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# Carbon Nanotube AFM Probe Technology

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## 1. Introduction

The invention of atomic force microscopy (AFM) is having a great impact on various areas, such as nano metrology, materials science, surface science and biology (Binnig et al., 1986). The lateral resolution of AFM is mainly determined by the probe's shape and physical property, especially the geometry and dimension of the probe end. Conventional AFM probe is pyramidal shape by micro-fabrication. The pyramidal probe would result in image resolution degradation by severe probe broaden effect, especially for the structures with higher aspect ratio, such as gratings and structures in MEMS.

To broaden the AFM applications, researchers pursue new kind probes that have longer lifetime, higher resolution, and better mechanical property. Carbon nanotubes (CNT) show many excellent properties, such as, high aspect ratio, high Young's modulus, excellent elastic buckling property, and electrical and thermal conductivity (Iijima, 1991). The above characteristics make carbon nanotube be ideal as probes in AFM. Carbon nanotubes have demonstrated considerable potential as AFM probes after the first CNT AFM probe was invented in 1996 (Dai et al., 1996).

This chapter would introduce the history of carbon nanotube AFM probes, including the CNT probes' fabrication and configuration optimization, the CNT probes' image artefact and its elimination study, the applications of these new kind probes and researches to improve their performance.

## 2. CNT probes' fabrication

There are two key processes in the fabrication of carbon nanotube AFM probe: attachment and modification. Firstly, the CNT must be fixed to the end of ordinary AFM probe to be the new imaging point; and then configuration or function modification to optimize the CNT probe's properties.

### 2.1 CNT attachment

#### 2.1.1 Direct manipulation method

Since carbon nanotubes were first applied as AFM probes in 1996 by Dai (Dai et al., 1996), various methods have been developed for their fabrications. The earliest method was to

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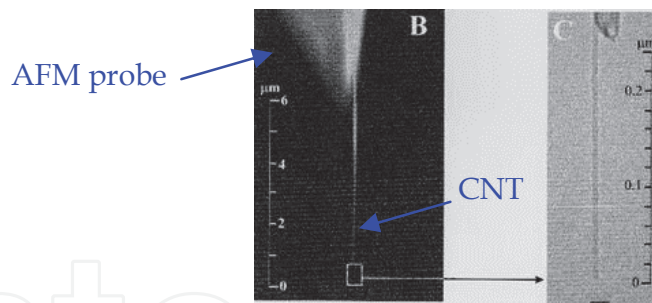


Fig. 1. SEM and TEM images of the first CNT AFM probe (Dai et al., 1996)

employ precise manipulation by picking and sticking a multi-walled carbon nanotube (MWNT) bundle to the silicon probe with an acrylic adhesive under direct view of optical microscope. This method can not be employed to well control the CNT probe's orientation. Further research extended this method using nanomanipulator in scanning electron microscope (SEM), and nanotube with smaller diameter can be selected and fixed to Si probe in SEM by electron beam induced carbon deposition (Nishijima et al., 1999) or Pt deposition (Fang et al., 2009).

Welding method was then developed for fixing CNT to Si probe end (Fang et al., 2007 ; Stevens et al., 2000). First, silicon probe and carbon nanotube were brought into a close distance by manipulating two microtranslators under direct view of inverted optical microscope. When carbon nanotube and silicon probe were in close proximity, an electric field of less than 20V was applied between them. The nanotube was attracted to the silicon probe and favorably aligned with the apex of silicon tip. Then the microtranslators are manipulated to make the protruding nanotube contact with the apex of silicon probe. The applied voltage is further increased between them to 30–60V until the nanotube was energetically disassociated by applying voltages and weld to the end of silicon probe. The carbon nanotubes grown in CVD method have small defects, at which points the resistance locally heats the nanotube until it is oxidized and divided. Fig. 2 is the schematic illustration of fabrication method.

The main drawback of the direct manipulation method is time consuming, and it is not an appropriate method for wafer-scale fabrication.

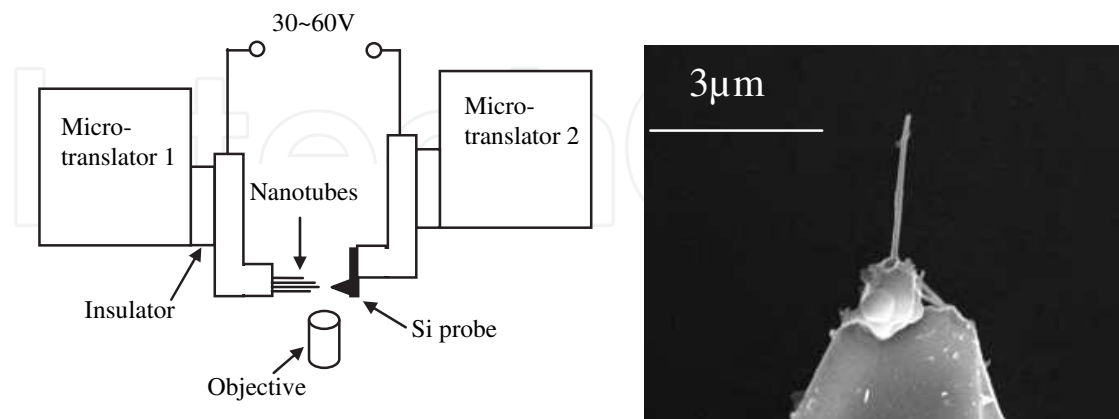


Fig. 2. Schematic illustration of welding process and CNT probe fabricated (Fang et al., 2007)

### 2.1.2 Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) method was used to grow carbon nanotubes on a catalyst deposited silicon probe surface in 1999 (Hafner et al., 1999). The CNT's growth length can be

controlled by adjusting the growth time (Edgeworth et al., 2010). Ye reported an innovative approach that combined chemical vapor deposition with nanopatterning and traditional silicon micromachining technologies to large-scale grow CNT probe through effective nanocatalyst protection and release before and after the microfabrication (Ye et al., 2004).

The key advantage of the CVD direct growth method is the possible route to batch fabrication. It was predicted that nanotube bundle AFM probes could achieve reproducibly be wafer-scale fabrication by this technique in the near future [Wilson & Macpherson, 2009]. While, the reproducible production of CNT probes with individual single-walled carbon nanotube (SWNT) is still the great challenge. How to accurately control the CNT probe's orientation becomes a key problem for the CVD method.

### 2.1.3 Pick-up method

In order to fabricate SWNT AFM probe, pick-up method was proposed in 2001 (Hafner et al., 2001). The SWNT could be picked up by the ordinary AFM probe with van der Waals forces during AFM probe scanning the SWNT substrate with nanotubes grow upwards. The pick-up method is flexible, while this method needed isolated and vertically aligned carbon nanotube samples.

### 2.1.4 Other approaches

Approaches have also been proposed to fabricate CNT probe in CNT solution under external fields, such as, using dielectrophoresis (Tang et al., 2005), alternating magnetic field (Hall et al., 2003). Tamara directly grew CNTs on the apex of AFM probe by selective heating of the catalyst under the microwave irradiation in the presence of ethanol vapor (Tamara et al., 2010). CNT probes were assembled by transplanting a CNT bearing polymeric carrier to a AFM cantilever (Kim et al., 2009).

## 2.2 Configuration modification

There are three key factors that determine the resolution and properties of the CNT probe, i.e., radius  $r$ , length  $L$ , and orientation  $\theta$  (CNT orientation angle with respect to the sample surface). It is vital that a precise control of these parameters allows the optimization of CNT probe to meet different applications' demand.

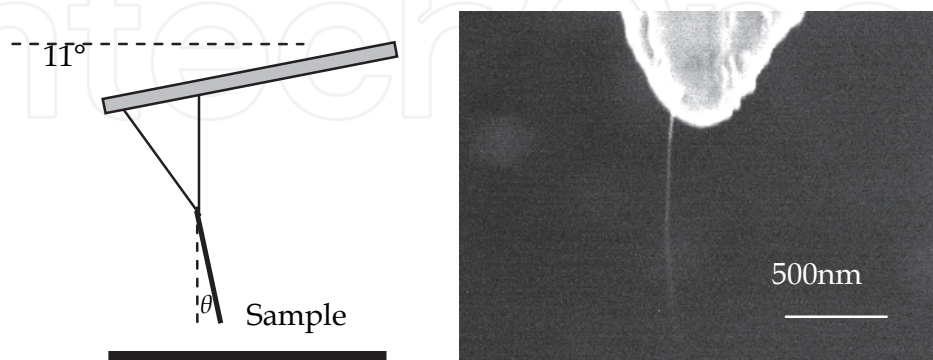


Fig. 3. Illustration of the CNT probe's thermally induced oscillations

A nanotube probe would be very gentle in lateral direction if the nanotube's aspect ratio ( $L/r$ ) is too large. Fig. 3 shows a scanning electron microscope (SEM) image of a long CNT

AFM probe. The blurring of the lower portion of the CNT is due to the thermally induced oscillations.

The lateral force constant ( $k_l$ ) of the CNT probe can be derived as the following

$$k_l = \frac{3YI}{L^3} = \frac{3\pi Y}{4} \cdot \frac{r^4}{L^3} \quad (1)$$

where  $I$  is the stress moment over the cross-section of the nanotube,  $Y$  is the Young's modulus of the carbon nanotube. The CNT probe bending response will dominate for a probe angle of even a few degrees with respect to the sample surface.

### 2.2.1 Orientation modification

The CNT probe's orientation should be vertical to sample surface theoretically for high resolution imaging. However, it is hard to accurately control the CNT probe's orientation during the CNT attachment process for most methods.

External electric field method was effective for CNT probe's orientation control (Fang et al., 2007). In the welding method, nanotube was attracted to the opposite Si probe and favorably aligned with the apex of probe under external applying voltage, as shown in Fig. 4. The attraction is due to the induced dipole moment in the nanotubes under external voltage. The largest strength of the electric field appears at the probe's apex, which will cause the CNT alignment with the apex. In the plasma enhanced chemical vapor deposition (PECVD) method, the CNT probe's orientation was controlled by an electric field present in the plasma discharge to align the nanotubes parallel to the electric field (Ye et al., 2004).

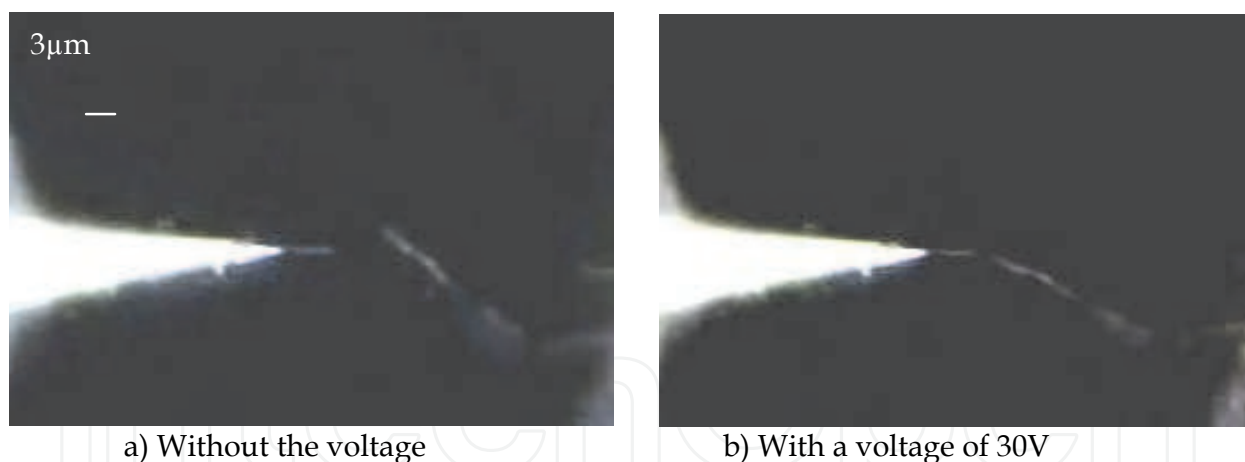
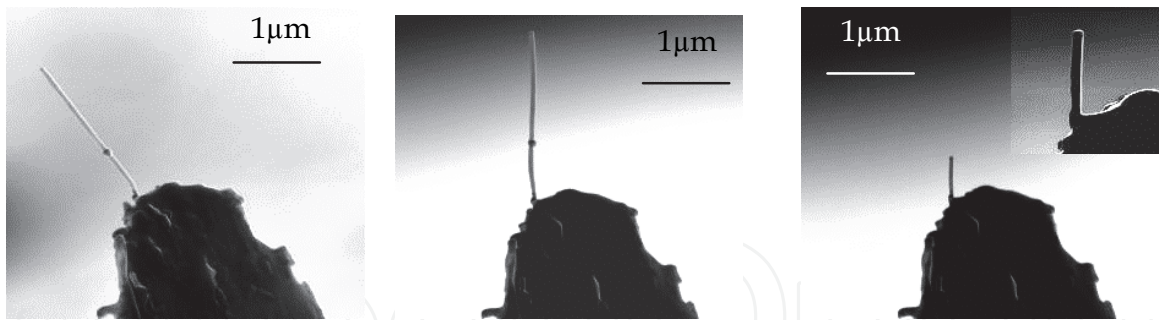


Fig. 4. The protruding nanotube favorably aligned with the probe apex (Fang et al., 2007).

Focused ion beam (FIB) irradiation method was recently proposed to modify the CNT probe orientation with high accuracy and reproducibility (Deng et al., 2006; Park et al., 2006). For the CNT probe's orientation alignment process, repeated single scans of the ion beam imaging were applied. The CNT probe was gradually aligned towards the FIB irradiation direction under every FIB scan and finally aligned parallel to the FIB irradiation direction, as shown in Fig. 5. The variables that affect the FIB-CNT interaction process include ion accelerating voltage, ion beam current, exposure time, and ion scan size (or the scan pixel density). Optimized combinations of these variable values can be made to achieve acceptable results (Fang et al., 2009).



(a) Misaligned CNT probe (b) Well-aligned CNT probe (c) CNT probe after shortening

Fig. 5. Nanotube probe's orientation and length are optimized by FIB irradiation and milling processes. The FIB alignment parameters in Figure 5(b) are 30kV and 50pA in the ion acceleration voltage and the ion current, respectively (Fang et al., 2009).

The CNT orientation changes are mainly due to the strain induced by the FIB irradiation and the CNT's excellent plastic ability. Experimental and simulation results have demonstrated that the carbon nanotubes can be considered as self-healing materials under electron or ion irradiation (Krasheninnikov & Nordlund, 2010). Two mechanisms govern the CNT defect annealing (Krasheninnikov et al., 2002). The first mechanism is vacancy healing through dangling bond saturation and by forming nonhexagonal rings. The second one is the migration of carbon interstitials and vacancies, followed by Frenkel pair recombination.

### 2.2.2 Length modification

The CNT probe's length should be chosen and modified for different applications. Shortening the CNT probe can decrease the thermal oscillation amplitude. Therefore, short CNT probe is required for the CNT probe's high resolution imaging or applications with high lateral force constant requirement, such as friction study (Lai et al., 2010). On the contrary, long CNT probe is useful for the high aspect ratio imaging, e.g., biological samples.

The first method to shorten the CNT probe was realized on AFM by electrical etching (Dai et al., 1996). Then the method of using electron bombardment under the electric field was applied in the direct manipulation methods under optical microscope or SEM, which can observe and control the shortening process in real-time (Fang et al., 2007).

A new 'nanoknife' method was proposed to precisely cut and sharpen CNT probe by local vaporization of carbon resulting from Joule heating (Wei et al., 2007). The 'nanoknife' was a short carbon nanotube adhered to a metal tip. The 'nanoknife' cutting process is controllable and repeatedly, as shown in Fig. 6. In the cutting process, a DC voltage of 5–10 V was applied between the CNT probe and the 'nanoknife', the 'nanoknife' was then manipulated to contact with the CNT probe at the selected position. When the contact was made, the CNT probe would be precisely cut at the contact position (Wei et al., 2009). The cutting position can be precisely controlled using the nanomanipulators. It is found that the cutting process happened within 0.01 second by measuring the current going through the contact.

In recent years, Focused Ion Beam milling method was used to precisely shorten the CNT probes (Fang et al., 2009). The C-C chemical bonds of CNT would be broken during the high energy ion milling. The end of the CNT probe after FIB shortening is found to be a round end with fullerene-like cap, which is independent with the FIB's parameters, as shown in Fig. 5 (c). Since the FIB's beam energy is a Gaussian distribution, the Gaussian tail would

produce many Carbon dangling bonds at the irradiation sites, where the dangling bonds would spontaneously close into a graphitic dome after shortening (Charlier et al., 1997).

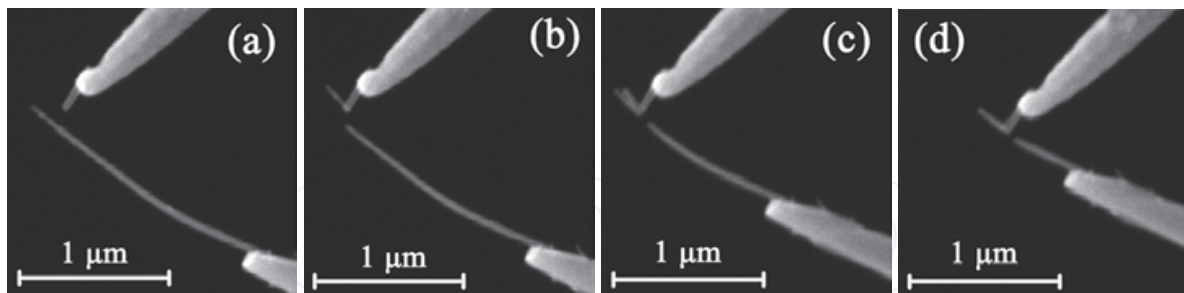


Fig. 6. SEM images showing a CNT (the lower one) is cut by a CNT 'nanoknife' repeatedly and becomes shorter and shorter (Wei et al., 2007).

### 2.2.3 High aspect ratio

Shortening the CNT probe can be useful to increase its resolution and stiffness. While a short CNT probe is not always the best choice for any applications. For high aspect ratio imaging, such as grating and biological sample imaging, the CNT probe should possess sufficient aspect ratio to avoid the imaging degradation by probe broadening effect. However, the force required to bend or buckle the CNT probe would greatly decrease as its aspect-ratio increase, which would be prone to result in image artefact at the sample step positions. A strategy to improve the mechanical integrity of CNT probe is to coat it with a thin layer film, such as polymers, Au or carbon (Yum et al., 2010).

For high aspect ratio imaging, the best CNT probe configuration should have sufficient probe lateral stiffness with portion CNT protruding at the probe end, which can get high image resolution and good probe rigidity. Method of using electron beam locally induced Pt deposition in-site to strengthen the nanotube probe with the nanotube end free of deposition was proposed (Xu et al., 2009).

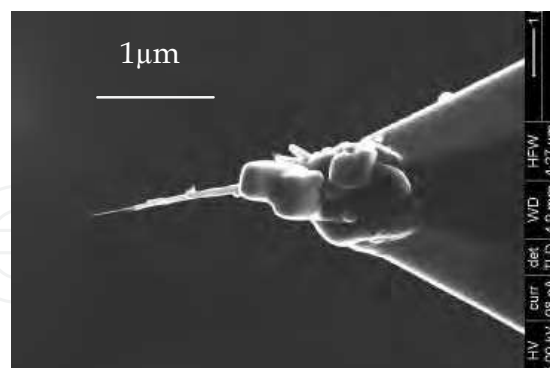


Fig. 7. CNT probe for high aspect ratio imaging (Xu et al., 2009).

Besides the configurations' demands, the attachment force of CNT probe should be large enough for versatile applications under different conditions. The probe-sample interaction forces for ordinary AFM probe are typically 10–100 nN in air. The bounding force of CNT probe can be roughly calculated by measuring the Si probe's deflection before and after the CNT is cut by nanomanipulation (Xu et al., 2009). The bonding force for CNT and Si probe with Pt deposition fix method is found larger than 500nN. The direct manipulation method and CVD growth method would have sufficient bounding strength than other methods.

Although the CNT probes have been developed, but they are still not widely adopted by the AFM users. The key issue that restricts the CNT probe's wide applications is that the CNT probe is much more expensive in comparison with ordinary tapping-mode AFM probe, which is mainly due to its complex fabrication technics and less productivity. It is vital to optimize the CNT probe's fabrication process with an accessible price and meeting versatile application demands. Moreover, the CNT probe's complex mechanical response during its working would also be an obstacle for its wide applications. For example, the CNT probe would be apt to produce image artefact during the high aspect ratio image. The CNT probe-sample interaction and its mechanical response are discussed in the following section.

### 3. CNT probe-sample interaction

The CNT probe is generally used in tapping-mode AFM (TM-AFM), where CNT probe intermittent contacts with sample surface and oscillating with high frequency during its scanning. Comparing with the ordinary AFM tappingmode probe, many new phenomena would appear when using a CNT probe. It is necessary to study the CNT probe interaction with sample and explain the new phenomena for CNT probe in advance.

#### 3.1 Introductions on tip-sample interaction force and phase angle

Fig. 8 depicts schematically the forces acting between the AFM probe and sample as a function of the probe-sample separation  $D$  (Clemens et al., 2006). As  $D$  decreases, the AFM probe firstly detects the attractive force. If the magnitude of the attractive force gradient  $dF/dD$  exceeds the probe's force constant  $k$  (point B), then the AFM probe cantilever will be unstable and jump into contact with the sample (point B'). The position B is called "snap into contact point". As the separation further decreases, the CNT probe-sample interactions would become repulsive force.

Thus in the experiment, the ability to precisely track the force versus distance curve for all tip-to-surface separations, mainly depends on the AFM probe's force constant. For example, the unstable phenomenon of "snap to contact" would appear if the CNT probe's lateral force constant is too low. On the contrary, if the probe force constant  $k$  is always larger than the sample force gradient  $dF/dD$ , the cantilever-dependent instability can be practically eliminated, thus enable a faithful measurement of the probe-to-sample interactions (Landman et al., 1990).

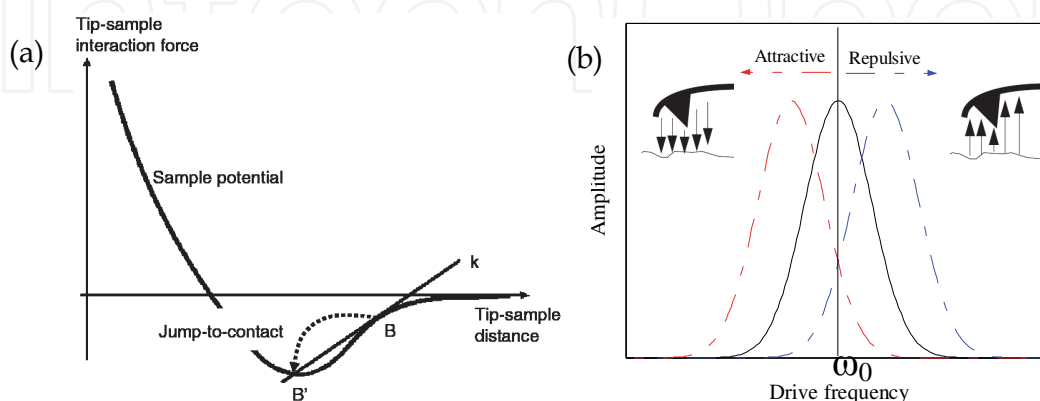


Fig. 8. Interaction force curve as the tip approaches the sample (a) (Clemens et al., 2006) and the AFM probe's resonance frequency shift under different forces (b).



The AFM probe-sample interaction forces variations can be sensitively detected by the cantilever's resonance frequency shift and phase angle. Any additional tip-sample force gradient would produce a shift of the cantilever's resonant frequency for the probe in tappingmode AFM. Attractive forces make the cantilever "softer" effectively, reducing the cantilever resonant frequency. In contrast, repulsive forces make the cantilever "stiffer" effectively, increasing the resonant frequency (Fang et al., 2008).

As a function of the driving frequency  $\omega$ , the phase angle  $\varphi$  of the cantilever oscillation relative to the signal sent to the piezoelectric driver can be derived as the following,

$$\tan \varphi = \frac{\omega \omega_0 / Q}{\omega_0^2 - \omega^2} \quad (2)$$

where the  $\omega_0$  is the probe's resonance frequency and  $Q$  is the quality constant of vibrating cantilever. From equation (2), the probe phase angle increases from  $0^\circ$  to  $180^\circ$  and the phase angle is  $90^\circ$  under the resonance frequency.

When the cantilever is far enough from the sample, there is no interaction between the AFM tip and the sample. Thus, the probe phase angle is  $90^\circ$  when the driving frequency is chosen as the cantilever resonance frequency according to equation (2). As the probe approaching the sample surface, the attractive forces first acting on the probe would decrease the probe's resonance frequency, where attractive forces make the cantilever "softer" effectively. Subsequently, the probe driving frequency becomes larger than the probe resonance frequency. Therefore, the probe phase angle is larger than  $90^\circ$  when the probe suffers attractive forces. Conversely, the phase angle is less than  $90^\circ$  when the probe works in repulsive forces region.

Therefore, the phase angle can be used to sensitively detect the probe-sample interactions. By mapping the phase of the cantilever oscillation during the AFM scan, phase imaging goes beyond simple topographical mapping to detect variations in composition, adhesion, friction, viscoelasticity, and other properties, as shown in Fig. 9. The phase images have been used to present the hydrophobic nature of single CNT by using the CNT probe with different AFM image parameters (Fang et al., 2008).

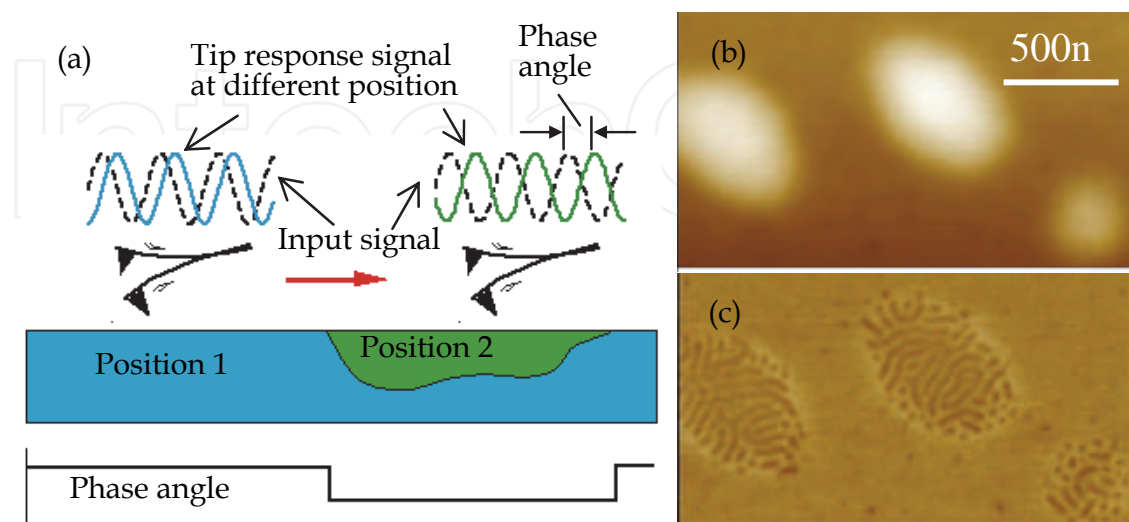


Fig. 9. (a) Phase angle in TM-AFM (b) topography and (c) phase images of copolymer. The height scale is 10nm and the phase angle scale is  $20^\circ$  (Fang et al., 2008).

### 3.2 Image artefact

For ordinary TM-AFM Silicon probe, its force constant is large enough to avoid the instability of “snap to contact”. However, in the case of CNT probe, it is very gentle in lateral directions and the CNT would elastically buckle if its lateral force exceeds the threshold value. In this section, we will discuss what the CNT probe’s mechanical responses and feedback would be if the CNT probe’s instability occurred. And the research works of how to overcome the instability would also present.

#### 3.2.1 Artefact at the steep positions

When the CNT probe scans sample positions with a great surface slope, such as a grating step, the nanotube would be nearly parallel with the grating edge, where the lateral force exerted to the CNT probe would increase dramatically comparing with scanning the flat positions (Akita et al., 2000b). Akita has done the CNT probe force curve (force-versus-distance curve) measurement performed near the pit edge and on a plane surface, as denoted in Fig. 10. The amplitude at a plane surface monotonically decreases with the probe-sample distance, which is similar to the conventional Si probes. The CNT probe’s oscillation is recovered at  $z < -40$  nm due to the reproducible buckling of the nanotube. While for the case near the pit wall, the probe’s oscillation is stopped abruptly, which indicates that the CNT probe snaps to contact with sample. These results from the trapping of the nanotube probe by attraction between the sidewalls of the nanotube and the pit. The adhesion force of the nanotube suffered near the pit edge is tested about 10nN (Akita et al., 2000a). At this point, it is impossible to control the position of the probe height for the AFM observation because that there is no distance dependence of the amplitude on the force curve. Therefore, the AFM image of the CNT probe at the pit edge is unstable with many ripple and wavelike distortion.

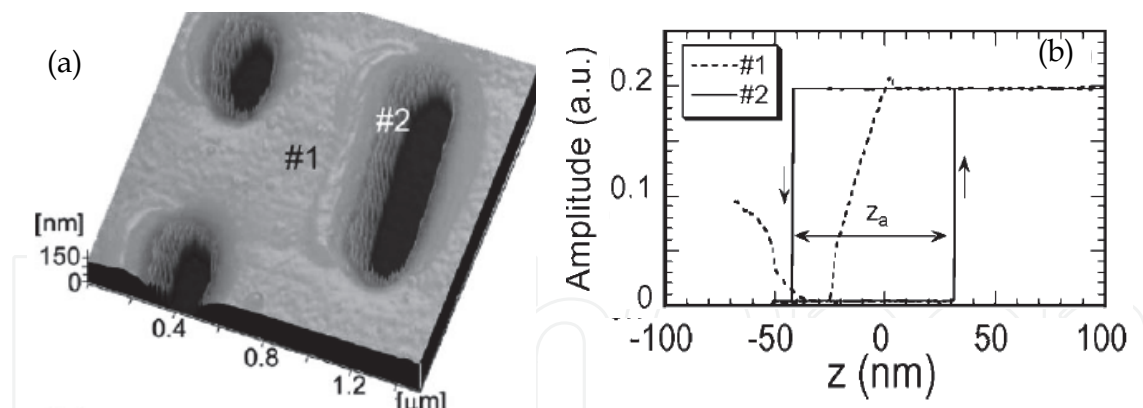


Fig. 10. The CNT probe image of a DVD surface (a), and the force curve measurement performed near the pit edge and on a plane surface (b) (Akita et al., 2000a).

It was found that the ripple and wavelike distortion is more easily occurred at the pit’s left edge than the right edge in general, as shown in Fig. 10. This are mainly attributed to the probe having a tilt angle of  $11^\circ$  when it scans a sample in AFM as shown in Fig. 3, where the vibrating probe suffers different repulsive forces at different pit edges (Fang et al., 2008).

What is the formation mechanism for the ripple and wavelike distortion at the grating edge? The phase angle data combining with height and amplitude data have been proposed to explain the image artifact, which is resulting from the CNT bent-adhesion-separation repeated process (Fang et al., 2008; Strus et al., 2005), as analyzed in Fig. 11.

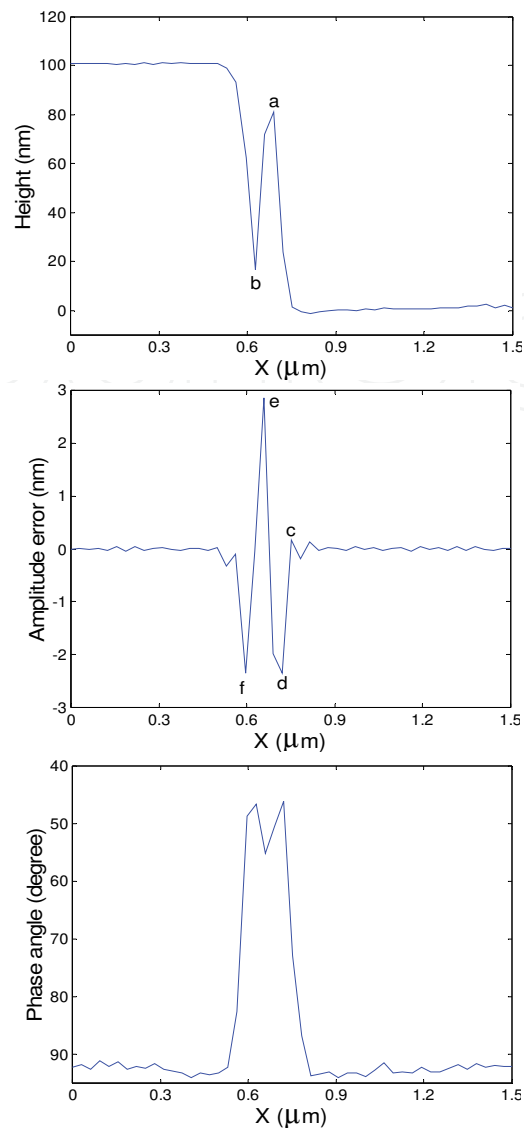


Fig. 11. Sectional view of height, amplitude and phase angle of the CNT probe image artifacts (Fang et al., 2008).

When the CNT probe contacts with the grating edge, the CNT-trench wall adhesion would bend the CNT probe and then reduce the vibration amplitude of the cantilever, as position *d* indicates in Fig. 11. The AFM controller perceives the sudden probe amplitude drop as a surface height increase and responds by quickly moving the probe away from the sample. At position *a*, the CNT has finally been broken free from the trench wall, and the cantilever vibrates at its free amplitude. There is about a  $10^\circ$  phase angle decrease around position *a* in the phase angle curve at the bottom of Fig. 11, which confirms that the CNT probe really moves away from the trench wall. In order to restore the original scan amplitude, the AFM controller again lowers the probe. At position *b*, the CNT probe contacts with the trench wall again and the amplitude also drops due to the bending of the CNT. Therefore, the image artifact at the trench wall results from the CNT probe bending-adhesion-separation repeated process (Fang et al., 2008). When the ripple and wavelike AFM results appear at the steep positions using CNT probe, we should carefully judge whether it is the real sample morphology or the image artefact resulting from the CNT probe's instability.

The CNT probe can be treated as a series system of the ordinary AFM probe combining with an end-fixed carbon nanotube. The effective force constant for this series system can be calculated as followed:

$$K_{eff} = \frac{F}{X} = \frac{F}{\frac{F}{K_s} + \frac{F}{K_c}} = \frac{K_s K_c}{K_s + K_c} \quad (3)$$

Therefore, the force constant of the Si probe would also affect the CNT probe's effective stiffness. Under many CNT probe fabrication experiments, the lateral force constant requirement of stable working for the CNT probe attaching to the triangular-shape AFM probe is found relative larger than the one to the rectangular shape probe. This is mainly due to the triangular shape AFM probe's less resistance ability to the lateral force (J. E. Sader & R. C. Sader, 2003).

### 3.2.2 CNT-sample boundary conditions

In general, CNT probes are harmonically excited near resonance and dynamically operated in either an attractive or repulsive regime using tapping-mode AFM. When CNT probes are operated in the net repulsive regime, CNTs have the potential to buckle, bend, adhere, and slide (Strus & Raman, 2009). Many studies highlighted that the CNT probe-sample boundary conditions and its mechanical responses would play a vital role in the CNT probe's stability.

A thermal noise forcing method was used to investigate the mechanical response of CNT AFM probes under the free sliding and pinned CNT contacts cases, as shown in Fig. 12. Generally, thermal noise forcing produces probe oscillation amplitudes only about angstrom. Therefore, the thermal noise spectrum is very sensitive to tiny variations of the contact properties between the CNT probe and the surface, thus providing an accurate picture of the CNT probe's mechanical response (Buchoux et al., 2009). Molecular simulations were proposed to explain the effects of CNT's slip and snap-to-contact on the resolutions (Solares & Chawla, 2010).

Strus suggested that the identification of CNT pinning and slipping during intermittent contact can be based on phase contrast images and energy-dissipation spectroscopy, as shown in Fig. 12. The pinning or slipping of the CNT depends on the scan surface and the CNT probe's stiffness. It is found that CNT probe is easier slipping on the graphite surface than on the graphene oxide and silicon oxide surfaces (Strus & Raman, 2009).

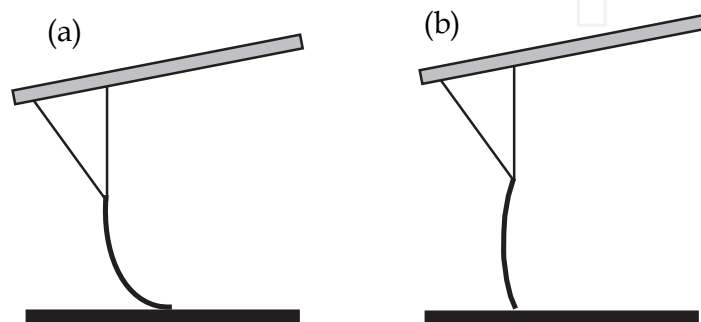


Fig. 12. Illustration of the CNT probes slide (a) and pin (b) CNT contacts cases.

The CNT probe's slipping effect was experimental studied (Fang et al., 2009). It is found that the CNT probe is apt to slide if it scans with a large vibration amplitude. There are many dark lines resulting from CNT's slide in the AFM image as arrows indicated in Fig. 13(b). Due to CNT's hydrophobic property and its high aspect ratio, the capillary force between the CNT probe and the sample surface is much smaller. Therefore, the CNT probe does not need to work at large amplitudes to break the capillary force as the Si probe does and it can work well under low scanning amplitude of less than 30 nm.

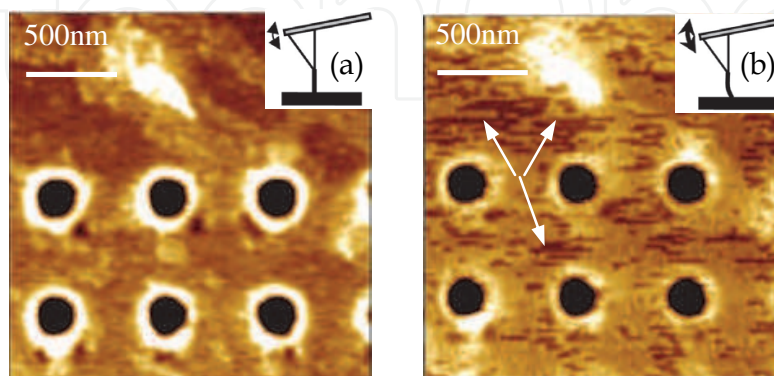


Fig. 13. Nanoholes images captured by CNT probe with 18nm (a) and 40nm (b) scan amplitudes (Fang et al., 2009).

The CNT slipping is an obstacle for accurate AFM topography measurements, while it can be treated as a potential method of analyzing surface composition by enhancing the probe-sample frictions contrast. AFM peeling force spectroscopy and theoretical studies have been used to quantitatively investigate the physics of adhesion and stiction of carbon nanotubes on different material substrates, such as, HOPG, polymer (Strus et al., 2008).

### 3.3 Artefact elimination

Studies have been conducted to lessen and avoid the CNT probe's image artefact. Larger scan amplitude ratio was employed to depress the ringing artefact, by increased from 66% to 96% of the 34 nm unconstrained vibration amplitude (Strus et al., 2005). Akita found that the CNT probe's image instability near the wall of the DVD surface pits can be avoided by slightly increasing the probe's free tapping amplitude to avoid the pit's attractions (Akita et al., 2000a). Solares has theoretically explored that spectral inversion method and dual-frequency-modulation method can mitigate the imaging artifacts when using short nanotube probes (<100 nm in length) in air. The two methods are capable of performing simultaneous imaging and force spectroscopy (Solares & Chawla, 2010).

The most effective method to overcome the CNT probe's image artefact is to strengthen the CNT probe, as discussed in the Section 2.2. For example, several micrometers long multiwalled CNT probes were prepared and strengthened with carbon molecular layers to overcome mechanical instabilities (Vakarelski et al., 2007).

## 4. CNT probe's applications

### 4.1 High resolution imaging

CNT's excellent properties make CNT probe be a favorable choice for AFM probe in topographic imaging. SWNT probe with several nanometers' radius shows great image

resolution over conventional Si probe (Cheung et al., 2000). CNT probes have also been showed higher image resolution for the high aspect ratio samples, such as, grating, cellular samples, etc (Dai et al., 1996; Fang et al., 2007; Hafner, 1999, 2001; Stevens et al., 2000). It is found that not only the CNT probe's radius would influence its resolution, its end configuration also showed impact on CNT probe's image ability (Fang et al., 2009).

CNT has a much higher Young's modulus and exceptional elastic buckling property, which results in the much better wear resistance ability of the CNT probes relative to the Si probes. The excellent wear resistance property makes CNT probes have consistent image resolution, which is very important for applications, such as, online inspection.

Electrostatic force microscopy (EFM) is one technique sensitive to the long-range electrostatic forces, which are useful in the study of semiconductor devices. Because of the long-range nature of electrostatic force, interpretation of EFM images is often complicated as the probe beyond the probe apex would also affect the EFM image results. This effect can be greatly reduced using high aspect ratio CNT probes (Wilson & Macpherson, 2009). For similar reasons CNT probes are also suitable for high resolution magnetic force microscopy. Iron-filled carbon nanotubes (Fe-CNTs) have been proposed for the application for magnetic force microscopy (Wolny et al., 2008).

#### 4.2 Nanofabrication

Carbon nanotube probe is not only a tool for imaging, but also for nanofabrication, as shown in Fig. 14. AFM nanolithography can be widely applied in fields such as data storage and device fabrication. Due to nanotube's excellent properties, carbon nanotube probes have been explored in fabricating oxide nanostructures on silicon surfaces (Dai & Franklin, 1998), a p-GaAs(100) surface (Huang et al., 2006), a metallic tantalum film (Choi et al., 2007).

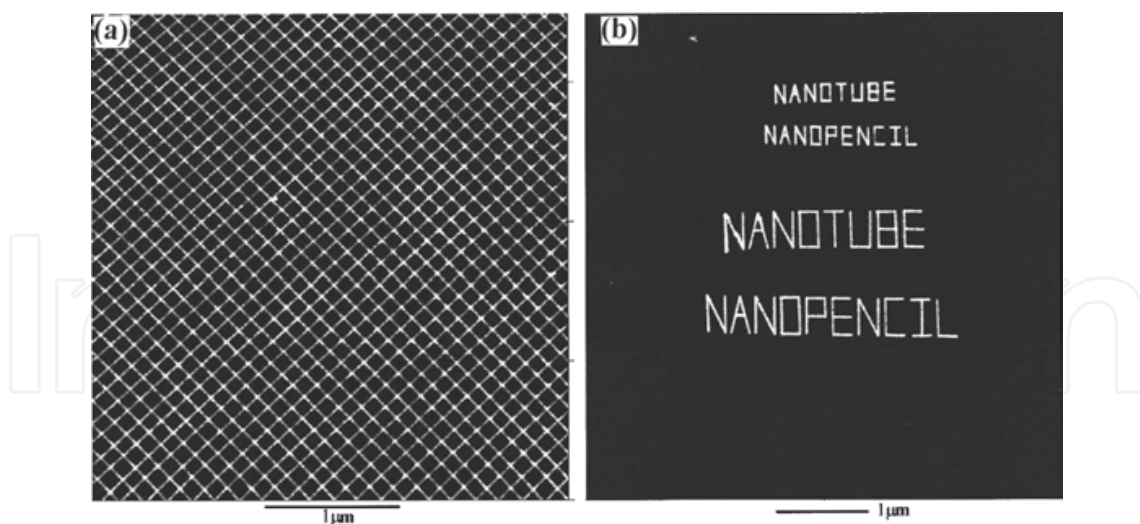


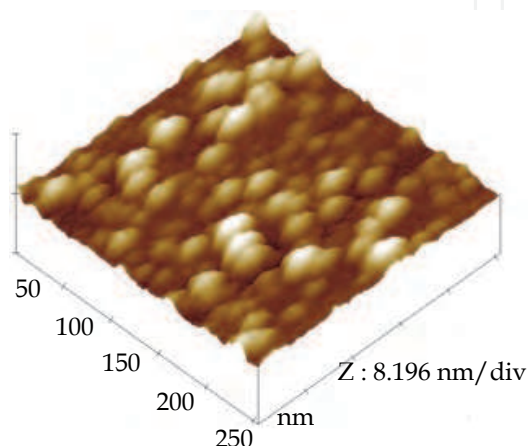
Fig. 14. AFM image of 2 nm tall, 10 nm wide, and 100 nm spaced silicon-oxide (light) lines fabricated by a nanotube tip using anodic oxidation method (Dai & Franklin, 1998).

It was found that hydrophobicity is a key factor in the improved reliability of CNT probes on the nanoscale oxide fabrication over conventional Si probes (Kuramochi et al., 2007). Okazaki studied the nano-gratings direct nanolithography on organic polysilane PMPS films using CNT probe (Okazaki et al., 2000).

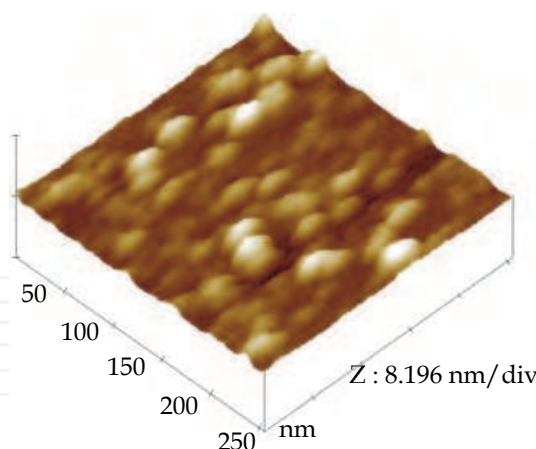
### 4.3 Biology application

Due to its excellent properties, CNT probe has been widely used in the biological application. It produces lower damage to the proteins than the Si probe during AFM scanning, as shown in Fig. 15 (Fang et al., 2007). CNT probe has been proven more suitable for imaging soft biological samples, such as, DNA, protein (Cheung et al., 2000).

Technology for introducing biomolecules and nanoparticles into living cells with minimal invasiveness is a key task to study the physical properties and biochemical interactions that govern the cell's behavior (Chen et al., 2007). Micro glass pipettes have been used for intracellular analysis research. However, due to their relatively large sizes and rigid structure, these probes cause severe damage to the cells (Niu et al., 2011).



(a) Measured by CNT probe



(b) Measured by Si probe

Fig. 15. AFM analyses of IgG protein. The Si probe has created a larger probe indentation to the soft proteins than the CNT probe (Fang et al., 2007).

Due to its nanoscopic dimensions, high mechanical strength, and functionalizable surfaces, CNT probe has been used as a “nanoneedle” in a nanoscale cell injection system to deliver cargo into cells. A multiwalled CNT probe was functionalized with cargo via a disulfide-based linker. Penetration of cell membranes with this “nanoneedle” was controlled by the

AFM. The following reductive cleavage of the disulfide bonds within the cell's interior resulted in the release of cargo inside the cells, after which the nanoneedle was retracted by the AFM control, as shown in Fig. 16 (Chen et al., 2007). The CNT probe "nanoneedle" technique causes little membrane or cell damage. Other biomolecules such as DNA and RNA, or synthetic structures such as polymers and nanoparticles can be delivered into cells in a similar fashion (Chen et al., 2007; Vakarelski et al., 2007).

Gold nanoparticle-decorated CNT probes are used to study intracellular environments in situ using surface-enhanced Raman spectroscopy (SERS), as shown in Fig. 17 (Niu et al., 2011). The high aspect ratio of CNTs displaces less intracellular volume than ordinary glass pipettes or optical fibers cell probes, thus perturbing the cell much less, especially when measurements performed over long periods of time. This might be a useful method for tip-enhanced Raman spectroscopy (TERS) application using CNT probe.

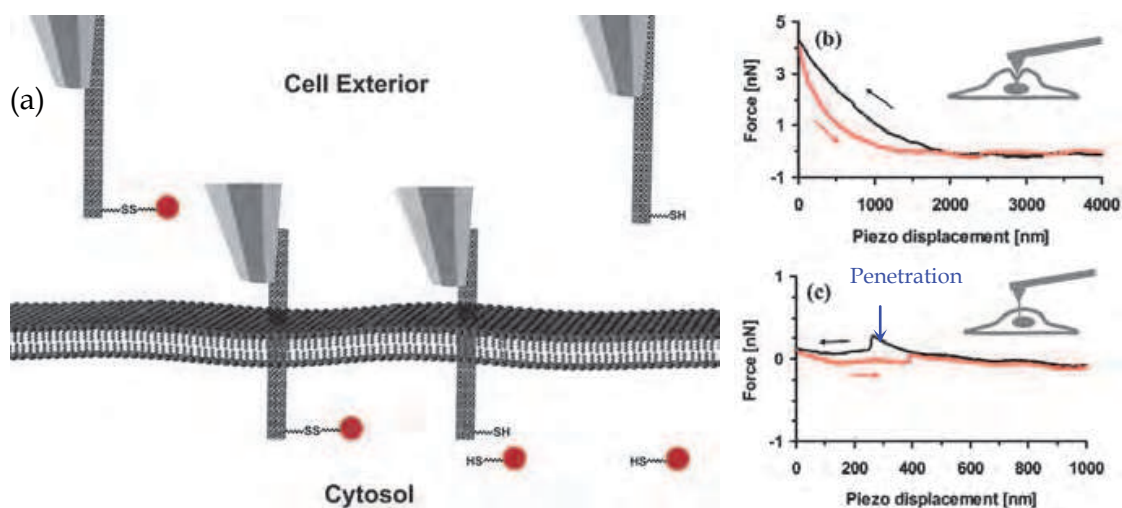
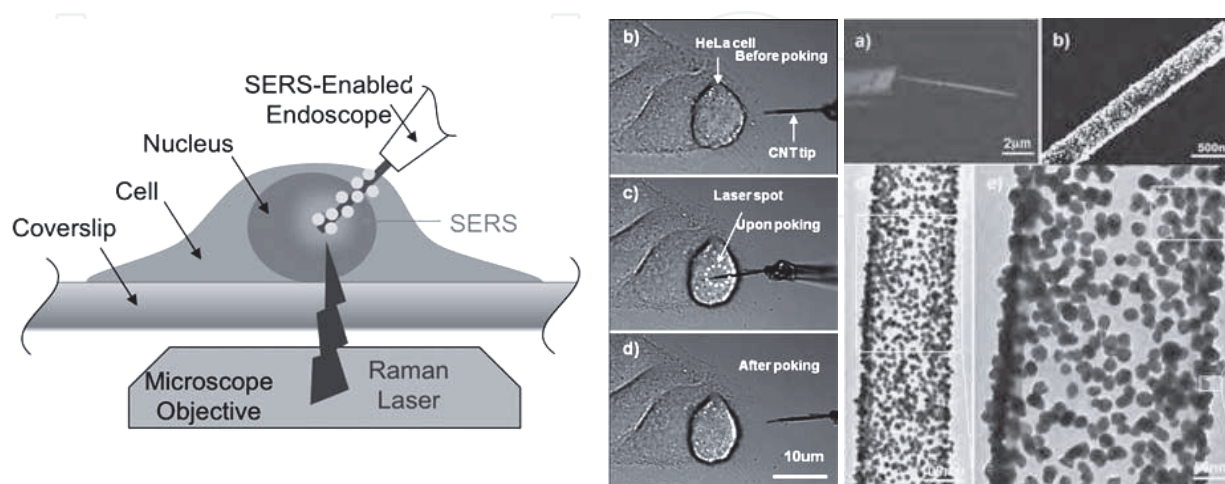


Fig. 16. Schematic of the CNT probe nanoinjection procedure. A CNT probe with cargo attached to the CNT surface via a disulfide linker penetrates a cell membrane (a) (Chen et al., 2007). Force vs piezo displacement curves for the indentation of a living cell using a pyramidal Si probe (b) and a C/Au-coated nanotube probe (c) (Vakarelski et al., 2007).



(a) Intracellular SERS study with a CNT probe (b) SEM of gold-decorated CNT probe

Fig. 17. Intracellular SERS study with a nanoparticle-decorated CNT probe (Niu et al., 2011).



## 5. Summary and outlook

Carbon nanotube probes open up a new AFM imaging world, increasing the probe's resolution and longevity, decreasing probe-sample forces, and extending the AFM application fields. It would also have a significant impact in key research areas, such as, nanometrology, surface engineering and biotechnology.

Future main attentions in the carbon nanotube AFM probes can be summarized as follows:

- CNT probe fabrication technics' optimization: the technics of high efficient fabrication with low cost; the fabrication's reproducibility and controllability.
- CNT probe imaging accuracy calibration: the CNT-sample boundary conditions and CNT's mechanical response effect studies on the CNT probe imaging resolutions in nanometer or angstrom levels; CNT probe's accuracy comparison with the others precision measurement techniques.
- CNT probe's unique applications: TERS; the biological application, such as, functionalized CNT probe as nanoneedle for intracellular studies and drug delivery.

## 6. Acknowledgement

The authors would thank the persons who have given kind helps in our CNT probe's researches, Dr. L. Q. Guo from Harbin Institute of Technology, Prof. Jason H. Hafner from Rice University, Prof. Hongjie Dai from Stanford University, Dr. Jason Cleveland from Asylum Research and Dr. M. C. Strus from Purdue University. Thanks go for Mr. Haifeng Gao and Miss Lihua Xu from Tianjin University for helping the typesetting.

The research work is supported by '111' project by the State Administration of Foreign Experts Affairs and the Ministry of Education of China (B07014), National High Technology Research and Development Program of China (863 No. 2009AA044305& 2009AA044204), National Natural Science Foundation of China (No. 50905126, 90923038&50935001), Ministry of Industry and Information Technology (No. 2011ZX04014-071), Natural Science Foundation of Tianjin(No. 10JCYBJC06400), and National Basic Research Program of China (973 Program, Grant No.2011CB706700).

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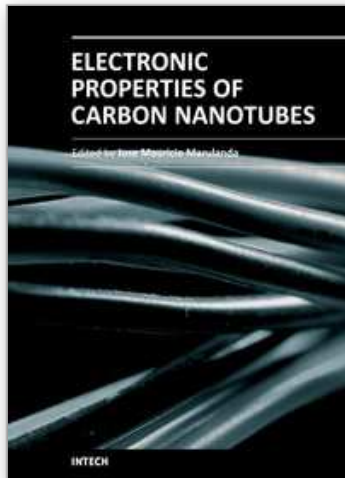
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## **Electronic Properties of Carbon Nanotubes**

Edited by Prof. Jose Mauricio Marulanda

ISBN 978-953-307-499-3

Hard cover, 680 pages

**Publisher** InTech

**Published online** 27, July, 2011

**Published in print edition** July, 2011

Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. These one-dimensional (1D) graphene sheets rolled into a tubular form have been the target of many researchers around the world. This book concentrates on the semiconductor physics of carbon nanotubes, it brings unique insight into the phenomena encountered in the electronic structure when operating with carbon nanotubes. This book also presents to reader useful information on the fabrication and applications of these outstanding materials. The main objective of this book is to give in-depth understanding of the physics and electronic structure of carbon nanotubes. Readers of this book should have a strong background on physical electronics and semiconductor device physics. This book first discusses fabrication techniques followed by an analysis on the physical properties of carbon nanotubes, including density of states and electronic structures. Ultimately, the book pursues a significant amount of work in the industry applications of carbon nanotubes.

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