Manipulation of the Transport Properties of Single-Walled Nanotubes by Alkali Intercalation and Local Charge Transfer

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Abstract. We have studied the effects of charge transfer on the transport properties of individual single-walled nanotubes. This was done in two ways. In the first, we expose devices made of individual nanotubes to alkali metal vapor. This causes no change in the conductance of devices made of metallic tubes, while it increases the conductance of semiconducting tubes and causes them to change from p-type to n-type. In the second method, we examine a single semiconducting nanotube over three leads with an impurity particle near one lead. Local charge transfer from the impurity to the tube causes the region with the impurity to act as a diode, while the other, 'clean', half displays symmetric transport behavior.

Single-walled nanotubes (SWNT’s) hold great promise as candidates for molecular-level electronic components. One possible route to construction of nanotube-based devices is through manipulation of their Fermi levels through charge transfer. It has been shown that the electronic properties of bulk ‘mats’ of tubes can be significantly altered by alkali-metal intercalation [1]. These bulk measurements are only the first step in understanding the details of how charge transfer affects the electronic structure of single tubes. Therefore, we have undertaken studies of the effects of charge transfer on single nanotubes. We will first describe studies of charge transfer by potassium intercalation, and then describe a device constructed of a single semiconducting nanotube that displays rectifying behavior due to the effects of a local impurity particle.

The samples used in this study are prepared by deposition of SWNT’s out of suspension onto pre-prepared Au leads on a degenerately-doped Si wafer with a 1 μm oxide layer. This geometry allows for application of both a bias voltage and an electrostatic gate voltage through the conductive silicon substrate. Examination of the samples by atomic force microscopy (AFM) shows that they are 1.4 nm in height, consistent with their being composed of a single nanotube, although it is also possible that a given sample comprises a few nanotubes lying flat in parallel.
After deposition, the samples are characterized by room-temperature transport measurements, primarily by examining low-bias conductance as a function of gate voltage. The samples display behavior that falls into two classes. 'Metallic' devices display a relatively high conductance (~1 \( \mu \)S) which is independent of gate voltage. 'Semiconducting' devices, on the other hand, display a much smaller conductance, which is strongly gate-voltage dependent. We choose samples that are clearly in either the semiconducting or metallic limit, and are thus most likely to be dominated by a single metallic or semiconducting nanotube.

Figure 1 shows the low-bias conductance of a semiconducting device as a function of gate voltage. As has been shown in earlier work [2,3], the conductance decreases dramatically as the gate voltage is swept from negative to positive. This behavior can be attributed to a depletion of p-type carriers from the area of the nanotube away from the contacts. Consistent with published results, all of the semiconducting nanotubes we observed displayed p-type behavior.

To 'dope' the nanotube devices with potassium, each chip containing a device was mounted into a pyrex tube with a feedthrough so that electrical measurements could be performed in situ. The apparatus was then baked out under dynamic vacuum and transferred to an inert-atmosphere glove box, where a small amount of potassium was inserted into the open end of the tube, which was then evacuated and sealed off. To expose the sample to potassium vapor, each end of the apparatus was heated independently; the sample side was kept hotter than the potassium side to prevent condensation of the potassium onto the sample.

When we first attempted to dope nanotube circuits in this way, we found that the semiconducting devices seemed to 'disappear' after baking out, while metallic ones were relatively unaffected. Therefore, we began to monitor the conductance of devices during the bake-out. The inset to figure 2 shows the conductance of a semiconducting nanotube as a function of time during bake-out at 100 °C. Over

![Graph showing conductance as a function of gate voltage](image)

**FIGURE 1.** Low-bias conductance of a semiconducting nanotube as a function of gate voltage. The decrease in conductance with positive gate voltage shows that the dominant carriers are holes. The saturation at negative gate voltage is most likely due to contact resistance.
FIGURE 2. Potassium-intercalation of a semiconducting nanotube. As the sample and K reach 190 and 170 °C, respectively, the conductance begins to increase. As the sample and K are held at fixed temperature, the conductance continues to increase. After 1 hour, the sample and K are slowly cooled; the conductance decreases with cooling, but remains significantly larger than the initial conductance. The inset shows the drop in conductance during bake-out prior to intercalation.

A period of two hours, the conductance of the nanotube drops to near zero. It is not known whether this drop in conductance is due to removal of carriers (i.e. that the tube is already doped in air) or a reduction in the mobility of carriers, perhaps due to a removal of species which may passivate local charged defects on the chip surface.

Figure 2 shows the conductance of the same semiconducting tube as a function of time during exposure to potassium vapor. Initially, the conductance of the nanotube was quite low (~5 nS). As the sample and potassium temperatures reached 190 and 170 °C, respectively, the conductance of the device began to increase. At this point, the temperatures were fixed. After one hour, the conductance had risen to 250 nS, and the sample and potassium were slowly cooled. Upon cooling the conductance decreased but remained significantly higher than the initial conductance. It is likely that this increase in conductance is due to charge transfer from the potassium to the nanotube. In subsequent studies of other devices we discovered that the doping process was reversible; heating only the sample side drives off the potassium and causes a reduction in conductance to a level similar to that of the undoped tube, at which point the tube can be doped again. Similar efforts were undertaken to dope metallic tubes, but no effect was observed.

To further examine the electronic structure of the doped semiconducting nanotube, we studied its conductance as a function of gate voltage, as shown in figure 3.
300
250 Semiconducting SWNT ~/

FIGURE 3. Low-bias conductance of a potassium-doped nanotube as a function of gate voltage. Charge transfer from the K to the nanotube has caused the tube to display n-type behavior: the conductance increases with increasing positive gate voltage.

FIGURE 4. AFM image of a single nanotube (1.4 nm in height) lying across three gold electrodes. An impurity particle can be seen near electrode A.

3. In contrast to the behavior seen in the as-prepared samples, the conductance of the alkali-doped device increases as the gate voltage is swept from -5 V to 5 V. The doped device is now n-type, consistent with transfer of electrons from the potassium to the tube.

The above results show that it is possible to dope single semiconducting nanotubes and change their behavior from p-type to n-type. One logical extension of this work would be to try to locally dope a tube, in order to make a p-n junction. Although we have not yet attempted to do this in a controlled fashion, below we describe a device in which this process seems to have occurred by chance.

Figure 4 is an AFM image of what is most likely a single nanotube lying across three gold electrodes, labeled A, B, and C. The segment of the tube lying across leads B and C seems to be 'clean,' i.e. there are no large impurities touching it. The segment across leads A and B, on the other hand, has a large impurity particle lying on top of it about 50 nm from lead A. As will be shown below, this impurity seems to have significant effects on the transport through the tube.

The left side of figure 5 shows the transport characteristics of the 'clean' segment of the nanotube. It shows a symmetric I-V curve characteristic of a semiconducting nanotube: low conductance at low bias and increasing conductance at high positive and negative biases. In addition, the gate voltage dependence (not shown) of the low-bias conductivity shows p-type behavior, as with previous devices.
The right side of figure 5 shows the transport characteristics of the nanotube between leads A and B. The impurity seems to be causing a drastic change in the I-V behavior: the device behaves as between B and C when a positive bias is applied, but does not conduct at any applied negative bias (where here A is biased and B is grounded). Thus the tube with a local impurity acts as a diode. We can understand its rectifying behavior as a result of local transfer of electrons from the impurity to the nanotube, using the TubeFET model of Tans et al. In the TubeFET, the difference in work functions between the leads and the tube pins the Fermi energy of the tube to the valence band edge at the contacts. The bands bend downward between the leads; application of a gate voltage increases or decreases this bending, reducing or enhancing the hole transport across the barrier created by the bent bands. In the nanotube diode, local charge transfer near the impurity creates a depression in the bands which interacts with the effects of the contact. The two effects combine to produce a larger barrier to hole transport at contact A than at contact B. At forward bias, the current is only limited by the barrier near contact B, and current flows as in the intrinsic device. At negative bias, on the other hand, transport is limited by the (now larger) barrier at contact A, and no current flows. It is interesting to note that, in this interpretation, the rectifying behavior depends on the interaction between the impurity and the contact: if the impurity were too far from the contact they would not 'see' each other and there could be no symmetry-breaking. Based on this idea, we can set a minimum characteristic screening length in the tube of about 50 nm, the distance between the impurity and lead A.

REFERENCES