

UC Irvine

UC Irvine Previously Published Works

Title

High Temperature Resistance of Metallic, Single-Walled Carbon Nanotube Devices

Permalink

<https://escholarship.org/uc/item/6fb4m5gz>

Journal

App. Phys. Lett., 9(083506)

Author

Collins, Philip G

Publication Date

2008

Peer reviewed



High temperature resistance of small diameter, metallic single-walled carbon nanotube devices

Alexander A. Kane, Kevin Loutharback, Brett R. Goldsmith, and Philip G. Collins

Citation: [Applied Physics Letters](#) **92**, 083506 (2008); doi: 10.1063/1.2885092

View online: <http://dx.doi.org/10.1063/1.2885092>

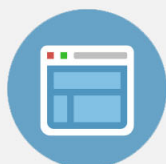
View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/92/8?ver=pdfcov>

Published by the [AIP Publishing](#)



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



High temperature resistance of small diameter, metallic single-walled carbon nanotube devices

Alexander A. Kane, Kevin Loutherbach, Brett R. Goldsmith, and Philip G. Collins^{a)}

Department of Physics and Astronomy, University of California, Irvine, California 92697-4576, USA

(Received 9 November 2007; accepted 26 January 2008; published online 28 February 2008)

The effects of high temperature cycling on the resistance of metallic single-walled carbon nanotube (SWCNT) devices is measured *in situ*. Individual, small-diameter SWCNTs contacted by palladium or titanium electrodes were measured from room temperature up to 1000 K in ultrahigh vacuum. Upon the first thermal cycling, the device resistances fluctuate and generally decrease. Pd-contacted devices typically become stable by 450 K, whereas Ti-contacted devices require higher treatments above 600 K. Once these temperatures have been exceeded, subsequent thermal cycling has minimal effects. Heat-treated devices exhibit linear temperature dependences, with Pd and Ti contacts producing average temperature coefficients of $-3 \times 10^{-4}/\text{K}$ and $1.1 \times 10^{-3}/\text{K}$, respectively. © 2008 American Institute of Physics. [DOI: 10.1063/1.2885092]

After a decade of intense study, electronic devices composed of single-walled carbon nanotubes (SWCNTs) are relatively well understood. However, a topic of continued experimental^{1–4} and theoretical^{5–8} investigation remains in the nature of the electrical connection between SWCNTs and macroscopic electrodes. As summarized in recent reviews,^{9,10} these connections depend critically on both the SWCNT diameter and the contacting metal. While transparent contacts can be made reliably to large diameter (>1.5 nm) SWCNTs using Pd metal,² contact resistances are much higher for both metallic⁴ and semiconducting³ SWCNTs with smaller diameters, varying considerably even for relatively small (0.1 nm) diameter changes. The origin of this resistance is of interest both fundamentally and for applications, such as SWCNT transistors, for which small diameter SWCNTs are needed to maximize current on/off ratios.¹¹ No model currently accounts for the large resistances observed between metals and small diameter, metallic SWCNTs.

In addition to SWCNT diameter and contact metal, processing history is equally important in determining the device properties and reducing device-to-device variability. Mild temperature treatments can produce dramatic changes in the SWCNT electrical properties,^{12,13} and reports of various annealing strategies suggest that heating plays an important role in the contact resistance.^{14–17} However, these reports do not provide sufficient detail either to optimize device properties or to understand the chemical and physical interactions at work.

This work investigates these effects by measuring SWCNT device resistances *in situ* during the annealing cycles ranging from 300 to 1000 K. These temperatures are insufficient to change the SWCNT crystallinity,^{18,19} but physisorbed and then chemisorbed species can both be removed from the device surfaces, and the contacting metals may be annealed. Accordingly, the measurements were performed in ultrahigh vacuum (UHV) and, since contact interfaces may also be effected, both Pd and Ti contact metals were compared.

Device preparation followed techniques standard in the SWCNT literature.^{20–22} Briefly, small diameter (1.1 ± 0.1 nm) SWCNTs were grown by chemical vapor deposition²⁰ of methane at 950 °C on *p*-doped, oxide-coated Si wafers. Thick oxides of 250–500 nm were necessary to maintain isolation between the SWCNT and the underlying substrate, due to the rapid gate oxide degradation during the voltage-biased measurements at high temperatures. Using standard photolithography,²³ contact electrodes were defined on top of the SWCNTs with an electrode separation of 2.5 ± 0.5 μm [Fig. 2(a), inset]. Next, 50 nm of either Ti or Pd metal was deposited by electron-beam evaporation, with a thin (~ 0.8 nm) Ti underlayer on the Pd samples. After deposition the resist was lifted off using Remover PG (Micro-Chem Corp.) with isopropyl alcohol, de-ionized water, and N_2 rinses. Postfabrication, atomic force microscopy (Pacific Nanotechnology Nano-R) was used to count the number of SWCNTs.

Metallic devices having little or no gate dependence were selected for further measurements, and Table I lists the characteristics of each device described here. Metallic SWCNTs are particularly intriguing because their contact resistance mechanisms are poorly understood.²⁴ To study the effects of heat treatment, metallic devices are also experimentally preferable to semiconducting SWCNTs, which have temperature-dependent and hysteretic doping levels and gate

TABLE I. Summary of samples discussed. The gate sensitivity denotes the percent variation in resistance for gate voltages between +10 and –10 V. Initial R denotes the samples' resistance preanneal measured *in situ* at room temperature, and final R is postanneal. dR/dT is the constant slope of $R(T)$ postanneal.

Sample	Pd-A	Pd-B	Ti-A	Ti-B
# of SWNTs	$<10^a$	1	2	16^a
Gate Sensitivity	41%	12%	14%	61%
Initial R (k Ω)	438	2230	1100	89 200
Final R (k Ω)	489	129	183	550
dR/dT (Ω/K)	54	–91	166	349

^aApproximately one-third of the SWCNTs are estimated to contribute to measurements on Pd-A and Ti-B.

^{a)}Electronic mail: collinsp@uci.edu.

thresholds.^{12,13} The selection of metallic SWCNTs excludes these artifacts from resistance measurements performed at fixed gate bias. Devices having nonzero gate dependence were measured at the point of lowest conductance to minimize any contribution from semiconducting SWCNTs.

Measurements were performed in a custom UHV apparatus with a base pressure of 5×10^{-9} Torr. Devices were held in place on a water-cooled BN heater by four or more long, tungsten needle probes. The high resistance contact needles allowed temperature excursions to 1000 K while simultaneously maintaining four-wire electrical connectivity. The SWCNT resistance $R(T)$ was determined using four probe measurements at alternating positive and negative biases, which eliminated extraneous noise and thermoelectric voltages. The resulting resistance errors are estimated to be $<1\%$. Temperatures were monitored and controlled to within 5% using a type *K* thermocouple mounted on the BN heater surface, with the error calibrated using a Pt reference thermistor (Lakeshore #PT-103-70J). Typical temperature cycling was either at a slow, uniform rate of 1 K/s or else at 300 K/s to soak setpoints spaced at 100 K intervals. The latter measurements required on-chip thermometry having temperature errors $<0.5\%$.

Figure 1 shows $R(T)$ for two Pd-contacted samples as they were first annealed *in situ*. The first, sample Pd-A, was heated continuously to 800 K and then cooled to 450 K [Fig. 1(a)]. $R(T)$ was relatively flat but exhibited two irreversible changes on the first heating cycle. The most noticeable effect was a slight increase in R as the temperature was ramped above 600 K. Subsequent $R(T)$ curves through the same temperature region were monotonic and linear, indicating that this increase was a permanent change. The second effect of heating was a visible increase in scatter of the data in the region $475 < T < 650$ K. We attribute this noise to thermal activation of a chemical process, possibly annealing of the metal that only occurs during the first heat treatment. The insets to Fig. 1(a) show the result of temperature excursions to 1100 K on the same sample. Increasing T above 900 K resulted in a large R increase, ultimately to an open circuit, as the Pd beaded up on the SiO_2 surface and became discontinuous. Pd electrodes are therefore limited to processing temperatures below 900 K, at least for bare Pd as used here.

Although moderate thermal cycling had a minimal effect on Sample Pd-A, as-fabricated devices with higher resistances are more susceptible to improvements. Sample Pd-B, for example, began with an anomalously high $R=2.2$ M Ω , but a temperature soak at 400 K for 250 s was sufficient to drop R to 76 k Ω . [Fig. 1(b)]. A second soak at 500 K initially increased R nearly threefold, followed by a slow decrease over the 500 s soak duration to a fluctuating $R \sim 80$ k Ω . A third temperature step to 600 K produced a modest resistance increase and, after approximately 200 s, a reduction of the device noise back to original levels. Both the overall increase in resistance and the appearance and disappearance of enhanced fluctuations reproduce the effects seen in the continuous temperature ramp on sample Pd-A. Finally, a curve of $R(T)$ acquired during cooling of sample Pd-B shows a relatively flat, slightly negative $R(T)$ that is reproducible over subsequent thermal cycles [Fig. 1(c)]. The negative slope suggests that a small, thermally activated barrier remains at the contact, since the SWCNT band structure is metallic. The final room temperature resistance of 129 k Ω corresponds to a conductance of $0.2 e^2/h$ and replicates pre-

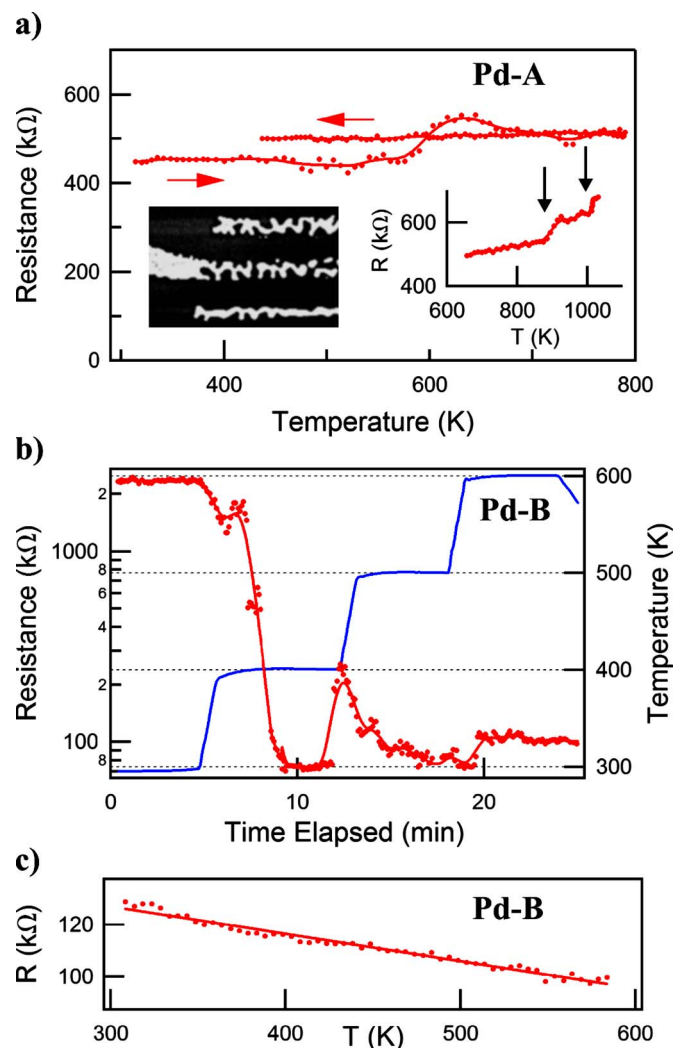


FIG. 1. (Color online) Heat treatment of two Pd-contacted samples. The points represent the measurements while the lines serve as a guide to the eye. (a) Temperature dependence of the resistance $R(T)$ of sample Pd-A. The arrows indicate heating and cooling directions. The device was previously annealed *ex situ* at 450 K. Insets: $R(T)$ as Pd-A was annealed above 1000 K, and a scanning electron micrograph of the connecting Pd electrodes afterwards. (b) The resistance (red, left axis) of sample Pd-B as the temperature (blue, right axis) was increased in steps of 100 K in a step/soak pattern. (c) $R(T)$ for Pd-B post-anneal and a linear fit.

vious examples of good Pd contacts to 1.1 nm SWCNTs.⁴

Figure 2 depicts similar effects observed on Ti-contacted SWCNT devices. Unlike Pd, for which sample Pd-B was an anomaly, Ti fabrication regularly produces high R devices that can benefit from thermal processing. Figures 2(a) and 2(b) depict the smooth thermal cycling of samples Ti-A and Ti-B and illustrate the large drops in R that occur on the first thermal cycle to 750 K. Sample Ti-A is a representative sample, a device consisting of two metallic SWCNTs in parallel. Its resistance did not change significantly until $T > 450$ K, when it decreased continuously until T reached 750 K. No significant hysteresis was observed in $R(T)$ from 800 to 1050 K, suggesting that 750 K is an appropriate processing temperature, but that higher temperatures can be used safely. As fabricated, sample Ti-B had a very high contact resistance and multiple SWCNTs in parallel. Furthermore, it began with a negative dR/dT characteristic of a semiconductor. Separate thermal cycles to 450 and 600 K each resulted in approximately tenfold R reductions, with the

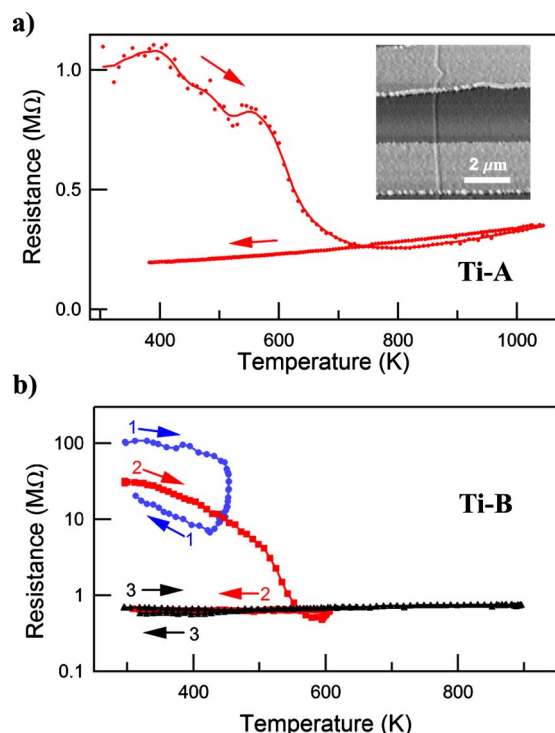


FIG. 2. (Color online) Heat treatment of two Ti-contacted devices. The numbers and arrows indicate the time sequence of the traces and the heating and cooling directions. The points represent data and the lines are provided as a guide to the eyes. (a) Sample Ti-A was annealed at a temperature of 1040 K and then cooled to room temperature. (b) Sample Ti-B was annealed at temperatures of 450, 600, and 900 K.

second cycle resulting in a constant, positive dR/dT . In contrast, processing from 700 to 900 K resulted only in a small, 7% decrease in R .

More than 12 Ti-contacted devices have been measured, and the temperature necessary to achieve a stable $R(T)$ was similar to that of Ti-A and Ti-B in each case, even though the initial R of the sample set spanned three orders of magnitude. Following thermal treatment, the range of the final R values was greatly reduced to approximately 300 kΩ per SWCNT, in agreement with the predictions of the ideal Ti-SWCNT contacts.^{3,4} Good agreement between the final device R and the number of connected SWCNT further suggests nearly uniform contact resistances after heat treatment.

While desorption of physisorbed species from the SWCNT may play some role in the effects measured here, the different responses of Ti- and Pd-contacted devices to heat treatments suggest that contact effects dominate the observed changes. Theoretical studies have shown that Ti should make a near-ideal contact to metallic SWCNTs, even for small diameter SWCNTs,^{5,8} due to the strong coupling between the Ti d orbitals and the SWCNT π orbitals; however, such studies assumed fully relaxed contact geometries. In addition, Ti is a much more reactive metal than Pd,⁸ and it is likely that chemical changes at the metal-SWCNT-oxide interface play a role in the resistance decrease, as well as structural changes in the Ti metal.

Finally, all of the heat-treated devices exhibited linear $R(T)$ with an average value of the temperature coefficient $\alpha = 1/R dR/dT$ is $(1.1 \pm 0.3) \times 10^{-3} \text{ K}^{-1}$. This value is more than an order of magnitude lower than the value for a good

bulk metal, which is close to $5 \times 10^{-2} \text{ K}^{-1}$.²⁵ For both Pd-contacted samples, α has a magnitude of 10^{-4} K^{-1} , significantly lower than that of the Ti-contacted samples. The substantial difference between Ti and Pd suggests that the temperature dependence remains dominated by contact effects and possibly the bulk α values of the metal electrodes. For example, in the ballistic limit, resistance is exclusively determined by thermalization of the carriers in the metallic electrodes, and this thermalization is mediated by acoustic phonons of the contacting metal, not the SWCNT.²⁶ Variations in the temperature coefficients between similar devices contacted by the same metal may be ascribed to the unavoidable physical and chemical variations at the SWCNT-metal interface.

This research was supported by NSF (DMR-0239842) and an ARCS Foundation fellowship.

¹W. Liang, M. Bockrath, D. Bozovic, J. H. Hafner, M. Tinkham, and P. Hongkun, *Nature (London)* **411**, 665 (2001).

²D. Mann, A. Javey, J. Kong, Q. Wang, and H. J. Dai, *Nano Lett.* **3**, 1541 (2003).

³Z. Chen, J. Appenzeller, J. Knoch, Y. Lim, and P. Avouris, *Nano Lett.* **5**, 1497 (2005).

⁴W. Kim, A. Javey, R. Tu, J. Cao, Q. Wang, and H. Dai, *Appl. Phys. Lett.* **87**, 173101 (2005).

⁵J. J. Palacios, A. J. Perez-Jimenez, E. Louis, E. San Fabian, and J. A. Verges, *Phys. Rev. Lett.* **90**, 106801 (2003).

⁶S. H. Ke, W. T. Yang, and H. U. Baranger, *J. Chem. Phys.* **124**, 181102 (2006).

⁷W. Zhu and E. Kaxiras, *Nano Lett.* **6**, 1415 (2006).

⁸Y. Matsuda, W. Q. Deng, and W. A. Goddard, *J. Phys. Chem. C* **111**, 11113 (2007).

⁹S. Heinze, J. Tersoff, and P. Avouris, in *Introducing Molecular Electronics*, edited by G. Cuniberti (Springer, Berlin, 2005), Vol. 680.

¹⁰H. Dai, A. Javey, E. Pop, D. Mann, W. Kim, and Y. Lu, *NANO* **1**, 1 (2006).

¹¹J. Guo, S. Datta, and M. Lundstrom, *IEEE Trans. Electron Devices* **51**, 172 (2004).

¹²K. Bradley, S. H. Jhi, P. G. Collins, J. Hone, M. L. Cohen, S. G. Louie, and A. Zettl, *Phys. Rev. Lett.* **85**, 4361 (2000).

¹³V. Derycke, R. Martel, J. Appenzeller, and P. Avouris, *Appl. Phys. Lett.* **80**, 2773 (2002).

¹⁴S. Rosenblatt, Y. Yaish, J. Park, J. Gore, V. Sazonova, and P. L. McEuen, *Nano Lett.* **2**, 869 (2002).

¹⁵W. Yunsung, G. Duesberg, and S. Roth, *Nanotechnology* **18**, 095203 (2007).

¹⁶D. Lifeng and R. Chebiam, *J. Appl. Phys.* **101**, 024320 (2007).

¹⁷A. Bachtold, M. Henny, C. Tarrler, C. Strunk, C. Schonenberger, J. P. Salvetat, J. M. Bonard, and L. Forro, *Appl. Phys. Lett.* **73**, 274 (1998).

¹⁸A. C. Dillon, T. Gennett, K. M. Jones, J. L. Alleman, P. A. Parilla, and M. J. Heben, *Adv. Mater. (Weinheim, Ger.)* **V11**, 1354 (1999).

¹⁹M. S. Dresselhaus and M. Endo, in *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*, edited by M. S. Dresselhaus, G. Dresselhaus, and P. Avouris (Springer, Berlin, 2001), p. 11.

²⁰L. An, J. M. Owens, L. E. McNeil, and J. Liu, *J. Am. Chem. Soc.* **124**, 13688 (2002).

²¹S. M. Huang, B. Maynor, X. Y. Cai, and J. Liu, *Adv. Mater. (Weinheim, Ger.)* **15**, 1651 (2003).

²²B. R. Goldsmith, J. G. Corneus, V. R. Khalap, A. A. Kane, G. A. Weiss, and P. G. Collins, *Science* **315**, 77 (2007).

²³Following a 15 min 200 °C prebake on a hotplate, LOR 1A (MicroChem) was spun on at 4000 rpm with a postbake hotplate temperature of 190 °C for 5 min. Shipley 1808 was spun on on top of the LOR at 4000 rpm and softbaked at 90 °C for 30 min in a convection oven.

²⁴M. Di Ventra and T. N. Todorov, *J. Phys.: Condens. Matter* **16**, 8025 (2004).

²⁵*CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (Taylor and Francis, London, 2007).

²⁶Y. Imry and R. Landaur, *Rev. Mod. Phys.* **71**, S306 (1999).