Robust operation and performance of integrated carbon nanotubes atomic force microscopy probes

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Abstract. We present a complete characterization of carbon nanotube-based atomic force microscopy (CNT-AFM) probes to evaluate the cantilever operation and advanced properties originating from the CNTs. The fabrication consists of silicon probes tip-functionalized with multiwalled CNTs by microwave plasma enhanced chemical vapor deposition. A dedicated methodology has been defined to evaluate the effect of CNT integration into the Si cantilevers. The presence of the CNTs provides enhanced capability for sensing and durability, as demonstrated using dynamic and static modes, e.g. imaging, indentation and force/current characterization.

Since the discovery of carbon nanotubes (CNT) [1] there have been many attempts to benefit from their entirely unique properties, motivating a revolution in the, at that time, emerging field of nanoscience and nanotechnology perhaps only comparable to the invention of atomic force microscope (AFM) [2] and scanning tunneling microscope (STM). [3] One of the most sought-after applications for CNTs is their use as scanning probe microscope (SPM) tips, taking advantage of unique dimensional high aspect ratio and ideal mechanical and electronic properties. The fabrication approaches vary as much as the number of combinations that can be implemented for the catalyst materials and preparation methods, synthesis techniques, attachment, etc. [4, 5, 6, 7] as do the resulting CNTs and the probes shape and performance characteristics. [8, 9]

We present a complete characterization of carbon nanotube-based dynamic mode AFM probes, both from the point of view of the operation of the cantilevers and from their advanced properties for sensing/microscopy due to the presence of the CNTs. The well-established technological approach consists of Si AFM probes functionalized near the tip with multiwalled CNTs grown by catalytic microwave plasma-enhanced chemical vapor deposition (MPECVD). [10, 11] First, a dedicated methodology has been defined to evaluate the effect of CNT integrative processing into the Si cantilevers. This information becomes essential for proper evaluation of imaging potential uses. [12] Then, we show how the presence of the CNTs provides enhanced capability for sensing with remarkable apex durability, as demonstrated by exemplary measurements in both dynamic and static mode. In particular, the specifications of CNT-interfaced topographical imaging, indentation, electrical conduction, mechanical response and adhesion are provided, while other capabilities for similar in-house fabricated devices have already been reported. [13]

The technological choice for the production of CNT functionalized tips is based on the integration of CNTs in commercial AFM probes using on-device synthesis of CNTs. Commonly, Si cantilevers with Al reflection coating are used as starting device (Budget Sensors Inc. Model: TAP300AL, 300±100 kHz, 40 N/m). After removal of native oxide in HF solution, locally controlled deposition of
thin, polycrystalline Pd layer is applied, as described in [14]. Subsequently, MPECVD is used for the
growth of a few thousands vertically oriented multiwalled CNTs (MWCNT), ordered and arranged as a
cover of tip’s original shape and dimensions. [15] Obviously, this may not seem the ideal product for
undertaking high spatial imaging resolution in high aspect ratio sample structures, as it is envisioned
for the use of long (small diameter) SWCNTs [16], but actually our devices have demonstrated, a
number of interesting properties that might balance this fact (viva infra). The collective nature of the
resulting number of CNTs comes directly from the dimensions of the area of Pd electroplating,
whereas the multiwalled structure derives from the effective particle size during PECVD, and
probably additional contribution coming from the use of microwave field. As reported in, [17]
different metal particles do present a specific heating efficiency to absorb microwave radiation, which
can be crucial for the growth process since it determines the particle state as a site for nucleation or
formation of CNT. Although the exact mechanism is not yet clear, in both cases, [18] the combination
of the catalyst and microwave CVD determines the CNT characteristics. Comparing the chemical
products of the synthesis for both approaches, the use of methane as the source of carbon may be
regarded as more hazardous, however, it is also noteworthy that methane has indeed been reported for
its remarkable capability to integrate SWCNTs for the fabrication of CNT field effect transistors
(CNT-FET) devices at wafer scale [19] or the development of MWCNT vertically aligned forests
without external field assistance for functional CNT-based electrodes. [20] In addition to a
morphological inspection by scanning electron microscope (SEM), recently we apply high resolution
transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) analysis
for a more precise determination of the structural and chemical properties of CNT-decorated tips,
which is important to support study of CNT synthesis process, and indispensable for the objective
of present investigation of CNT-probes for AFM sensing (Figure 1). Therefore, the knowledge of catalyst
position and element, the quality of outer amorphous carbon layer and its interface to the metal, etc is
applied to the discussion and understanding of force, electric and mechanical interactions and imaging
experimental results. For any kind of catalyst, the CNTs consist of a few tens of layers, MWCNT,
being indicative of the growth technique, the MPECVD. In the case of Pd, we systematically observe
that inner structure is bamboo-like. Using EDS we confirm the purity of catalyst particles.

![Figure 1. a) HRTEM is used to determine the structure of the CNTs. MWCNT images obtained from as-purchased Au coated probes. b) EDS provides chemical determination of catalyst particles.](image)

Although our basic probe device is based on the specific dynamic mode probes related above, other
cantilevers dimensions and starting materials have also been used and similarly studied for the
production of particular functionality CNT-integrated probes. The same procedure has been used when
testing local electrodepositing of Pd and MPECVD in as-purchased metal-coated softer probes (e.g.
model SI-DF3-A, Rh or Au coated, 1.5 N/m, from SSI Nanotechnology Inc, Japan) as a test of the
generality of the method. Provided that they could be more sensitive to the harsh fabrication
conditions due to their increased length, and hence, mechanical fragility [21], they actually showed
similar guarantee for the cantilever mechanical resonating properties after the CNT on tip synthesis.
Results also indicate the strong dependence of the catalyst material nature in the obtained CNTs in
terms of multilayer arrangement, probably linked to particle issues, such as diameter, etc (further study is ongoing). After the in-depth study of a few tens of CNT-AFM probes in terms of resonating mechanical operation of the cantilevers, morphological, chemical and structural determination, and test of performance and analysis for AFM applications, we describe and summarize the properties of our devices as follows.

For the quality control of the whole CNT-integrative fabrication process, we establish a procedure for monitoring the resonance figures of merit, so that we have access to the state of intrinsic properties of the cantilever. The resonance calibration is the fundamental step for the actual use of the probes by DFM. For doing this, we apply the automated resonance calibration routine of our SPM system (Seiko Instruments NanoNavi II E-Sweep) after, i) HF etching, ii) Pd electrodepositing, and iii) MPECVD (CNT growth), and register resonance frequency peak, together with related characteristics, such as quality factor or excitation voltage. The detection of the peak of oscillation is determined at resonance (instead of slightly shifted to, about 3 kHz lower, as commonly used for dynamic mode operation), for a target amplitude of 1 V. The calibration measurement is executed first, in air and normal pressure, then, in a vacuum (∼10⁻³ Pa), and finally, at atmospheric pressure in a N₂ ambient, for the study of pressure, humidity and vibration dissipation, which will strongly determine the CNT-probe performance, thanks to the SPM chamber system for relative humidity (i.e. including pumping).

![Figure 2. a) Example of resonance frequency calibration obtained in a vacuum. Peak width is below 30 Hz. Perfect coupling between CNTs and tip supports a proper performance during dynamic mode imaging. b) Tendency of resonance frequency as a function of MPECVD process time. The decrease correlates with the mass loading on the tip due to the formation of CNTs.](image)

The summary of the resonance frequency peak monitoring demonstrates that the calibration of the oscillation can be uniquely determined, for the user fixed target parameters, and for any of the tested environmental conditions with no unexpected divergences. The resonance frequency peak in a vacuum is sharp and precisely reliable, with a width of no more than a few tens of Hz (Figure 2, a)). In the case of normal pressure determination, we observe the usual broadening of the peak (FWHW about 0.5 kHz), within the specifications of as-purchased probes, and, importantly, without major difference between air versus N₂, which will be convenient for demonstration of universal DFM imaging.

Closely related to the frequency determination, the quality factor is a measure of the oscillation attenuation due to a series of factors. [22] It is indispensable to have a minimum value for normal conditions of operation [23], while it should be adjusted in absence of damping for a controllable actuation and detection. In brief, our results register no degradation of the cantilever quality factor (complementary description in [15]). In the case of the vibration voltage, the conditions of the technological approach results in no clear tendency, but remarkably (almost) always the target amplitude value could be reached within the voltage limits of the instrument (10 V). In fact, the determination of the vibration voltage for the target actuation is intrinsically less precise or more unpredictable. Even when no modification or technological process is applied to the probes, it contains an additional source of error as it can depend on slight variations of, for instance, photo detector alignment and signal.
This quality control strategy has been applied to the intermediate steps, for completeness, while strictly, the main objective as been the determination of the product specifications for the final CNT-probe devices. The results indicate that the probes intrinsic properties do not suffer any modification that could make unfeasible their application for imaging, nor additional degraded characteristics after CNT integration. The sharpness of the resonance peak in vacuum suggests that high resolution AFM could be tested using proper system (frequency modulated detection [24, 25]). In this case, probably, the CNT diameter characteristic of our MWCNTs would be the limiting factor for atomic resolution. The good resonance frequency determination is rooted in the fact that no dangling CNTs conform the CNT-modified tip (as it could be the case of a single long SWCNT), but collective arrangement coverage of the tip cone is present. Therefore, CNTs support each other and show perfect coupling to the Si original device. This point is a strict requirement for a reliable linear response when executing topographical imaging in order to guarantee a precise dimensional calibration. Partially summarizing, the possibility to be properly operated in a vacuum in terms of excitation, detection and linear response indicates that present CNT-based probes may be tested in atomic resolution SPM systems to test their ultimate properties for force or conductivity probing techniques, AFM or STM.

As stated in [15], the resonance frequency shift after the CNT synthesis indicates and quantifies the carbon mass loading due to the MPECVD process. Effectively, it correlates with the local accretion of mass as a consequence of CNT formation and allows study of the synthesis growth rate. As shown in Figure 2, b), the decrease of resonance frequency [26, 27] (due to mass loading) as a function of MPECVD process time shows a linear dependence tending to the saturation for synthesis longer than 30 minutes. Certain deviation from linearity is attributed mainly to the variability of the MPECVD and the use of more or less concentrated catalyst solution together with the concise resulting electrodeposited area of Pd for each tip. The extrapolated amount of MWCNTs (~3000) formed is in agreement with the SEM observed MWCNT structures and density. Although a fine fitting of present case is hard and inherently imprecise to be established, this procedure, together with an even more local CNT-functionalized nanomechanical device can be envisioned as an ultimate resolution mass sensor, for example, if properly integrated for optimal operation (CNTs are reduced) and signal conditioning, as in [28, 29].

After comprehensive determination of CNT role and performance on AFM probes subsequent to CNT integration in terms of technological approach, examples of their actual function as a tool for AFM in several of the sensing modes are presented. The measurements include both non-contact and contact sensing and demonstrate the wide-range of applications capability of our CNT-AFM probes.

Figure 3. Tapping mode imaging using CNT-probe on an epoxy resist containing Au nanoparticles. a) The quality of the image corroborates the proper performance of the integrated CNT-tip. b) Same location inspected after indentation of the polymer with the CNT-probe, while consecutive image is also acquired by the same CNT-tip.

The proper imaging performance is easily demonstrated in Figure 3. Topography image (Figure 3 a)) has been acquired in dynamic mode on a thin layer (about 10 nm) of epoxy resist deposited on a Si substrate. The resist contains embedded Au nanoparticles (commercially available, with an average size of 6.5 nm). It is clear from the image quality and the dimensions of the observed particles inside
the resist matrix that they are absolutely correct and well resolved. More remarkably, following the topography image an indentation test using CNT tip is executed, and consecutive imaging of the resist carving (bump in the center of the image) is acquired also with the same CNT-AFM probe (Figure 3 b)). As the tip has no acute cone shape, but MWCNTs ‘grass-like’ conformal coverage of the very same tip shape and 20-30 nm in diameter (average size of present Pd-based MWCNTs), the tip is not able to completely resolve inside the indentation hole, however, the rest of the image area is not significantly altered in terms of quality of resolution, in-plane (xy) nor vertical dimension (z). As it will be further demonstrated next, the durability of the tip apex in our CNT-AFM probes represents a truly advantage for the tip technology.

Similarly to the results presented in [18], one of the promising applications of CNT-functionalized tips is their potential suitability for measurements in contact, in particular, for force spectroscopy or electrical conductivity. In this case, the potential is a two-fold one, since CNT-probes can be applied to the determination of the sample substrate properties, or the study of very same CNT characteristics. Figure 4, a) shows a retraction force curve executed on mica, which is a standard hard substrate for analysis or calibration of cantilever elastic properties. The mechanical response is modulated (milder contact) due to the presence of the CNTs with respect to the one obtained for bare tip on same conditions. Particular adhesion interactions attributable to the CNT-interfacing are under study. In figure 4, b), an example of relatively high voltage electrical conduction measurement is presented (sample-tip approach). The simultaneous force/current data acquisition provides deeper insight on the events of mechanical and electrical contact: stable electrical current is established at very low loading forces of about 7 nN and not abruptly. In both cases, further measurements could go behind the measurement tests reported in the figures, thanks to the unaltered tip apex and the MWCNTs completely elastic deformation. More detailed communications about the performance of CNT-probes, specifically, for mechanical and electrical conduction properties will be soon published in [30].

![Figure 4](image)

**Figure 4.** a) Iterative retraction curves performed with CNT-probe on a mica substrate. Controlled RH is set to 5%, whereas forces related to tip-sample adhesion interaction are still observed. b) Simultaneous acquisition of approach force curve and electrical current at tip-sample bias 7 V, as a function of z, stable current is 200 nA. Establishment of correlation between mechanical and electrical contact can be studied (RH 35 %). Sampling substrate is Si covered by a thin Pt layer.

In summary, the present communication shows the complete and comprehensive description of integrated MWCNTs into AFM silicon probes. After a detailed description of the operational performance of the CNT-probes from the point of view of devices for dynamic mode AFM application, representative results of their actual use for different sensing modes is shown. A procedure for the quality control of the fabrication process has been established, enlightening some aspects of the CNT synthesis process and framing the technology robustness for its exploitation for probing. The utility of the CNT-probes is demonstrated for both contact and dynamic modes of operation, with outstanding force sensing sensitivity of (probably) any kind of interaction. By AFM, conducting, semiconducting or insulating materials can be investigated and further exploitation of the CNT-AFM probes is envisioned for phase imaging, electric modes (electric force microscopy, Kelvin probe force microscopy, magnetic force microscopy, etc), force spectroscopy, electrical conductivity...
measurements, surface manipulation or nanolithography. The durability of the tip apex represents remarkable robustness, combined with the convenient CNT elasticity, for probing all sorts of substrates (either hard or soft materials).

Acknowledgments
G. Rius is grateful for the granted financial support of Strategic Research Foundation Grant-aided project for Private Universities from MEXT, Japan. The funding for JST-Sentan Project: MultiProbe Microscopy System is also acknowledged.

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