Initial Studies Using a Combined TEM - Scanning Tunnelling Microscopy (STM) Side Entry Sample Holder

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Abstract. A combined TEM-STM holder has been evaluated and the STM tip has been used to investigate the mechanical and electrical properties of individual carbon nanotubes with simultaneous observation and analysis in the TEM.

1. Introduction
Standard Scanning Probe Microscopy (SPM), particularly Scanning Tunnelling Microscopy (STM), has been used extensively to study the properties of nanostructures. However, during the last few years SPM has been integrated into TEM specimen holders for in-situ three dimensional SPM imaging, probing (e.g. current-voltage determination) and indentation of nanometre-scale features with simultaneous two dimensional TEM observations. This provides the advantage of actually observing the SPM tip as well as exactly where it is during the probing of a nanostructure. In this work, an integrated miniature STM built within a conventional TEM holder developed by Nanofactory Instruments [1] has been evaluated and used to study the electronic properties of carbon nanotubes. A great advantage of this set-up is the ability to carry out high resolution TEM and EELS investigations in conjunction with I-V measurements of individual nanotubes.

2. Experimental Method
Fig. 1 shows the STM-tip unit within a side entry TEM sample holder designed to fit in both a Compustage (FEI CM200 Supertwin FEGTEM) and non-compustage (FEI CM20 Twin LaB₆ TEM) goniometer [1]. On the bench, the sample is mounted in a fixed position using conductive glue onto a gold wire, while the gold or tungsten STM tip is mounted in a six-legged tip holder ‘hat’ which is connected to a piezoelectric scanner via a conductively (titanium silicon carbide) coated sapphire ball as shown in Fig 1b. For samples on a substrate the wire is bent and the sample is mounted vertically in the holder, whilst for powders and nanotubes, the wire is covered in conductive glue and dipped into the sample. STM tips may be prepared by either simply cutting a 0.25 mm diameter gold wire with pliers or electrochemical etching (either ac etching of gold wire in HCl or dc etching of tungsten wire in NaOH or KOH [1]).

The piezoelectric scanner allows both a course inertial sliding and a fine piezo movement of the tip in all three dimensions. However, since the course movement is finite it is important to ensure that the sample and the tip are sufficiently close in X, Y and Z prior to operation – this may involve repositioning either the sample or the tip. The alignment of the probe and the nanostructure is critical and is performed in two stages: (1) the vertical (Z) alignment is achieved by adjusting the specimen to
the eucentric height using the TEM goniometer, the Z position of the STM probe is then adjusted to the same height so as to minimize the relative movement between the sample and the tip whilst continuously tilting the goniometer; (2) then the XY position of the STM probe in the specimen plane is adjusted using the piezoactuator. The approach of the probe to the nanostructure is then controlled by the piezoactuator which can be adjusted manually or using a feedback control during scanning. Note the inertial slider does not give unidirectional movement which means that a course movement in Z will also move the tip in X and Y.

3. Results of the Evaluation
3.1 STM Tip Preparation
The gold tips produced were found to be relatively large compared with the nanostructures of interest (Figure 2). This made it difficult to carry out any imaging but the tips were a few 100 microns in diameter with several sharp edges which were sufficient for I-V measurements. Mechanically cut tips tended to have many multiple tips [2] whereas etched tips were better defined.

Figure 1. Images of TEM-STM holder. In Figure 1b: 1) tip holder 2) sliding ball 3) sliding rods 4) support ball 5) piezo tube (Courtesy of Nanofactory [1]).

Figure 2. An SEM image of a STM tip produced by ac etching of gold wire (scale bar=2µm; (right) TEM image of the tip after it has been damaged (scale bar = 200nm).
Once sharp, clean tips have been produced, they are very easily damaged and contaminated either when mounting the tip into the holder or when aligning the tip to be in contact with the sample. When investigating electrical properties, it is necessary to keep the tip clean in order to obtain good electrical contacts with the nanotubes. Therefore, contamination (e.g. dust and carbon structures that detach from the sample and attach onto the tip) was easily removed using an aerosol duster; molecular contamination would have little impact on the I-V measurements due to the relatively large contacts areas employed. Damaged tips are easily straightened with a pair of tweezers. However, this resulted in the tips losing the relatively smooth curvature and forming more jagged edges as shown in Fig. 2. Other cleaning techniques will be investigated such as plasma cleaning as well as ‘in-situ’ cleaning by flashing the tip with a high bias voltage.

3.2 Mechanical Deformation of Nanotubes
It has been possible using this technique to visualise the elastic properties of carbon nanotubes as seen in Fig. 3. A small bundle of nanotubes was bent almost 90° without breaking or introducing deformations in the form of kinks etc. However, repeated deformation did produce kinks which were limited mostly to one point along the tube. In certain instances the nanotubes were seen to break into separate pieces, mostly for very short carbon nanotube (CNT) bundles.

![Figure 3. TEM images of bundles of nanotubes a) before contacting the tip and b) during bending.](image)

3.3 I-V measurements
Preliminary I-V experiments were carried out on a gold tip-gold wire sample and an I-V curve is presented in Figure 4a. The I-V plot is linear (indicating metal and also a good contact) with a resistance of approximately 70Ω. Figure 4b shows the I-V measurement on a SWCNT bundle which shows a metallic behaviour in agreement with studies of the nanotube chirality. From the differential plot of I-V, dI/dV vs V, it is possible to obtain density of states information, as has been presented by Wildoer [3] and Odom [4].

![Figure 4. Graph showing the I-V relationship of a) a gold tip-gold sample wire and b) a gold-tip-CNT bundle.](image)

Using the STM-tip it is possible to investigate the changes in electronic properties of CNTs when a bundle is straight, when it is bent and with the introduction of kinks. Figure 5b shows the I-V curves...
for a bundle of CNTs when straight and when bent. It appears that resistance does change as strain is introduced to the bundle. However, care must be taken when carrying out such measurements as the contact between the tip and the CNTs is also changing and affecting the I-V curve produced as can be seen in Figure 5a.

To investigate the affects on bonding during deformation, EELS analysis has been carried out at the magic collection angle (angle at which orientation effects are minimized) on bundles of CNTs at certain stages during deformation, and preliminary results are presented in Figure 6. In the C-K edge, there appears to be a slight decrease in the $\sigma^*$ peak when the CNT bundle is bent compared with the straight CNT bundle.

![Graph showing the I-V curves from a bundle of nanotubes a) for a bad contact between tip and CNTs and b) for a bundle of tubes that is straight and bent.](image)

**Figure 5.** Graphs showing the I-V curves from a bundle of nanotubes a) for a bad contact between tip and CNTs and b) for a bundle of tubes that is straight and bent.

![Graph showing the C-K edge EEL spectra of the bundle of CNTs in Figure 3 when the bundle is straight and while it is bent with the tip.](image)

**Figure 6.** Graph showing the C-K edge EEL spectra of the bundle of CNTs in Figure 3 when the bundle is straight and while it is bent with the tip.

3.4 STM imaging

Imaging CNTs has been attempted using the constant current mode and the constant height mode. However, both have been unsuccessful mostly due to the elastic nature of the tubes; during an acquisition the nanotubes became stuck to the tip during the imaging process. Therefore, imaging was also attempted on a gold wire with etched features. This was also unsuccessful but attempts are being made to optimise the settings, as well as reduce the noise, and increasing the resolution, by producing much finer tips.

4. Summary

An integrated miniature STM built within a conventional TEM holder has been used to study the electronic properties of carbon nanotubes. The system is fairly straightforward to use. The ultimate is to obtain reliable I-V curves from isolated SWCNTs and use the TEM, to image the nanotubes in order to identify the symmetry of the tube. Attempts have also been made to investigate the field emission characteristics of SWCNTs.
References

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