Electrical cutting and nicking of carbon nanotubes using an atomic force microscope

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An atomic force microscope (AFM) has been used to modify the electrical properties of carbon nanotube devices. By applying voltage pulses from a metal-coated AFM tip, electrical breaks (''cuts'') or tunneling barriers (''nicks'') can be created at any point along a tube. These methods are applied to make single tube devices by cutting uninteresting nanotubes or create small quantum dots with large charging energies by placing two tunneling barriers 50 nm apart along a nanotube.
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Since their discovery,[1] carbon nanotubes (NTs) have been extensively studied because of their exceptional electrical and mechanical properties.[2] For example, single walled carbon nanotubes behave as nearly ideal one-dimensional electronic systems that are either semiconducting or metallic, depending on their chirality.[2] NTs also possess extraordinary stiffness and resistance to fracture, making them promising for structural applications.[3] These unusual electrical and mechanical properties, combined with their small size, make NTs excellent candidates for many technological applications, including field effect transistors (FETs),[4] field emission displays,[5] and nanosensors.[6]

Scanning probe microscopy has been an indispensable tool in exploring the properties of NTs. Scanning tunneling microscopy (STM) has been used to investigate the size, chirality, and the density of states of NTs[7,8] as well as electrically to cut NTs lying on a metal surface.[9] STM, however, cannot be used to probe NTs on insulating surfaces, *e.g.*, in a NT transistor. Here, atomic force microscopy (AFM) is used. Electric force microscopy (EFM) has been used to investigate the voltage distribution inside NTs[10] and scanned gate microscopy has been employed to image scattering centers inside them.[10–12] Physical manipulations of NTs with the AFM tip, like rolling, sliding, bending, and buckling, have been used to investigate the mechanical properties of NTs.[13,14] Such manipulations have also been utilized to modify the electrical properties of NTs, creating junctions,[15] FETs,[16] and quantum dots.[17–20]

In this letter, we demonstrate that voltage pulses from a metal-coated AFM tip can be used to permanently modify the electrical properties of NT devices. By adjusting the properties of the voltage pulses, we can either electrically break (''cut'') NTs or create tunneling barriers (''nick'') at any point along them. We demonstrate the utility of these techniques by creating single NT devices through the cutting of unwanted extra NTs, and making ultrasmall NT quantum dots can be created by nicking a NT at two places along its length.

The NT devices used in this work were prepared following an approach similar to that of Kong *et al.*[21] First, catalyst islands containing $Fe(NO_3)_3 \cdot 9H_2O$, $MoO_2(acac)_2$ and alumina nanoparticles were defined on a degenerately doped silicon wafer with 200-nm-thick thermally grown oxide. Photolithography and etching were used to pattern a poly(methylmethacrylate) layer, which was subsequently used as a lift-off mask for the catalyst. NTs were then grown by chemical vapor deposition.[21] Metal electrodes consisting of Cr(5 nm) and Au(50 nm) were patterned over the catalyst islands using photolithography and a lift-off process, with a spacing between source and drain electrodes between 1 and 3 μm. This process allowed the parallel production of hundreds of NT devices using only optical lithography. The samples were annealed at 600 °C for 45 min in an Ar environment to decrease the contact resistance between the NTs and the electrodes. Typical NT conductances obtained were $0.2-2e^2/h$.

A commercial AFM (Digital Instruments Dimension 3000) was used to perform the electrical modification. The sample stage was modified to allow mechanical probes to make electrical contact to the sample pads during imaging. Metallized AFM tips (Pt-Ir coated) were employed, to which a voltage could be applied using the AFM controller electronics.

Figure 1(a) shows a topographic image of a single NT on the oxide surface, as imaged by the AFM operating in tapping mode. This NT is connected to two metal electrodes that are not visible in this image. The NT can be cut by applying a voltage pulse to the metal-coated AFM tip. After identifying NTs by topographic imaging, the tip is placed over the NT. The AFM feedback is turned off, the tip is lowered until

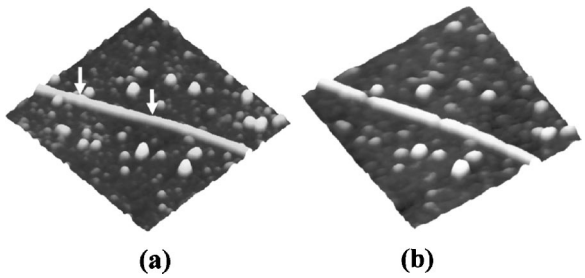

FIG. 1. Perspective views of a carbon NT on an oxide layer imaged in tapping-mode AFM (a) before and (b) after cutting by applying two voltage pulses of −6 V for 100 ms (left) and 50 ms (right) to the points marked by arrows in (a). Image size is 500×500 nm^2 and the height of the NT is 3 nm.

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it is in or very near contact with the NT, and a voltage pulse is applied for a specified period while the NT is grounded. Figure 1(b) shows the result of two such voltage pulses of -6 V for 100 ms and 50 ms, applied at the locations indicated by the arrows. Two gaps in the subsequent topographic image clearly show that the NT has been broken by the two pulses.

The size of gap resulting from this cutting process can be controlled by the height and duration of the voltage pulses. The conductance G of the NT was used to monitor the process; a cutting event can be easily seen as a sudden decrease of G to zero. Tip voltages more negative than -4 V for durations between 10 to 100 ms are most effective in cutting. Short pulses typically result in small gaps, such as the right one in Fig. 1(b). Shorter pulses (less than 10 ms) often result in gaps invisible in AFM images, but can nevertheless cut the NTs, as determined from G. Positive voltage pulses with similar properties did not lead to cutting.

By applying smaller and shorter voltage pulses with the tip further away from the NT, we are able to nick a NT instead of cutting it completely. This nicking is manifested as a drop of G of the NT to a lower, but nonzero, value. Voltage pulses more negative than -3 V for 0.1 to 10 ms were most effective. Control of the tip–NT distance is more critical for nicking than cutting. To give greater control, the tip can be first moved $\sim$10 nm laterally away from the point where the nick is to be made and then brought to the oxide surface. Voltage pulses are applied while the tip slowly approaches the NT from the side until a desired resistance change occurs. In this way, the effects of an uncontrolled drift of the AFM tip relative to the NT are minimized. Successful nicking resulted in typical resistance changes of 50 kΩ to 10 MΩ. With practice, the yield of this technique (nicking without cutting) can be as high as 50%. It has been used successfully on both metallic and semiconducting NTs.

The microscopic mechanism of cutting and nicking by the AFM tip is not understood. The cutting of NTs on gold substrates using an STM tip[9] was attributed to the breaking of carbon–carbon bonds by electrons tunneling between the tip and NT. The voltage required to cut the NT ($|V_{\text{tip}}|>3$ V) was similar to that reported here, but both positive and negative pulses were equally effective in cutting NTs, unlike in our experiments. Another possibility is the local oxidation of the NT by the breakdown of water in the liquid meniscus formed between the tip and the NT. This oxidation process has been widely used to modify surfaces with an AFM tip.[22] Creating of defects by mechanical pushing[18,20] can be excluded as a possible mechanism for nicking, since nicking was not observed without voltage pulses. Further work is necessary to clarify the origin of the cutting and to determine the nature of the microscopic barriers created by nicking. Regardless of their origin, however, these cutting and nicking techniques are very useful, as shown in two examples below.

Strategies for parallel production of NT devices such as the one described above often result in more than one NT bridging an electrode pair, as in Fig. 2(a). Electrical cutting is a simple and fast way to remove undesired NTs. EFM[10] is helpful in identifying NTs to remove. An EFM image of the voltage distribution in the device when a voltage is applied

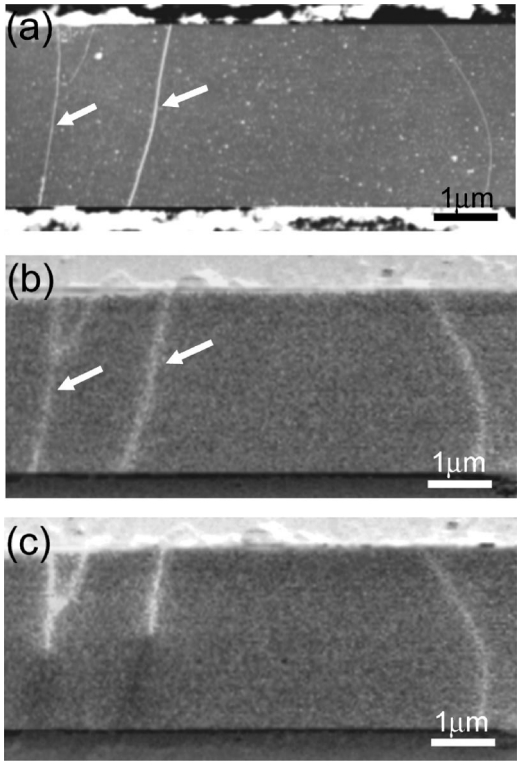

FIG. 2. (a) Topographic image of three NTs between two Au electrodes, (b) EFM image of (a) before cutting, and (c) EFM image after cutting two NTs on the left by applying voltage pulses at the points marked by arrows in (a) and (b). White represents higher voltage on the NT in the EFM images.

to one of the contacts reveals the contact resistance of NTs with metal electrodes as well as any defects or breaks along them. Figure 2(b) is an EFM image of the device in Fig. 2(a), with a voltage applied to the upper contact. Figure 2(b) shows three bright lines that correspond to three conducting NTs in parallel. Voltage pulses of -7 V for 50 ms were then used to cut two NTs on the left at the points as marked by arrows in Fig. 2(a). The topographic image after the cutting is indistinguishable from that in Fig. 2(a), but the cutting is clearly evident in EFM image in Fig. 2(c). The cuts in these NTs result in complete voltage drops at the points where pulses were applied. The conductance of the device now reflects the properties of only the rightmost NT.

A second application uses nicks to create a quantum dot along the length of a NT, as shown schematically in the lower inset of Fig. 3. A NT with an initial conductance $G=0.1\,e^2/h$ was nicked at two points 50 nm apart with voltage pulses of -6 V for 10 ms. The conductance dropped to 0.05 e^2/h after the first nick and to 0.025 e^2/h after the second, indicating two barriers in series with approximate conductances of 0.1 and 0.05 e^2/h each. In Fig. 3, G versus gate voltage V_g of this device is shown at $T=20$ K. Coulomb oscillations associated with the addition of single electrons to this dot are clearly evident. The upper inset shows the differential conductance dI/dV of this device as a function of V_g and source–drain voltage (V_{sd}), plotted as a gray scale. Coulomb diamonds are observed, with a charging energy of $e^2/C\sim 75$ mV. This charging energy is similar to the value expected for a 50-nm-long NT as a quantum dot.[23]

The techniques described above have significant advantages over the mechanical ones previously employed to

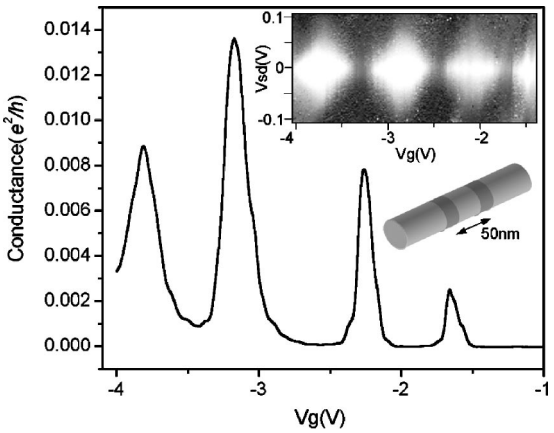

FIG. 3. Conductance as a function of gate voltage of a NT quantum dot at 20 K. The quantum dot was made by nicking two times 50 nm apart on the NT. The upper inset shows differential conductance dI/dV as a function of V_g and V_{sd} at $T=20$ K. White represents low dI/dV, while black corresponds to high dI/dV. The size of coulomb diamonds indicates a charging energy of ~75 meV. The lower inset shows the schematic of the NT quantum dot, with the dark bands representing tunneling barriers created by nicking.

break NTs[19] or to bend them to make tunnel barriers.[15,18,20] In mechanical manipulations, the forces applied to the NT are quite large and can disrupt the electrical contact between the NT and the metallic contacts.[15] In addition, creating multiple kinks in a NT is quite challenging, since the manipulation required to make one kink can disrupt the other. With electrical cutting, in contrast, the contacts remain unaffected and the creation of one nick does not appear to influence the properties of others.

In summary, we have demonstrated that the electrical properties of NT devices can be locally modified by applying voltage pulses with a metal-coated AFM tip. These techniques, in combination with mechanical manipulation, hold great promise for creating more complex NT devices such as multiple quantum dots, NT–NT junctions, and Aharonov–Bohm rings. In addition, the gaps formed in NTs by cutting could be used as nanometer-scale electrodes to probe nanocrystals or single molecules.

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