Electron beam detection of a Nanotube Scanning Force Microscope

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Atomic Force Microscopy (AFM) allows to probe matter at atomic scale by measuring the perturbation of a nanomechanical oscillator induced by near-field interaction forces. The quest to improve sensitivity and resolution of AFM forced the introduction of a new class of resonators with dimensions at the nanometer scale. In this context, nanotubes are the ultimate mechanical oscillators because of their one dimensional nature, small mass and almost perfect crystallinity. Coupled to the possibility of functionalisation, these properties make them the perfect candidates as ultra sensitive, on-demand force sensors. However their dimensions make the measurement of the mechanical properties a challenging task in particular when working in cavity free geometry at ambient temperature. By using a focused electron beam, we show that the mechanical response of nanotubes can be quantitatively measured while approaching to a surface sample. By coupling electron beam detection of individual nanotubes with a custom AFM we image the surface topography of a sample by continuously measuring the mechanical properties of the nanoresonators. The combination of very small size and mass together with the high resolution of the electron beam detection method offers unprecedented opportunities for the development of a new class of nanotube-based scanning force microscopy.

Nanoscience and nanotechnology rely on the ability to manipulate and probe objects with a resolution in the deep nanometer range1–4. In the last three decades, advances in the field have been possible mainly thanks to the development of Atomic Force Microscopy (AFM)5–7. The idea behind the technique is at the same time very simple to understand and impressive in the attainable results: a tiny mechanical oscillator with a sharp tip at the extremity is approached to a surface and the evolution of the mechanical properties of the probe is monitored to get information about the sample topography and properties. Generally the mechanical oscillator used in AFM is a micrometer sized silicon cantilever presenting a very sharp tip at the extremity8. The need to increase the force sensitivity and spatial resolution, pushed the researchers to develop alternative mechanical oscillators based on self-assembled structures with submicrometer dimensions. Prominent examples are silicon based nanowires9, 10 and carbon or boron nitride nanotubes11–14 and even bidimensional suspended membranes15, 16. These new probes, because of their minute size and mass and almost perfect cristallinity, couple high spatial resolution and force sensitivity reaching the zepto-newton (10⁻²⁴ N) range17 for carbon nanotubes working in cryogenic environment. The major drawback for the further development of this new kind of probes is the extreme difficulty to detect their position and motion. It is worth mentioning that the mechanical properties of suspended nanowires have been elegantly measured via optical interferometry18 leading to a first proof of concept of nanowire based scanning force microscope19. Despite the effort and recent progress, optical detection schemes can be hardly applied to nanotubes which are the ultimate mechanical oscillators and force sensors: their diameter, in fact, ranging from 1 nm to few tens of nanometers, is too small to be possibly detected with optical techniques. Very recently, electron microscopy has been shown to detect the thermally induced resonant properties of nanomechanical resonators with picogram effective masses5 and even attogram scale carbon nanotubes20.

In this study we demonstrate that electron beam detection of mechanical oscillators can be harnessed to develop the first example of scanning force microscope based on individual suspended nanotubes. The individual nanotube is mounted on top of a custom AFM working in situ in a Scanning Electron Microscope (SEM) at a pressure of ≈10⁻⁵ mbar. The highly focused electron beam of the SEM is positioned, in the so-called “spot mode”,
on the externally driven nano-oscillator and the inelastically scattered electrons (SE) are monitored to measure
the resonator motion with a spatial resolution of 0.4 nm. As in standard non-contact AFM, the mechanical
response of the nanotube is monitored via amplitude and phase locking, while approaching a sample, allowing to
reconstruct the surface topography. This new technique allows to take advantage of the exceptional properties of
nanotubes as force sensors for scanning microscopy. For standard electron microscopy, the spatial resolution,
given by the electron beam size, is below 1 nm and it represents a three orders of magnitude improvement with
respect to optical techniques. The high focusing of the electron beam further increases the motion detection res-
olution for unidimensional systems²⁰. We therefore demonstrate for the first time, that one dimensional oscillators
can be used for scanning force microscopy.

In this work we used boron nitride multiwalled nanotubes (BNNTs) realized via Chemical Vapour Deposition
(CVD)²¹. CVD BNNTs present a very high structural purity with no evident defects in a spatial region reaching
the micrometric range. The nanotubes are glued at the extremity of an electrochemically etched tungsten tip, fixed
on a three axis piezo inertial motor mounted inside a SEM (FEI-Nova nanoSEM). In Fig. 1 we present a scheme
of the experimental set-up and a SEM picture of one nanotube used in this study in front of an electrochemically
etched tungsten tip. The electron beam is set fixed at a chosen working point along the section of the NT. This
working point is chosen so that the variation of the SE intensity around this working point stays linear, see Fig. 1e.

To counteract the drift of the nanotube with respect to the electron beam, a feedback loop acts directly on the
SEM deflection coils to control the position of the electron beam and keep constant the low frequency compo-
nent of emitted secondary electron (SE) intensity detected via a Everhart-Thornley Detector (ETD). This allows
to maintain, for the whole duration of the experiment, the electron beam at a constant working position. The
intensity of the emitted SE are recorded via a Specs Nanonis SPM electronics and analyzed to extract the DC and
AC fluctuating components.

BN nanotubes are mechanically excited with an external piezo dither and the variations of SE, related to the
relative displacement of the NT around the working point, are recorded as a function of the excitation frequency.

When excited by an external sinusoidal force \( F_{\text{ext}}(\omega) = F_{\text{ext}} \cos(\omega t) \), the nanotube behaves in first approximation as a
spring-mass system with oscillation amplitude and phase with respect to the excitation given by:

\[
A(\omega) = \frac{F_{\text{ext}}}{m_{\text{eff}}^2(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}
\]

\[
\phi(\omega) = \arctan\left( \frac{\gamma \omega}{m_{\text{eff}}(\omega_0^2 - \omega^2)} \right)
\]

with \( m_{\text{eff}} \) the oscillator effective mass, \( \omega_0 = \sqrt{\frac{k}{m_{\text{eff}}} \omega_0} \) the resonant frequency and \( \gamma \) the damping factor. \( k \) is the spring
constant that is for this nanotube in the order of \( 10^{-4} \) N/m to compare to the typical spring constant for mul-
walled carbon nanotube that is in the range of \( 0.001-0.05 \) N/m²². Using single wall nanotube, the value of the
spring constant can be substantially pushed down to value of \( 10^{-6}-10^{-5} \) N/m. These values have to be compared
to what generally achievable with standard Silicon cantilever that is at best in the order of few mN/m. However
general dynamic mode cantilevers have spring constants in the range of few tens of N/m which give a force reso-

nution for unidimensional systems²⁰. We therefore demonstrate for the first time, that one dimensional nanotubes
used during this work.

To confirm that the detected resonance is due to the mechanical motion of the nanotube, we switch the SEM
operation mode from “spot mode” to the conventional full frame imaging: when excited at the resonance the
nanotube position exhibits the standard resonant profile for the fundamental mode of a single clamped oscillator,
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In Fig. 2a we present the response of a nanotube with diameter \( D \approx 50 \) nm and length \( L = 18 \) \( \mu \) m, when
varying the frequency of excitation. The mechanical response is characterised by a resonance at \( f_0 = \omega_0/2\pi \approx 270
\) kHz and a quality factor, defining the inverse of the damping rate, \( Q \approx 250 \). In contrast to previous studies on
nanowires and single walled carbon nanotubes⁹, ¹⁹, ²⁰, we do not observe a double resonant peak due to non degen-
eracy of polarisations. This further confirms the high structural quality and geometrical symmetry of BN nano-
tubes used during this work.

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operation mode from “spot mode” to the conventional full frame imaging: when excited at the resonance the
nanotube position exhibits the standard resonant profile for the fundamental mode of a single clamped oscillator,
as described by the Euler-Bernoulli equation. In Fig. 2c we plot the SEM images for different excitation ampli-
tudes confirming that for the range of excitations used during the experiment, the oscillator stays in its linear
regime.

As the interaction of the oscillator with its environment is modified, one observes a change in both the fre-
quency and the amplitude at resonance. The shift in resonance frequency \( \delta f \) is related to the conservative force
response, whereas the broadening of the resonance (change of quality factor \( Q_i \rightarrow Q_f \)) is related to dissipation²³

\[
\delta f = \frac{\partial F_{\text{ext}}}{\partial \omega} = \frac{2k}{f_0} \delta f_{\text{ext}} \quad \text{and} \quad P_{\text{D,I}} = \frac{k}{\sqrt{3}} \left( \frac{1}{Q_i} - \frac{1}{Q_f} \right)
\]

where the index \( i \), indicates the component of the position vector. In practice, during a typical experiment, two
feedback loops allow us to work at the resonance and maintain constant the oscillation amplitude \( a_{\text{ext}} \). Monitoring
the frequency shift \( \delta f \) and the resonance quality factor \( Q_f \) obtained from the excitation voltage or the oscillation
amplitude, thus provides a direct measurement of real and imaginary parts of the mechanical impedance.

To demonstrate the possibility to use a nanotube as the force sensor of a scanning probe microscope, we firstly
approached a very sharp tungsten tip to the oscillating nanotube. While approaching the tungsten tip down to
the contact we record the evolution of the phase between the nanotube oscillation and the exciting dither and of the oscillation amplitude. This first experiment is performed in an open-loop configuration: any variation of the interacting environment is directly measured by a change of both the oscillation amplitude and the phase with respect to the excitation. Once the mechanical response of the NT is modified by the tip-NT interaction, we kept the distance constant and we performed a scanning picture of the tungsten tip, as in standard AFM. As shown in Fig. 3a, the amplitude and phase shift as a function of the position of the tip correctly detect the spatial force field induced by the tungsten, and consequently reconstruct the tip shape.

As a further demonstration of the potentialities of the NT-SFM, a BNNT (diameter \(D = 80\) nm and length \(L = 18\) \(\mu\)m) with resonant frequency \(f_r \approx 350\) kHz and oscillation amplitude of \(\approx 10\) nm scans at a distance of \(\approx 10\) nm a (100) silicon surface while a double feedback loop acts on both the phase and the amplitude. In Fig. 3b we plot a cartography of a 1 micron silicon terrace, recording at the same time the excitation voltage applied to
keep constant the amplitude and the frequency shift. Variations of both quantities allow to reconstruct the surface
topography with a resolution of $\approx 100$ nm, given by the size of the nanotube apex.

Finally taking benefit from the versatility of the NT-SFM and in addition to what presented above, we show in
Fig. 3c, a static AFM and a SEM picture of gold nanoparticles deposited on a HOPG sample. In this case, by static
we mean that the nanotube is neither excited nor oscillating: this operation mode is the analog of the static mode
employed in standard Atomic Force Microscopy. The static AFM picture is obtained by recording the deflection
of the nanotube during the scan; experimentally this quantity is given by the voltage command to the deflection
coils to keep constant the SE emission intensity. When the nanotube deflects because of the interaction with the
surface, its relative position with respect to the electron beam changes, therefore modifying the SE emission
intensity. The feedback loop acting on the beam position allows to reconstruct precisely the displacement of the
nanotube and consequently the surface topography.

In addition, it is worth mentioning the complementarity of this operation mode with the AC mode presented
before: by recording the deflection of the nanotube it is in fact possible to quantitatively measure the total force
which the nanotube is submitted to. Considering the experimental set-up, with the nanotube oscillating parallel
to the substrate, the conventional force curve cannot be easily acquired. However, it is in principle doable by
following the position of the beam controller to keep the secondary electron emission constant. Together with the measurement of the conservative force gradient via the frequency shift and the dissipative forces via the change in the quality factor, this method allows to completely characterise the force environment with an unprecedented resolution.

Altogether our pioneering work demonstrates that one dimensional oscillators such as boron nitride nano-
tubes can be harnessed as probe sensors for Scanning Force Microscopy. By using a highly focused electron beam
we can detect and record the mechanical response of an individual nanotube. Coupling atomic force microscopy
technology together with high resolution electron beam detection, allows to measure, in real-time, conservative
and dissipative interactions as well as the complete static interactions of a nanotube with its environment. We

Figure 2. Electron beam detection of the mechanical response of a BN nanotube. (a) Amplitude and phase of
the nanotube mechanical response as a function of the exciting frequency. The frequency is scanned around the
resonant frequency; for a BN nanotube with $D = 50$ nm and $L = 18$ $\mu$m the resonance is measured at
$f_r = \omega_0/2\pi \approx 270$ kHz and the quality factor $Q \approx 250$. Red curves are best fit based on equations (1) and (2).
(b) Scanning Electron Microscope pictures of the nanotube for different excitation amplitudes: from left to right
0 mV, 500 mV, 1 V, 2 V; the mode shape reproduces well the standard Euler-Bernoulli profile for the fundamental
mode of a single clamped tube.
elegantly exploited this new detection method to measure the surface topography of samples approached by the extremity of an individual nanotube.

In this first proof of concept of nanotube based atomic force microscope, we have performed measurements with a nanotube whose diameter and therefore apex is approximately 50 nm. As in standard atomic force, the spatial resolution is given by the probe apex and in this first work is in order of tens of nanometers. This limitation is only due to the choice of nanotube and thanks to the potentiality of the detection scheme, smaller nanotube can be used and even single wall nanotubes with diameters in the range of few nanometers. Using single wall nanotubes will consequently decrease the spatial resolution at the level of cantilever functionalised with nanotube at the extremity. When using ultimate resonators, thermal noise will be a limiting factor to take into account; large thermally induced oscillation amplitude exceeding the diameter of nanotubes have been measured on individual carbon nanotube using electron beam detection and this will be limiting the actual spatial resolution of a single wall nanotube based force microscopy. However we believe that thermal noise can be also turned to advantage allowing to develop a vectorial thermal noise-based force spectroscopy. In practice this would mean to extend what has been elegantly shown with Silicon Carbide nanowires to individual nanotubes. This is however beyond the limit of this work. More in general, the highly focused electron beam allows to detect oscillators with diameters in the nanometer range, drastically increasing the force sensitivity and spatial resolution compared to standard atomic force microscope cantilevers and even more recent nanowires. Our work represents a proof of concept and open the path for the development of a new class of ultrasensitive nanotube-based scanning force microscopes.

**Methods**

**Implementation.** Nanotubes are prepared by gluing them individually on an electrochemically etched tungsten tip. BNNTs are culled under optical observation and glued with carbon tape under optical microscope. On the sample holder of the Scanning Electron Microscope (NovaNanoSem 450), the prepared nanotubes and the sample are placed face-to-face on the same dedicated nanomanipulation station. The tip-nanotube is placed on a three axis steppers motors (3*Smaract SLC17-1720). The sample is placed on a three axis piezoscanner with sub-nanometric resolution in displacement (MicroTRITOR Piezosystemjena). The nanotube and the sample are placed perpendicularly in the so-called pendulum configuration; i.e. the oscillations of the nanotube are parallel to the substrate. A piezo-dither (PA3JEW Thorlabs) is glued underneath the tip-nanotube to excite mechanically the nanotube at its natural frequency.

**Control in Real-Time.** During the experiments, measurements and controls are performed in Real-time by a complete Specs-Nanonis package (RT5, SC5 and OC4). The position of the electron beam of the SEM is controlled with the Specs-Nanonis electronics by directly controlling the voltage applied to the beam deflector lenses.
The secondary electrons emitted by the nanotubes are collected with a standard Everhart-Thornley Detector, which includes a strongly biased grid and a high bandwidth scintillator. The signal from the detector is then acquired and analysed via the Specs-Nanonis electronics.

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Additional Information

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