Hands-on tools for nanotechnology

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We describe some mechanical and electrical measurements on carbon nanotubes. We discuss
electron beam lithography techniques to form metal wire contacts to the as-found nanometer
structures. Starting from a unique collaborative perspective, we suggest some improved design and
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I. INTRODUCTION

The quest since the first transistor and the first integrated circuit has been towards smaller devices and smaller circuits. Moore's law has been an accurate description for decades so that current devices are hundreds of nanometers. By the end of the century the same trend will have carried the device sizes down to the scale of atoms—which, in light of current processing technology, hardly seems a plausible target. The steps along that path are not even clear. Certainly no one can imagine reaching such targets with current lithography and processing technology. Ultimately the devices will be very different in form and function probably relying on oxidation states of individual molecular structures. Storing bits of information on individual molecules offers enormous potential for storage density (one can place the world's literature in a 1 ℓ container), and given refined self-assembling chemistry, alleviating the complement of Moore's law for the costs of fabrication facilities.

The "spacers" between such individual charge storage sites might take any number of chemical and physical forms. One possibility is to use chemically stable macromolecules and carbon nanotubes are the quintessential manifestation of such species. The nanotubes themselves have their own unique and attractive electrical properties being ballistic conductors with tunable energy gaps (from zero up to several hundred meV).[1] Given some—as yet undiscovered—specific functionalization methods, they might form the basis for molecular electronic devices. Nanotubes certainly provide the ultimate in strength to weight ratio among man-made materials, so they are good choices for the connection "struts" mentioned above even if they do not add electrical functionality.

The mechanical and electrical properties of carbon nanotubes have been studied in some depth. Scanning tunneling microscopy measurements[2,3] have demonstrated that the local electron density of states is very close to the predictions based on fairly simple arguments[4] based on the symmetries in the chiral structures formed by wrapping graphene sheets into cylinders. Measurements of the nanotube's conductance along its length from overlapping metal pads at either end have proven that the semiconducting nanotubes can act as transistors (albeit probably not with useful gain in any foreseeable technology).[5,6] The strength and toughness of nanotubes have been assayed in a variety of experiments[7,8] and calculated from models based on reliable potentials[9] known from extensive research on graphite, which shares the same basic lattice structure.

In the following sections we will review first some of the experiments we have done to illuminate the physics of nanotubes as well as the physics coupling them to their environment. After that we will describe lithographic techniques to make electrical contacts to nanotubes in whatever random conformations that have been cast onto the substrate.

II. EXPERIMENTS ON NANOTUBES

Our experiments fall into two main categories: the first set aims at the mechanical properties of nanotubes (and other objects in this size range) including strength and friction, and

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the second category is electrical response. Since both of these effects depend critically on the overlap of orbitals between atoms on the outside of the nanotube and neighboring lattices, there are strong linkages between the two classes of investigation.

A. Mechanical studies

Extensive studies of toughness[10] lead us to conclude that the nanotubes can be deformed almost arbitrarily without structural damage. A very small fraction of the manipulations that we have been able to accomplish through forces applied by an atomic force microscope (AFM) tip have created irreversible damage in the scores of nanotubes that we have studied. These data support calculations from a variety of sources that the mechanical strength and toughness of these materials is unique.[11,12]

On graphite, which matches exactly the honeycomb lattice unit in the nanotube, the nanotube should respond differently depending on the alignment of the graphite honeycomb with that on the surface of the nanotube. Data indicate that there is an order of magnitude difference in force required to move the nanotube across the surface depending on the nanotube's alignment with the underlying lattice. In addition, the experiment showed that any particular nanotube tends to "lock in" at angles separated by $\pi/3$ as we might expect for the honeycomb structures. The force to push the nanotube around on the surface increases by about an order of magnitude within a very small window near the lock-in angle as if the nanotube were snapping into place on a peg board. In addition, the force to push the nanotube across the graphite surface in the lock-in angle has a distinctive sawtoothed pattern indicating progressive straining and then releasing of bonds to the surface. The pattern repeats reliably for a given nanotube as illustrated by the multiple traces in Fig. 1, and it is periodic in the nanotube's diameter. In short, it is clear that the nanotube is rolling along the surface with the carbon–carbon bonds between the nanotube and the graphite substrate acting in gear-like interlock. Each individual nanotube has a particular lock-in angle, which then varies across the population of nanotubes as the nanotube chiralities vary.[13]

All of these experimental discoveries are supported by calculations.[14,15] In addition to supporting the experimental results, calculations have made great strides in explaining the physics by discovering that the large diameter nanotubes used in the first experiments tend to reduce their net structural energy by forming faceted structures,[15] which in turn accounts semiquantitatively for the rather large energy scale in the rolling force curves.

B. Electrical interactions

The nanotube offers interesting intrinsic properties for device components in that it is a ballistic conductor with a tunable band gap. The practical use of the nanotube in a circuit requires coupling it to the rest of the circuit and hence coupling it chemically and electronically to the environment. There are a large number of difficulties to be overcome be-
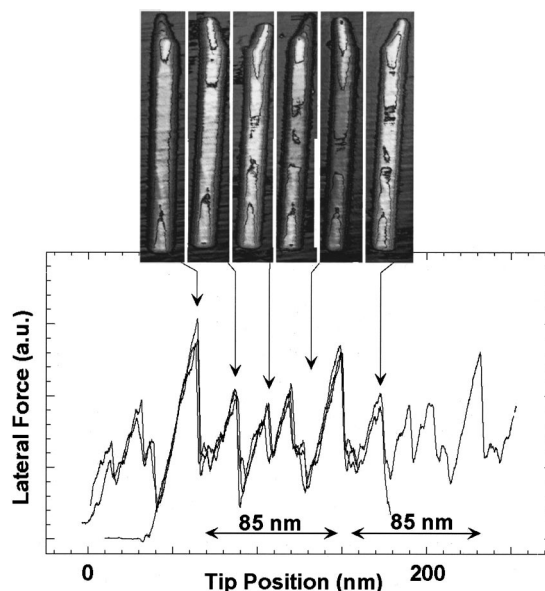
FIG. 1. Images and lateral force measurements obtained while a nanotube was rolled on a graphite lattice. The pattern repeats on a period equal to the circumference of the nanotube. Rolling is clearly visible in the images of the nanotube at the top.

fore such a technology will be available, and we report here a few experiments that illuminate some of the subtleties enmeshed in the coupling problem.

1. Effect of separation between lattices

A very simple experiment involves overlaying two nanotubes on an insulating substrate and studying the electrical conductance between them. We have performed such experiments and the results of one of them are displayed in Fig. 2. An insulating AFM tip was used to deform parts of the nanotubes while the conductance was measured between the leads marked by 1 and 2. Applying pressure to any part of the nanotubes except at the junction has very limited effect—in fact, too small to separate from the noise in our measurements. Applying a vertical force to the junction by pressing
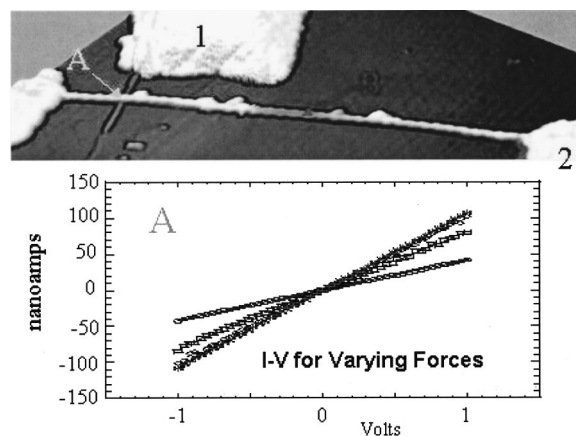

FIG. 2. Image of crossed nanotubes and the *I–V* curves illustrating the change conductance from one nanotube to the other as a function of the force applied to the junction.
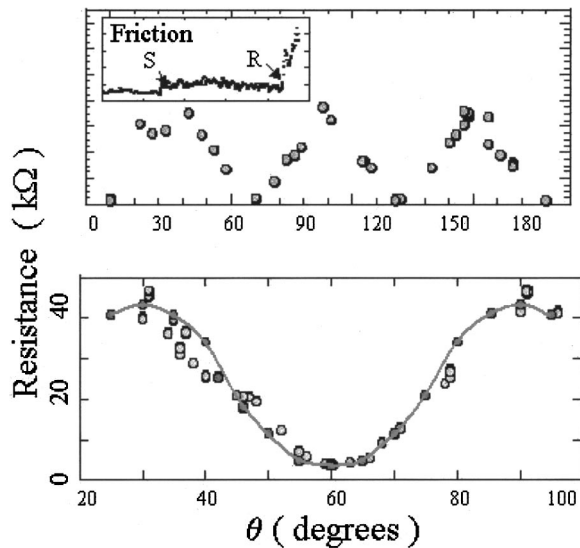
FIG. 3. Illustration of the dependence of the resistance between the nanotube and the graphite substrate on the angle θ between their lattices.
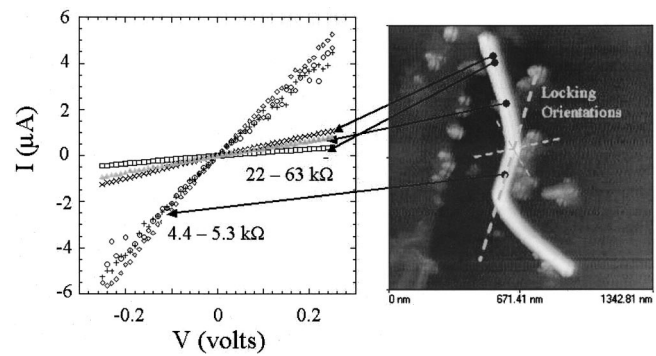

FIG. 4. Resistance measurements at different places along a bent nanotube depend on whether that particular section of the nanotube is in registry with the graphite substrate.

down on the top nanotube increases the conductance between the tubes by a factor of 2 for forces in the range of 250 nano-Newton. Since the force is changing the resistance by changing the separation between the two nanotubes, it is clear that any technology that relies on nanotubes in proximity to each other may have to control the degree of proximity to quite stringent tolerances.

2. Effect of alignment of lattices

Since the nanotube has the same honeycomb structure of lattice units as graphite has, a nanotube laid onto a graphite sheet serves us as a model system for the contact between two nanotubes. By rearranging the orientation of the nanotube on the surface we have learned that the resistance varies by at least an order of magnitude depending on the relative alignment between the nanotube lattice and the graphite lattice as shown in Fig. 3.[16] In fact, the results follow (perhaps somewhat fortuitously) the predictions of a self-consistent model calculation based on reliable potentials and wave functions as well as simple considerations based on unrelaxed models.[17] The resistance oscillates smoothly as the angle between the nanotube lattice and the graphite lattice is changed through a cycle of $\pi/3$ as expected from the lattice (honeycomb) symmetry. This result may be viewed either from the perspective of overlap between orbitals in real space or of conservation of crystal moment by the carriers who have preferred directions of motion in the honeycomb lattice. Again this accentuates the point that control over all details of the linkages will be required to make certain technological uses of these macromolecular structures.

3. Coupling of modes within a nanotube

The order-of-magnitude difference between the two situations above (in lattice alignment and out of alignment) permits a different kind of experiment. As discussed above, the nanotubes can be bent into more-or-less arbitrary conforma-

tions on the surface. In particular, the nanotube can be placed so that part of the nanotube is registered with the graphite lattice and part is not as in Fig. 4. One can then measure the vertical resistance from the AFM tip through the nanotube into the graphite without difficulty for different regions of the *same nanotube*. Moreover, the same tube can be rearranged again and again to observe that it is not the particular location on the nanotube nor the presence of permanent irreversible deformations that leads the observed anomalies in resistance. As illustrated by Figs. 4 and 5, the resistance from the AFM through the transverse conduction path (circumferential around the axis) appears to be largely decoupled from the axial conductance modes. We infer this because the conductance through the out-of-registry sections does *not* depend on the distance away from the nearest section that is in registry—i.e., the conductance through the upper section of the nanotube in the figure above is independent of how close the measurement point is to the middle section. One would expect that good coupling between transverse and axial
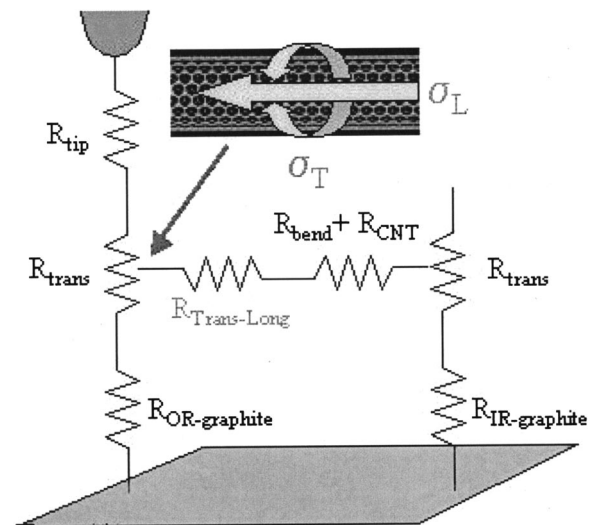

FIG. 5. Schematic to describe the various resistances used to model the experiment on vertical resistance through the bent nanotube. The longitudinal mode (R_{CNT}) and the circumferential mode R_{trans} appear not to couple to each other.

modes of motion would make it more advantageous for the charge to flow along the tube and out through the very low resistance section of the nanotube that is in lattice registry with the graphite. Seeing no such behavior and recognizing that the bends in the nanotube are unlikely to contribute much resistance,[18] we infer poor coupling between the longitudinal and transverse modes. In light of what is known about the electronic transport modes in nanotubes, this is a very surprising result and may indicate that the measurements are driving the carriers out of equilibrium.

III. ONE-STEP CUSTOM PATTERN GENERATION AND LITHOGRAPHY

A. Unique lithography environment

Electron beam lithography with features smaller than 100 nm is now routine for devices where all stages of fabrication are defined by electron beam methods. Our experiments, however, require connections from lithographically defined features to as-cast nanometer scale objects. The nanotubes cannot be deposited or grown on the device substrates we use with much accuracy, so we have to adapt our devices to their placement on the surfaces. The principles of the methods are straightforward. First one must deposit alignment marks and other coarse scale features such as bonding pads. We are using Au or AuPd metal for both pads and marks (2-μm-wide crosses), but none of this is critical in the following discussion. Second, one deposits the nanotubes by standard means from a solvent that leaves a sparse covering of the surface with nanotubes at random orientations and typical spacing of several μm. Third, a registration image is made of the sample with an AFM to ascertain the positions of the nanotubes relative to the pads and alignment marks. In principle, one could use the scanning electron microscope (SEM) to make this image and sometimes we do, but the AFM affords us the potential to rearrange the nanotubes into desired device structures[8] such as overlapped or abutted joints, etc. Next, poly(methylmethacrylate) (PMMA) is spun onto the samples after routine cleaning procedures. A lead pattern design based on the registration image is written by Nabity's pattern generation system (NPGS) in an Hitachi 4700 SEM.

This process has several disadvantages compared to the normal "all ebeam" process where all details of all patterns are defined in the same units (typically pixel size at a certain magnification in the lithography tool). As in most processes, we have found the most time consuming difficulties to be drawing the one-off patterns, but there are other time intensive steps here involving file conversions from AFM to NPGS to ebeam image types. In addition, one must adjust the horizontal and vertical gains (and sometimes a shear coefficient) in either the AFM image or in the SEM image to align them (i.e., to convert pixel sizes). This amounts to a simple affine transformation of one image to match the other. All of this conversion of image type and image shape eventually became so frustrating that we devised a different approach.
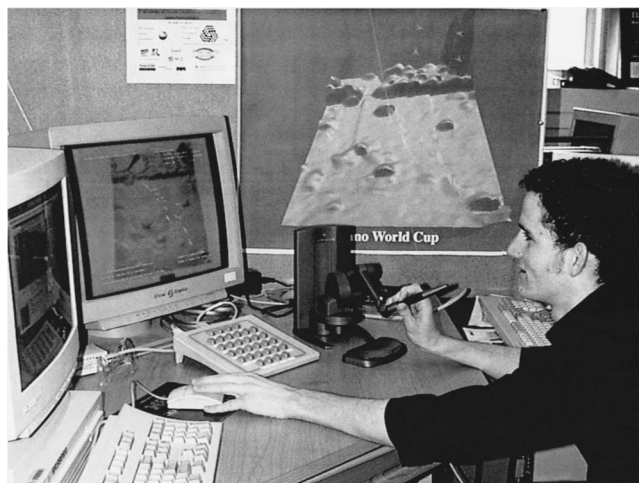

FIG. 6. Operator of the nanoManipulator sees and feels the information from the microscope in real time.

The approach involves extending the "hands-on" (visual and haptic virtual world as shown in Fig. 6) interface developed originally for the AFM.[19] This interface comprises a code written here to connect the rendering capability to permit shaded specularly illuminated visual surface models (mainly through an SGI Onyx) and three-dimensional haptic sensing and rendering (through a SensAble Devices PHANToM)[20] to invoke sense of touch and the server for the commercial AFM (exclusively ThermoMicroscopes).[21] This "nanoManipulator" combination[22] is deceptively seamless and provides huge gains in speed to perform many experiments, which are difficult to impossible in conventional microscopes, by placing the operator into the feedback loop that controls the AFM.

The AFM has been augmented with a SEM in the latest version of the instrument. The bare use of the combination instrument already implies a quest to translate the AFM im-
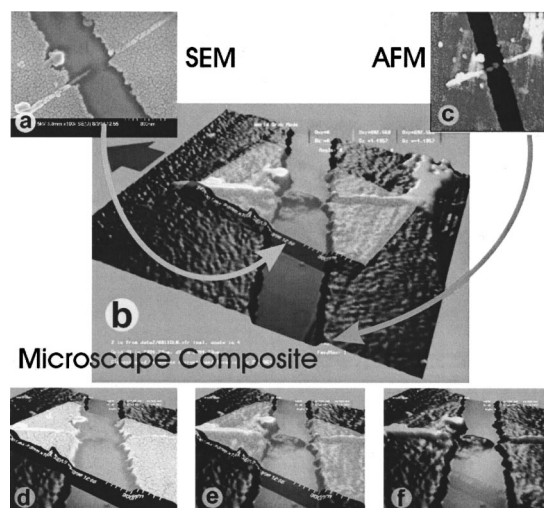

FIG. 7. Schematic depiction of the process of aligning the AFM and the SEM images into the same composite frame (b). Varied transparency [(d), (e), (f)] accentuates different features in particular constituent images.

age into the SEM pixel space as in Fig. 7. In fact, the issues of the combined instruments are much more than just transforming and overlaying two images. In fact, the issues of the combined instruments are much more subtle, and it is possible to use one microscope to counteract artifacts in the other so that the combination provides an image that gives more accurate data than either microscope can yield independently. In addition, of course, the combination provides an environment for manipulating nanometer scale objects viewed in real time through the SEM. The overlaying of the AFM data with the SEM image is straightforward but tedious: one selects by hand features that are prominent and recognizable in both images and makes an affine transform of one image to "fit" the complementary image. Such an operation can be completed in a few seconds by the operator, but there is no reason that the computer alone cannot perform a well-defined optimization that accomplishes the same alignment with less tedium. Such optimization code has been developed and implemented in our research group and works adequately for many pairs of images.[23]

B. Our approach

Formerly the registration image, which marked the positions of nanotubes relative to alignment marks, had to be converted from AFM output to an image that could be loaded into DesignCAD, which was the "front end" for NPGS. There a pattern was designed that connected the optically defined gross features with the nanometer scale objects. Then exposure parameters were set from experience (typically we use a 200 nm of soft-baked PMMA and 264 $\mu C/cm^2$), the sample was exposed and then the "developed" in a MIBK-IPA solution and later stripped in warm acetone.

Attempting to avoid the tedium mentioned above, we have developed streamlined methods to reduce or remove some of the more tiresome aspects. After the nanotube positions are registered (this step cannot be skipped since the nanotubes are too small to see beneath the PMMA), the samples are coated with PMMA and baked. The samples are then installed into the SEM and the custom lithography code is started. Parameters are set so that a new image can be made without detrimentally exposing the resist. The different image defines that location of the pads and the nanotubes for the fine scale lithography exposure. The registration image can then be aligned to the SEM image through either manual or automated techniques. The automated alignment may invoke less-damaging prejudice about specific highlights in the images. For instance, the operator might focus all attention on the alignment marks because they are easiest to see in the SEM image and ignore important subtleties in the field of interest near the nanotube. By contrast the computer can be coded to perform image processing until the nanotube's location is determined reliably, then to ignore the alignment marks altogether and to focus all attention on registration of the nanotube to the electrical pads. It is also much more capable in optimizing based on more than three points (which left as ideal markers define the affine transform), so
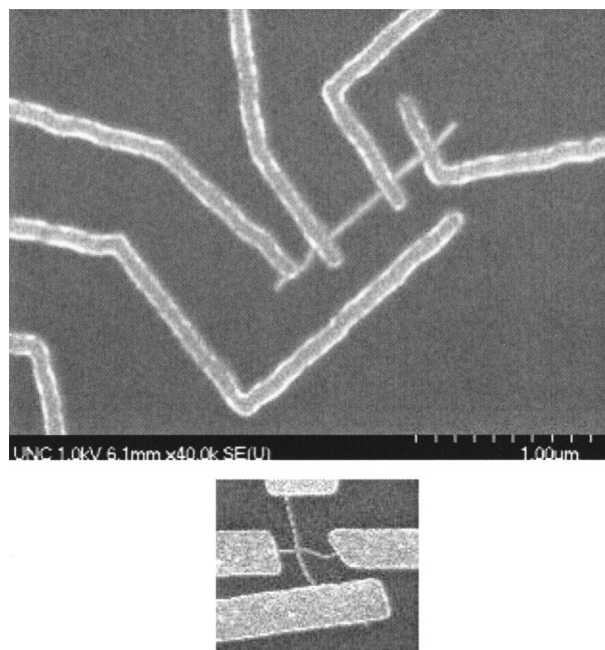

FIG. 8. Examples of the electron beam defined lithography of metal contacts to carbon nanotubes. In the top panel, the contacts are about 80–100 nm wide and a factor of 4 or so larger in the bottom. Both are drawn larger than our limitations to reduce electrical contact resistance to the nanotubes.

that once again operator prejudice can be eliminated with the same reliability as available in standard all-e-beam processing.

In the same code we are implementing drawing tools and a pattern generator that will replace the commercial tools so that one simply sits before the console and marks up the SEM image with free-hand wires or simple rectangular shapes that are then written directly with the appropriate exposure parameters. This method has the potential to save hours of time per experiment by eliminating the file conversion and transformation steps from the human operator's work load. Since none of these tasks requires anything but routine attention and reaction, the computer is likely to be a much more reliable performer. In the end we may have the computer do the drawing tasks as well, since the optimization rules will be very simple (certainly less complex than modern printed circuit board wiring code must implement). Devices of the kind shown in Fig. 8 should take no more than 20 min to conceive, draw, align and expose.

IV. CONCLUSION

The experiments and techniques reviewed here are a sampling of the exciting results that have been obtained in the nanometer domain through an interdisciplinary collaboration that includes computer scientists, materials scientists, social scientists and educators. The nanoManipulator provides a hands-on paradigm for materials science,[24] biological science,[25] educational methods[26] and distance collaborations are being explored[27] as well as providing a varied set of hard driving problems for computer science.[28]

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