a result of the electrodeposition, the electrodes were covered with a 6-nm thick layer of Au that covered the sections of the nanotube contacting the electrodes (Fig. 1b). Our previous electroplating experiments with metallic SWNTs or small bundles of SWNTs containing at least one metallic nanotube showed the nucleation and growth of Au nanodots on the sidewalls of the nanotube (Fig. 3). However, for this semiconducting nanotube, these Au nanodots did not form, possibly indicating that the regions of the nanotube between the electrodes may have remained free of Au deposits. This might be expected in this region of the nanotube since the electrons in this p-type element reside at too low an energy to reduce the Au ions in solution. However, the Fermi level is pinned at the valence level for the portion of the SWNT on or near the electrode [4], and Au may be reduced on this region of the SWNT.

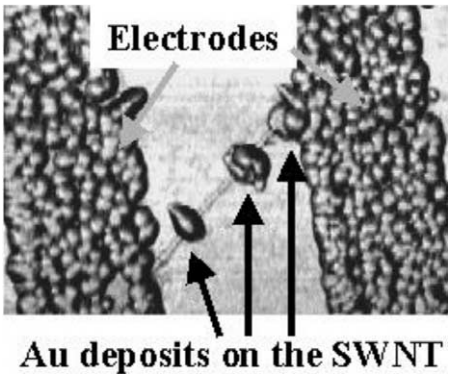


Fig. 3. The electrodeposition of Au on a SWNT. These obvious Au nanodots are always present on samples where we see Au deposition on the portion of the nanotube between the electrodes.

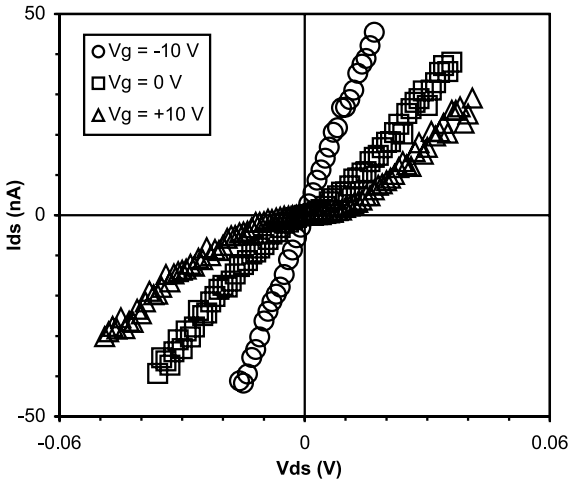


Fig. 4. Charge transport measurements after electrodepositing Au onto the drain and source electrodes. The contact resistance was 270 kΩ. Note that the range for $V_{DS}$ in this figure is only 10% of that in Fig. 2.

The post electroplating charge transport measurements (Fig. 4), acquired under the same ambient conditions as the initial measurements, show a significant reduction in the contact resistance. The electroplating resulted in a reduced two-probe resistance of 270 kΩ, more than a factor of six less than the initial 1.7 MΩ. Fig. 5 demonstrates that the low-voltage resistance of the electroplated device can be modulated over seven orders of magnitude.

After electroplating the SWNT remained a p-type semiconductor (Fig. 4), indicating that either no Au was deposited on the nanotube outside of the electrode region, or that anything deposited did not change the fundamental semiconducting nature of the SWNT. However, the *I–V* characteristics of the CNTFET were considerably altered. Before electroplating, the *I–V* curve with the gate voltage set to zero had a gap of ~0.4 V symmetrically placed around $V_{DS} = 0$ where conduction was very low (Fig. 2). However, for identical bias condition after electroplating, this gap was only ~20 mV (Fig. 4). This behavior may be explained by band bending in the SWNT in-

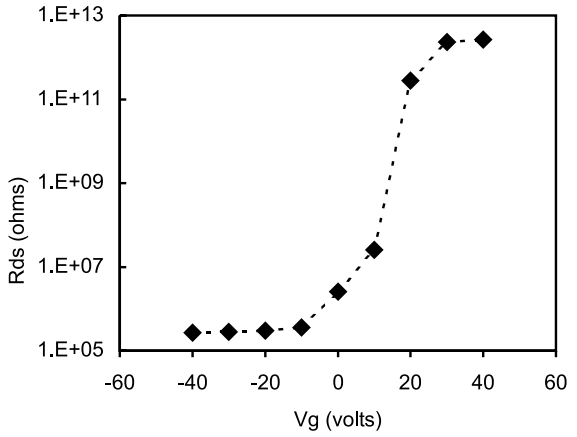


Fig. 5. The low-voltage resistance of the CNTFET of Fig. 1b can be modulated by seven orders of magnitude by the gate voltage.

duced by electrode/nanotube work function differences. While a Pd electrode CNTFET generated the curves in Fig. 2, the significant change in contact resistance would suggest that the electroplated Au controlled the nanotube/electrode junction during the generation of the curves in Fig. 4. While literature values of work function for Au and Pd are available, the work functions of the materials as used here are likely to vary from these values due to surface impurities. However, changes in band bending at each end of this short SWNT segment due to the different work functions of the two electrode materials may explain the change of $I$–$V$ characteristics after electroplating as described previously [4].

A possible alternate explanation would be a change in the mechanical configuration of the nanotube/electrode junction. The SWNT was draped across the electrodes that extended 36 nm above the substrate, causing two bends in the nanotube at each electrode (Fig. 1c). This bending is especially noticeable at the source electrode in Fig. 1a. However, Fig. 1b indicates that Au encased these bends after electroplating as shown schematically in Fig. 1c. Since mechanical bending of SWNTs is known to alter charge transport in SWNTs [10], encasing these bends in the electrode metal may alter the $I$–$V$ characteristics of the CNTFET.

While our two-terminal resistance of 270 kΩ is still relatively high, low resistance metal/nanotube contacts have been reproducibly fabricated using metals such as Ti and Ni [11]. This suggests that our technique could achieve greater reduction in the electrode/nanotube contact resistance by electrodepositing a metal with a smaller grain size.

In summary, we have successfully electrodeposited Au over the sidewalls of a SWNT deposited across prefabricated electrodes. This technique resulted in a significant reduction in the electrode/nanotube contact resistance. Furthermore, the electroplating did not perturb the semiconducting behavior of the SWNT. However, the $I$–$V$ characteristics of the CNTFET were significantly altered, possibly due to the work function difference between the original electrode material and the electroplated material or a mechanical change in the electrode/nanotube junction.

## Acknowledgements

The authors would like to thank Pam Flemming for her help in preparing the patterned electrode structures. This work was supported under a National Science Foundation Graduate Fellowship and by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory. The research was carried out at ORNL, managed by UT-Battelle, LLC, for the US Department of Energy under Contract No. DE-AC05-00OR22725, and in part at the Cornell Nanofabrication Facility (a member of the National Nanofabrication Users Network) which is supported by the National Science Foundation under Grant ECS-9731293, its users, Cornell University and Industrial Affiliates.

## References

[1] C. Dekker, Phys. Today 52 (1999) 22.
[2] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, Nature (London) 386 (1997) 474.
[3] M. Bockrath, D.H. Cobden, P.L. McEuen, N.G. Chopra, A. Zettl, A. Thezss, R.E. Smalley, Science 275 (1997) 1922.

[4] S.J. Tans, A.R.M. Verschueren, C. Dekker, Nature (London) 393 (1998) 49.
[5] R. Martel, T. Schmidt, H.R. Shea, T. Hertel, Ph. Avouris, Appl. Phys. Lett. 73 (1998) 2447.
[6] V. Derycke, R. Martel, J. Appenzeller, Ph. Avouris, Nano Lett. 1 (2001) 453.
[7] H.T. Soh, C.F. Quate, A.F. Morpurgo, C.M. Marcus, J. Kong, H. Dai, Appl. Phys. Lett. 75 (1999) 627.
[8] A.A. Puretzky, D.B. Geohegan, X. Fan, S.J. Pennycook, Appl. Phys. Lett. 76 (2000) 182.
[9] A. Bezryadin, A.R.M. Verschueren, S.J. Tans, C. Dekker, Phys. Rev. Lett. 80 (1998) 4036.
[10] T.W. Tombler et al., Nature 405 (2000) 769.
[11] Y. Zhang, N.W. Franklin, R.J. Chen, H. Dai, Chem. Phys. Lett. 331 (2000) 35.