Formation of highly transmissive liquid metal contacts to carbon nanotubes

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We have developed a method to produce liquid metal contacts to carbon nanotubes that allows direct measurement of the influence of the contact on the nanotube conductance. Gallium is deposited onto standard gold nanotube contacts, where it gradually spreads to coat the contact region. The two-terminal multiwall nanotube conductance increases by as much as $1.2e^2/h$ during the transition from gold to gallium contacts, and approaches $2e^2/h$ at room temperature, with a current density of 2×10^8 A/cm^2. Surprisingly, the conductance is independent of the contact area or contact separation, providing evidence that transport is ballistic in multiwall nanotubes. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1807946]

Due to their outstanding electrical and structural properties, carbon nanotubes have been considered for a variety of nanometer scale electronic device applications.[1] One problem hindering nanotube device development, however, is the difficulty in making reproducible low resistance electrical contacts to either single wall or multiwall carbon nanotubes. Recent experiments suggest that a possible solution is to use metals that are liquid near room temperature, such as Ga or Hg for electrical contacts. Frank *et al.*[2] observe that the room temperature conductance of a multiwall nanotube (MWNT) measured between a STM tip and a liquid metal contact is $2e^2/h$ (corresponding to a resistance of 12.85 kΩ), independent of the nanotube length or structure. The quantization of the conductance in the Frank experiments suggests that electron transport through MWNTs occurs with no scattering, (i.e., ballistically). By contrast, experiments on multiwall nanotubes having gold contacts in a standard planar geometry give a range of conductance values.[3,4] This variation in contact resistance makes it difficult to distinguish the nanotube device properties from the contact resistance. It has been proposed that due to its ability to wet the nanotube, the liquid metal produces an unusually reproducible and transmissive contact, allowing for the true transport properties of the nanotube to be revealed.[5] This proposal has yet to be tested in a planar configuration due to the difficulty in incorporating the vertical measurement geometry into a standard device design.

In this letter, we present a developed method to produce liquid metal contacts to carbon nanotubes in a planar geometry. Using a molten mixture of gold and gallium we are able to create highly transmissive contacts to multiwall nanotubes. By monitoring the nanotube conductance during contact formation we can directly measure the change in contact transmissivity during the transformation from a standard gold contact to a liquid metal contact. The two-terminal conductance increases by as much as $1.2e^2/h$ during the formation of a single liquid metal contact. We find, in agreement with Frank *et al.*,[2] that the conductance is independent of the contact area or contact separation. Through bias annealing, the contact resistance decreases further, resulting in a MWNT conductance that approaches $2e^2/h$ at room temperature, and a maximum current density of 2×10^8 A/cm^2.

A schematic drawing of our device structure is shown in Fig. 1(a). A standard contact metallization layer consisting of 20 nm Cr/70 nmAu is sputter deposited onto the surface of an oxidized silicon wafer, and patterned using optical lithography. Pairs of contact leads are defined having a separation distance of 1 μm. The leads are in turn connected to large

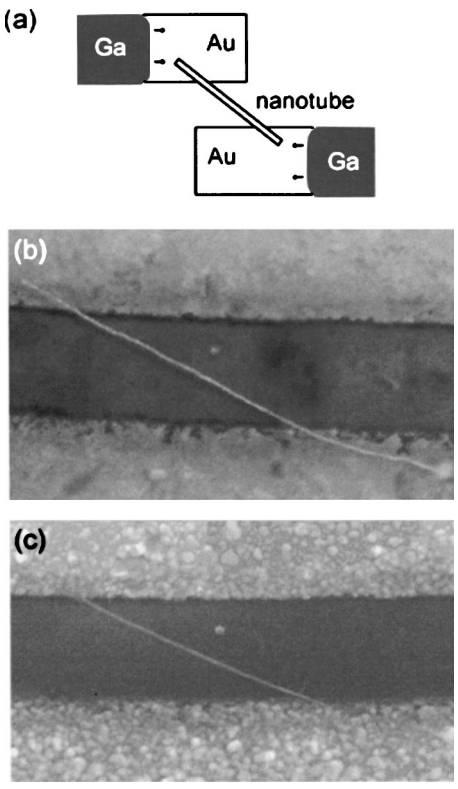

FIG. 1. (a) Schematic drawing showing our device layout. The conductance across the nanotube is monitored as gallium flows along the nanotube leads. Scanning electron microscope images of a nanotube device (b) before and (c) after gallium flows across the gold leads. The contact separation is approximately 1 μm. The contact resulting following gallium flow is an alloy of gold and gallium throughout its entire thickness.

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contact pads. A DMF solution containing multiwall nanotubes is then dispersed onto the sample surface. (We use multiwall nanotubes produced by the arc-discharge method that are 20–30 nm in diameter and 3–6 μm in length.) The dispersed nanotubes distribute randomly to create conducting pathways across the gaps separating the pairs of contact leads. We can adjust the nanotube concentration in solution so that on average one or two nanotubes bridge each pair of leads. The chip is inspected using a scanning electron microscope, and the leads that contact either side of a nanotube are located. A drop of liquid gallium is then placed on the pads that connect to these leads and the sample is loaded into a variable temperature probe station and the sample chamber brought under vacuum (chamber pressure approximately 10^{-6} Torr).

We observe that the gallium droplets placed on the contact pads do not spread out across the entire surface of the chip, as might be expected, but instead follow the path defined by the patterned gold. Over time, the gallium flows to completely cover the gold leads, but does not come in contact with the silicon dioxide surface or fill the gap between the leads. The rate at which the gallium spreads along the length of a gold lead varies, depending on the lead width and thickness, and the sample temperature. For a 10-μm-wide and 60-μm-thick gold lead at 50 C the flow rate is measured to be approximately 7.5 μm/h. Initial investigations suggest that the gallium/gold mixture forms an alloy that drives the gallium diffusion.[6] A detailed study of this process is currently under way.[7]

This "natural alignment" of the gallium with the gold allows us to directly determine the influence that the change from a gold to a gallium contact has on the nanotube conductance. Figure 1 shows an electron micrograph of a MWNT device (b) before and (c) after the spreading of the gallium takes place. After spreading, the gallium/gold mixture completely covers the gold leads, but does not alter the position of the nanotube significantly, or fill the gap inbetween the contacts. Figure 2(a) shows the zero bias differential conductance of a single nanotube as a function of time after the gallium is dropped onto the contact pads. Before the gallium reaches the nanotube, contact to the nanotube is made through the gold, and the two terminal conductance is approximately $G=0.3e^2/h$ ($R=86$ kΩ). As the gallium comes in contact with the nanotube on one of the two leads, the conductance increases abruptly to $0.9e^2/h$. The gallium then comes in contact with the nanotube on the other lead, and the conductance increases to $1.2e^2/h$. Figure 2(b) shows the results of this experiment performed on a pair of leads bridged by two nanotubes. Four jumps in conductance can be seen, each corresponding to the point at which the gallium modifies one of the four nanotube contacts. We have performed similar experiments on 10 different samples containing a total of 24 nanotube contacts. The increase in conductance due to the gallium contact formation varies between $0.1e^2/h$ and $0.6e^2/h$. An increase within ±10% of $0.2e^2/h$ is observed in 12 of the contacts. The main mechanism for the decrease in contact resistance is thought to be the improvement in contact wetting by the presence of the liquid metal. This effect is particularly pronounced because the nanotube has poor contact wetting when lying on top of the gold surface. Since gallium and gold both have similar work functions ($\Phi_{Ga}=4.0$ eV and $\Phi_{Au}=4.3$ eV) the contact barrier should not be influenced appreciably by the influx of gallium. At low bias, the conductance is stable after the formation of the gallium contact. The conductance can be increased however, by placing a large bias (>5 V) across the device, resulting in a maximum observed conductance of $1.9e^2/h$ and a maximum current density of 2×10^8 A/cm^2. This further increase in conductance is presumably due to melting and annealing of the gallium contact by Joule heating, resulting in enhanced wetting between the contact and the nanotube.

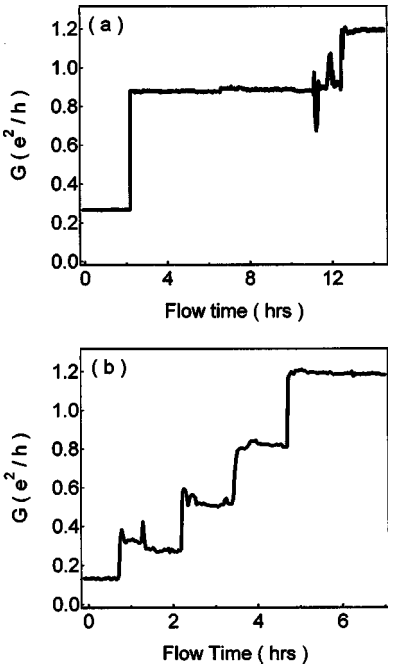

FIG. 2. Zero bias differential conductance of multiwall carbon nanotube measured at $T=320$ K as a function of gallium flow time. A jump in conductance is observed each time the gallium makes contact with one end of a nanotube. (a) A single MWNT lies across a pair of gold leads, (b) two MWNTs lie across a pair of gold leads.

As shown in Fig. 1(a), each nanotube overlaps the gold leads by a distance of 1–2 μm on either side of the gap. The area of the nanotube covered by gallium thus increases as the gallium flows along the gold leads. We would expect that the resulting increase in contact area and decrease in contact separation should produce a gradual increase in conductance. This is not observed, however. As seen in Fig. 2, after the initial jump in conductance when the gallium reaches the nanotube, the conductance stays constant, or even decreases slightly as the contact area increases with time. In the measurements of Frank *et al.*[2] of the MWNT conductance using a liquid metal contact, a conductance of $2e^2/h$ is observed, independent of the distance the nanotube is dipped into a liquid contact. Because the conductance does not change with the nanotube length, Frank *et al.* conclude that electron transport is ballistic through a MWNT at room temperature. In our experiment, the two-terminal conductance is less than $2e^2/h$ and varies from device to device. However, the total conductance is again observed to be independent of the nanotube length, in support of the conclusion of Frank *et al.* The sample-to-sample variation in conductance that we observe is most likely due to the variation in nanotube surface conditions in the contact region.

Two terminal nanotube conductance measurements as a function of bias and temperature are often used as a method to map out the nanotube tunneling density of states.[8,9] Such

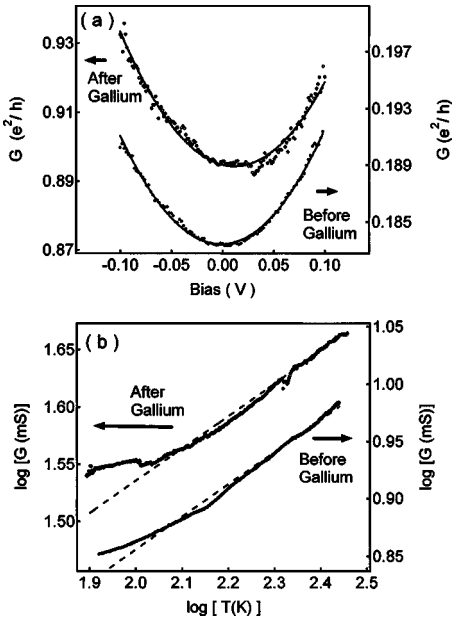

FIG. 3. (a) Differential conductance as a function of bias of a MWNT measured before and after the formation of the gallium contacts at 77 K. (b) Zero bias differential conductance as a function of temperature of a MWNT measured before and after the formation of the gallium contacts. The results are plotted on a log–log scale to bring out the power law dependence of the conductance on temperature.

measurements make the unproven assumption that the contacts to the nanotube are tunneling contacts and not Schottky contacts,[10] so that the energy dependence of the transmission across the contact can be neglected. Our gallium contacting techniques provide a method to directly test this assumption. Figure 3(a) shows the bias dependence of the conductance of a MWNT before and after gallium contact formation, measured at 77 K. The conductance of the gallium contacted nanotube is almost five times greater than the gold contacted nanotube. Despite this, the influence of the bias on the conductance is very similar in both cases: a conductance minimum observed near zero bias and a 4%–5% increase in conductance as the bias increases to 100 mV. Figure 3(b) shows that the temperature dependence of the conductance is also unchanged by the gallium contact. Both before and after gallium contact formation, the conductance G increases with increasing temperature T, and can be fit to the form $G = aT^{\alpha}$, where a and α are constants.[9] For the fits shown in the figure, the parameter a increases from 0.29 to 0.97 as the contact changes from gold to gallium, but α remains constant at 0.28. These results suggest that both gold and gallium form tunneling contacts, rather than Schottky contacts, and that the gallium acts to increase the contact barrier transmissivity, but does not alter the contact barrier height. The bias and the temperature dependence of the two-terminal conductance can thus be safely used to map out the nanotube tunneling density of states.

To summarize, we have demonstrated a straightforward method to make low resistance nanotube contacts by incorporating liquid metal into a planar nanotube device structure. The contacting technique provides a method to determine the influence that contact formation, contact area, and contact transmissivity have on the nanotube conductance. With further enhancements, we expect this technique will allow the reproducible fabrication of nanotube devices whose measured conductance is no longer limited by the contact resistance.

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