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Gold contact to individual metallic carbon nanotubes: A sensitive nanosensor for high-pressure

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A strong and universal piezoresistive effect is evidenced for individual metallic carbon nanotubes contacted to gold electrodes through high contact resistances. The effect is well explained through a pressure modulation of the tunnel barrier width at the contact. The pressure dependence (−16%/GPa) is much stronger than for standard resistive high pressure gauges, and it depends neither on the initial resistance nor on the pressure transmitting medium. © *2010 American Institute of Physics*. [doi:10.1063/1.3507389]

Carbon nanotubes have raised a lot of interest for their mechanical[1–3] and electronic[4–7] properties, which can be combined in electromechanical sensors[8–10] or actuators.[11] In particular, they show very sensitive piezoresistive effects, which origin can be attributed either to interactions with contacts[12] or to an intrinsic evolution.[13,14] In this latter case, a dependence on the chirality is predicted[13] and observed.[14] In the high pressure domain, different sensors have been designed experimentally[9] or theoretically.[15] For example, a pressure sensor was built by depositing a nanotube on a flexible membrane.[9] The differential pressure across the membrane was then measured through the change in the nanotube conductivity. Another pressure sensor was also theoretically designed on the base of the diameter dependent pressure collapse of the nanotube cross-section.[15]

When based on the intrinsic evolution of the tube, e.g., change in the gap, the pressure dependence will depend on the tube chirality or at least on its diameter.[15,16] This is interesting for tuning the device properties but it relies on the possibility to choose among the nanotube chiralities or diameters. Unfortunately, this is still complicated, despite the important progress that have been made in separating different types of carbon nanotubes.[17,18] Here we show that using metallic nanotubes deposited on gold contacts, for which the contact resistance is well above the intrinsic resistance, we can obtain a sensitive and general evolution that does not depend on the nanotube initial resistance. This result opens the possibility of developing high-pressure miniaturized sensors based on carbon nanotubes.

To show this, we have fabricated nanotube devices where individual metallic nanotubes are lying on top of gold electrodes, as depicted in Fig. 1. The resistance of these devices was then measured under high gas pressure up to 1 GPa. Nine pressure experiments were carried out on five different nanotubes having different initial total resistances (resistance of the nanotube plus the contact). Two of them were measured both in argon and helium as pressure transmitting medium (PTM). At each pressure step, the resistance was measured by the linear dependence of the current on the bias voltage, avoiding errors due to offset voltages or currents. The initial measured resistance at atmospheric pressure depended on the considered nanotube, with values ranging from 86 kΩ to 1.3 MΩ. Further experimental details can be found in Ref. 19.

For all experiments, the resistance is found to decrease linearly with pressure, which allows adjusting the pressure evolution of the resistance by a linear fit. The relative change in resistance with pressure is then obtained by normalizing each data set by its fitted initial resistance. These relative changes in resistance are plotted in Fig. 2. Remarkably, we observe that all the experimental data fall on the same linear decrease, within experimental error. The mean value of the resistance evolution is −16%/GPa ($-0.16\ \mathrm{GPa}^{-1}$). All the experimental conditions and pressure dependencies relative to this graph are listed in Table I.

In order to characterize the physical origin of the observed evolution, we write the total resistance of a nanotube as $R_{\mathrm{tot}}=R_Q(1+l/l_m)+R_C$, where R_Q is the quantum contact resistance, l is the length of the tube, l_m is the mean free path of electrons, and R_C the nonquantum contact resistance. $R_{\mathrm{int}}=R_Q(1+l/l_m)$ can be seen as the intrinsic resistance of the tube, including the quantum contact resistance which arises from the limited conducting channel number. In nanotubes, $R_Q=6.5\ \mathrm{k}\Omega$, while l_m has been estimated to be between 0.5 and 1 μm at ambient conditions.[7,20,21] The lengths of our nanotubes are typically between 1 and 10 μm, so that the

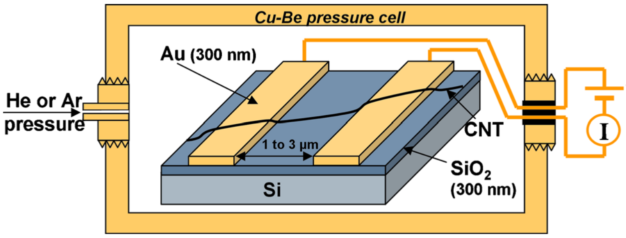

FIG. 1. (Color online) Scheme of the experimental setup. Carbon nanotubes (CNT) are grown directly on top of gold electrodes which are deposited by photolithography on an oxidized silicon wafer. The device is then placed inside a high pressure cell providing electrical feed through for resistance measurements.

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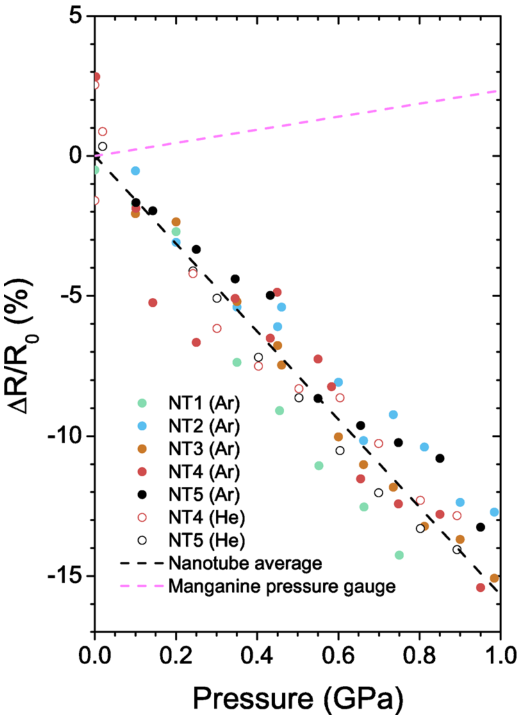

FIG. 2. (Color online) Relative change in the nanotube resistances with pressure. The parameters of the pressure experiments are detailed in Table I. The dotted line across the points is the average slope of −16%/GPa. The dotted line on top of the figure is the evolution of the manganin pressure gauge (+2.3%/GPa), the standard gauge that we employed to measure the pressure.

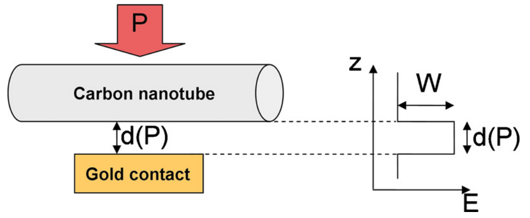

FIG. 3. (Color online) Scheme of the rectangular tunnel barrier accounting for the nonquantum contact resistance. The width of the barrier (d) is the distance between the gold contact and the nanotube; the height (W) is equal to the mean work function of gold and nanotubes. The piezoresistive effect comes from the pressure dependence of the gold-nanotube distance $d(P)$.

intrinsic resistances can range from 13 to 140 kΩ. As shown in Table I, the initial resistances range from 86 kΩ to 1.3 MΩ, which are well above the intrinsic resistance. The nonquantum contact resistance is thus predominant in the total resistance. Moreover, the change in resistance with pressure ranges from 13 to 200 kΩ, which in average is also well above the expected intrinsic resistance of the nanotube. This means that the observed evolution should dominantly find its origin in changes in the nonquantum contact resistance.

In a first approximation, it is possible to model the nonquantum contact resistance by a rectangular tunnel barrier, which width is the distance d between the tube and the gold contact, and which height is the mean work function W at the gold-nanotube contact. The corresponding scheme is depicted in Fig. 3. The work function of gold is $W_{\mathrm{Au}}=5.1$ eV while the one of nanotubes is estimated to $W_{\mathrm{NT}}=4.8$ eV.[22–24] So actually, a trapezoidal shape barrier should be needed to take into account the different work functions of gold and nanotubes. But due to the small difference in work functions, the result is the same as for a rectangular shape. Therefore, the barrier height can be estimated to the mean value of $W=4.95$ eV. The distance d and its evolution with pressure have been estimated for nanotubes buried into gold contacts. It can be written as $d=d_0(1-\alpha P)$, with $d_0=2.78$ Å and $\alpha=26.5$ TPa^{-1}.[25] In the case of a single walled carbon nanotube deposited on top of gold contacts, which correspond to our case, the ambient pressure d_0 has been predicted with a value of 2.9 Å.[26] In such geometry, there is no calculated value for the α coefficient, so as an ansatz, we adopt the graphite c-axis variation with pressure, which is $\alpha=25$ TPa^{-1}.[27]

TABLE I. Summary of the following different sets of measurement on metallic nanotubes: surrounding PTM, fitted initial resistance of the contacted nanotube (R_0), and fitted pressure coefficient of the relative change in resistance (slope). The nanotubes are labeled as in Fig. 2.

Device	PTM	R_0 (kΩ)	Slope (GPa^{-1})
NT1	Ar	407	−0.193
NT2	Ar	86	−0.133
NT3	Ar	172	−0.158
NT4	Ar	1337	−0.157
NT5	Ar	341	−0.137
NT4	He	1326	−0.153
NT5	He	276	−0.167
Average			−0.157
Manganin pressure gauge			+0.023

With these assumptions we obtain the scaling of the tunnel resistance as follows: $R_T \propto e^{2kd}$, where $k=\sqrt{2m_eW}/\hbar$, m_e being the mass of an electron, and $\hbar$ the reduced Planck constant. Given the values of k, d_0, and the studied pressure range, this exponential behavior can be linearized to $\Delta R_T/R_T=-\gamma P$, where $\gamma=2kd_0\alpha$. We obtain a pressure coefficient for the tunnel resistance that is $\gamma=0.17$ GPa^{-1}. We can note that for the buried case, the above mentioned values for d_0 and α also give a pressure coefficient of $\gamma=0.17$ GPa^{-1}. Both these values are in excellent agreement with our experimental results of $\gamma=0.16$ GPa^{-1}. Therefore, the observed evolution is well explained by a variable tunnel barrier at the gold-nanotube contact. Moreover, this behavior may be extended to all gold to metallic nanotube contacts, especially the buried case. However, one can expect this evolution to be less pronounced when the total resistance is closer to the intrinsic resistance, as should be the case when the nanotube is buried.

It is also interesting to note that although a modification of the nanotube cross-section is expected under pressure, it most likely cannot account for the observed evolution of the resistance. Indeed the cross-section modification is known to occur between two critical pressures corresponding, respectively, to the onset of the ovalization and the final collapse of the nanotube cross-section.[28,29] Therefore this would result in at least one clearly visible region with no or smaller pressure evolution, similar to what is observed in Ref. 19. Here it seems that either the effect of the cross-section modification is not significant compared to the one describe above, or the critical pressure of ovalization is situated above our pressure range (which we mainly expect for the studied range of diameters).

The observed general evolution is very interesting if we think in terms of pressure sensing devices. It means that whatever the chirality of the tube and the quality of the contact, the behavior will be as expected provided the nanotube is metallic and the contact resistance is high enough. The separation of metallic from semiconducting tubes is readily possible,[18] and high resistance contacts are easier to produce, especially when the nanotubes are deposited on top of the contacts. Therefore, such a device would be easy to produce. Another interesting feature is the pressure coefficient of 0.16 GPa^{-1}, which is almost one order of magnitude higher than the coefficient of the manganin pressure gauge (-2.34×10^{-2} GPa^{-1}) used for experiments in the high-pressure domain. The use of other metals for the contact is possible, but the pressure coefficient will be different, depending on the rate at which the nanotubes get closer to the contact with pressure. Among gold, platinum, and palladium, gold should be the most sensitive material, as its confinement potential is predicted to be the shallowest.[26]

The process here evidenced is also interesting because it essentially implies a Van der Waals bonding scheme, which forms a tunnel barrier that is easily deformable with pressure. We could thus virtually build such devices with many different materials. However, the case of the gold contacted nanotube is very favorable, not only because gold is better than platinum or palladium, but also because a nanotube is unidimensional, which favors a high contact resistance. However, there are two main issues that need to be addressed. The first one is the precision of the device. If used as previously, the precision would be ± 0.1 GPa, which is much too high, compared to the measured pressures. The second issue is the fact that the evolution should change when the contact resistance becomes of the order of magnitude of the intrinsic resistance. Therefore, a compromise should be found between a high resistance (favoring the pressure range) and a low resistance (favoring the precision). The precision may also be improved by an optimized geometry that prevents from environmental noise (charge transfer, electromagnetic fields).

To summarize, we measured a general pressure behavior for the resistance of gold contacted metallic carbon nanotubes. It is well explained by a rectangular tunnel barrier, which height is the mean work function of gold and nanotube and which width is the distance between the nanotube and the contact. This effect can be used to design pressure gauges that are easy to build and sensitive, although the precision should be increased. It is worth noting that within the experimental uncertainties, the pressure coefficient depends neither on the initial contact resistance, nor on the PTM (for the two inert gases that we probed). It seems also unaffected by the nanotube diameter and chirality, at least within the distribution obtained with our chemical vapor deposition method. This can greatly simplify the fabrication process of such a sensor, as well as its calibration. Other contacting metals could be used to obtain different pressure coefficients, but gold should be the most sensitive among gold, platinum, and palladium.

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