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Ultrasensitive Mass Sensing with a Nanotube Electromechanical Resonator

B. Lassagne,† D. Garcia-Sanchez,† A. Aguasca,‡ and A. Bachtold*,†

CIN2(CSIC-ICN) Barcelona, campus UAB, E-08193 Bellaterra, Spain, and Universitat Politecnica de Catalunya, Barcelona, Spain

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ABSTRACT

Shrinking mechanical resonators to submicrometer dimensions (~100 nm) has tremendously improved capabilities in sensing applications. In this Letter, we go further in size reduction using a 1 nm diameter carbon nanotube as a mechanical resonator for mass sensing. The performances, which are tested by measuring the mass of evaporated chromium atoms, are exceptional. The mass responsivity is measured to be 11 Hz·yg^{-1} and the mass resolution is 25 zg at room temperature (1 yg = 10^{-24} g and 1 zg = 10^{-21} g). By cooling the nanotube down to 5 K in a cryostat, the signal for the detection of mechanical vibrations is improved and corresponds to a resolution of 1.4 zg.

Electromechanical resonators are a widely employed technology to detect tiny amounts of mass.[1−4] They are routinely used for monitoring deposition rates from evaporation sources and also for more specific applications, such as high-sensitivity detection of bacteria,[5] evaluation of hydrogen storage capacity,[6] measurement of the stoichiometry of surface compounds,[7] and monitoring of air pollution.[8] These applications have triggered an intense research endeavor aimed at scaling down electromechanical resonators and improving measurement schemes. Mass resolution down to ~7 zg has been achieved using microfabricated silicon resonators at 4.2 K.[4]

Even though the measurement techniques are rather challenging, the mass sensing principle remains simple. Electromechanical resonators can be described by harmonic oscillators with an effective mass m_{eff}, a spring constant k, and a mechanical resonance frequency

$$f_0 = \frac{1}{2\pi}\left(\frac{k}{m_{\mathrm{eff}}}\right)^{1/2}$$

Mass sensing consists of monitoring the shift δf_0 of f_0 induced by the adsorption onto the resonator of the atomic species to weigh. δf_0 is related to the deposited mass δm by[9]

$$\delta m = \frac{2m_{\mathrm{eff}}}{f_0}\delta f_0 \qquad (1)$$

The quantity $(2m_{\mathrm{eff}}/f_0)^{-1}$, defined as the mass responsivity $\mathscr{R}$, is an important parameter to evaluate the performance of a resonator for mass sensing. High $\mathscr{R}$ enables better sensitivity (see eq 1). Mass responsivity up to 1 Hz·zg $^{-1}$ has been previously measured.[4]

Carbon nanotubes are a material of choice to fabricate ultrasensitive mechanical resonators.[10−17] The mass of a nanotube is ultralow, typically a few attograms, so even a tiny amount of atoms deposited onto the nanotube makes up a significant fraction of the total mass. Nanotubes are also ultrarigid mechanically, which is a key material property to push up the resonance frequency. Low mass and high resonance frequency are expected to result in exceptional mass responsivity, but it has not been measured so far. Despite high expectations, the mass resolution δm_{min} that has been achieved up to now remains modest, on the order of attograms.[15,18] In this Letter, we report on mass sensing experiments in which chromium atoms are evaporated onto a nanotube resonator (Figure 1a). The measured mass responsivity and mass resolution are excellent; they surpass the values reported previously for resonators made of nanotubes and of any other material.

Nanomechanical nanotube resonators are fabricated by means of standard nanofabrication techniques. Single-wall carbon nanotubes are grown by chemical-vapor deposition on a highly doped Si substrate coated with a 1 μm thick SiO_2 layer.[19] Using electron-beam lithography, nanotubes are connected in a transistor geometry to two Cr/Au electrodes. Wet etching in buffered hydrofluoric acid is performed to suspend the tube. An annealing treatment at 400 K during 1 h in a flow of Ar and H_2 is carried out to remove impurities resist residues and other contaminants). Figure 1b shows a scanning electronic microscopy image of one device after the fabrication process.

The carbon nanotube resonator is actuated by means of electrostatic interaction. When a voltage V_g^{ac} oscillating at a frequency f is applied on the backgate of the wafer, an

* Corresponding author: adrian.bachtold@cnm.es.
† CIN2(CSIC-ICN).
‡ Universitat Politecnica de Catalunya.

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oscillating electrostatic force is generated on the nanotube at the same frequency

$$F_{el} = C_g' V_g^{dc} V_g^{ac} \cos(2\pi ft) \quad (2)$$

where C_g' is the derivative of the capacitance between the nanotube and the backgate and V_g^{dc} is the dc voltage applied on the gate.

The motion δz of the nanotube induced by F_{el} is detected via a capacitive technique. δz modulates C_g, and, in turn, it modulates the charge in the nanotube, $\delta Q = V_g^{dc}\delta C_g$. To track the high-frequency charge modulation, we employ a mixing technique[12] by applying $V_g^{ac}\cos(2\pi ft)$ on the gate and $V_{SD}\cos(2\pi ft + 2\pi\delta ft)$ on the source (Figure 2a). This results in a mixing current I_{mix} on the drain at δf, which reads

$$I_{mix} = \frac{1}{2} V_{SD} \frac{dG}{dV_g}\left[V_g^{ac}\cos(\alpha) + V_g^{dc}\frac{C_g'}{C_g}\delta z \cos(\theta_m - \alpha)\right] \quad (3)$$

where dG/dV_g is the transconductance of the nanotube, α is the phase coming from the electronic circuit, and θ_m is the phase between F_{el} and the mechanical motion. The first term in eq 3 has a purely electrical origin ($\delta Q = C_g V_g^{ac}$) and results in a background current observed at any actuation frequencies. The second term originates from the mechanical vibrations and is effective only when f matches f_0 for large oscillating motion. Figure 2b shows a color scale plot of I_{mix} as a function of the actuation frequency and of the dc gate voltage. Two mechanical resonances are observed. Their frequency increases with V_g^{dc} due to the enhancement of the mechanical tension—the static electrostatic force bends the nanotube.[12−14] The tuning of f_0 with V_g^{dc} ensures that the resonance has a mechanical origin and is not a simple electric resonance occurring in the circuit.

An important parameter of a harmonic oscillator is the quality factor Q, which quantifies energy dissipation. The motion depends on Q as

$$\delta z = \frac{1}{(2\pi)^2} \frac{F_{el}}{m_{eff}} \frac{1}{\sqrt{(f^2 - f_0^2)^2 + \frac{f^2 f_0^2}{Q^2}}} \quad (4)$$

Q is obtained by fitting eqs 3 and 4 to the shape of the resonance following the fitting procedure in refs 12 and 14 (Figure 2c). We have studied several nanotube resonators for which Q ranges from 50 to 200 at room temperature, in agreement with previous works.[12,14] Upon lowering the temperature down to 20 K, we find that Q increases up to 800−2000. The microscopic mechanism of dissipation is currently not understood. However the enhancement of Q is crucial for most electromechanical experiments, such as mass sensing, as it allows for a better sensitivity.

We now turn our attention to the mass sensing experiment. Cr atoms are deposited onto the nanotube resonator by joule heating of a Cr bar in a metal evaporator. We choose Cr because it has a high binding energy on the nanotube wall (see below). Figure 3a shows the shift in the mechanical resonance frequency each time ∼160 zg of Cr (∼1860 Cr atoms) is deposited onto the nanotube. The mass is determined as follows. The evaporation time for each step is 1.5 s, and the deposited area equals the diameter d multiplied by the length L of the nanotube ($d = 1.2$ nm and $L = 900$ nm). The evaporation rate is set to the lowest detectable value of the quartz crystal in the evaporator, which is ∼10 pm•s^{-1}.

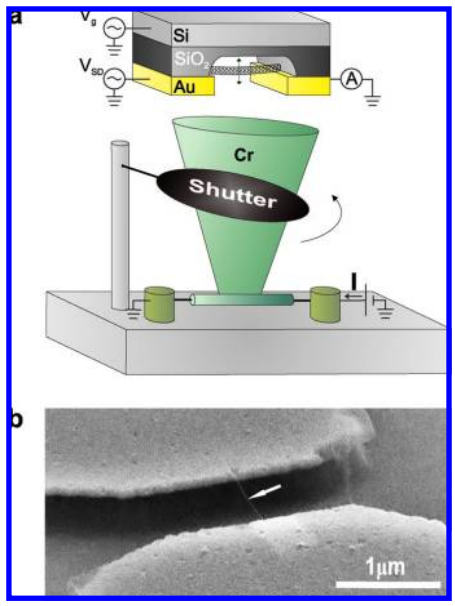

Figure 1. Experimental setup for mass sensing. (a) Schematic of the setup. Chromium atoms are deposited onto the nanotube resonator in a Joule evaporator and the mass of the atoms adsorbed on the nanotube is measured. (b) Scanning electron microscopy image of the nanotube resonator.

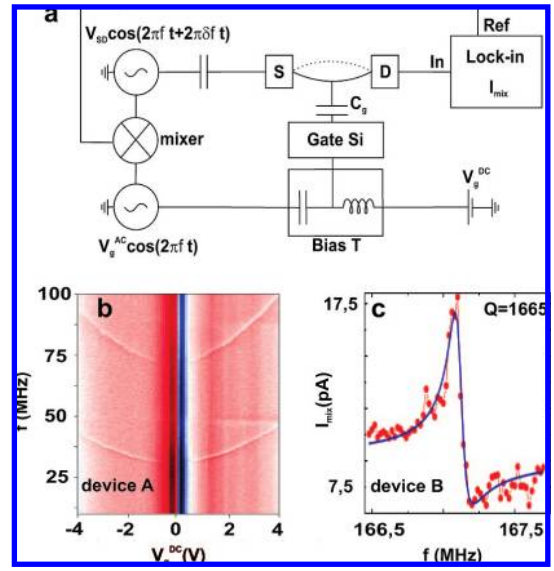

Figure 2. Diagram of the measurement circuitry and characteristics of nanotube resonators. (a) Diagram of the experimental setup. A voltage V_g^{ac} oscillating at frequency f is applied to the Si backgate to actuate the motion. The motion is detected using a mixing technique, which consists of applying an oscillating voltage V_{SD} at $f + \delta f$ on the source and measuring the current at δf from the drain. δf is 10 kHz, and the lock-in time constant is 100 ms. (b) Mixing current as a function of gate voltage and frequency at 300 K and ∼10^{-6} mbar. $V_{SD} = V_g^{ac} = 25$ mV. (c) Mixing current as a function of frequency for $V_g^{dc} = 2.2$ V and $V_{SD} = V_g^{ac} = 1$ mV at 20 K and ∼1 mbar. The resonance peak shape is fitted using eqs 3 and 4 (blue curve). Equations 3 and 4 can be written as $I_{mix} = A + B\cos(\theta_m - \alpha)/[(f^2 - f_0^2)^2 + f^2 f_0^2/Q^2]^{1/2}$ with $\theta_m = \arctan(ff_0/Q(f^2 - f_0^2))$. The parameter A corresponds to the background current signal, which is extracted from the experimental data far from the resonance. B, α, f_0, and Q are fitting parameters. The result does not depend on the starting value of the fitting parameters.

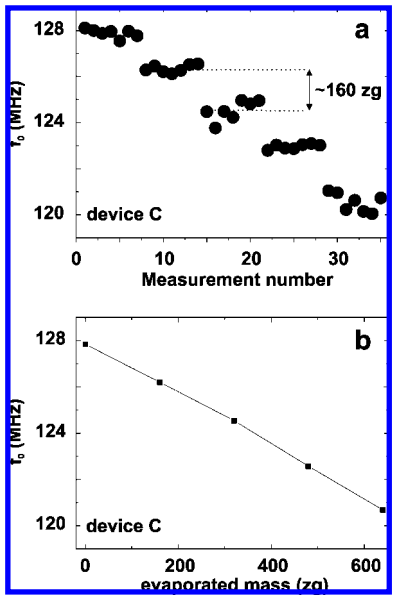

Figure 3. Mass sensing experiment. (a) Resonance frequency measured sequentially at 300 K and ~5 × 10^{-6} mbar. f_0 shifts down stepwise each time ~160 zg of chromium is evaporated onto the nanotube. f_0 is obtained by measuring I_{mix} as a function of frequency, such as in Figure 2c. The time between two points is 40 s except when chromium is evaporated (5 min). We notice that the resonance frequency does not drift in time between two evaporations, so it is not a thermal effect. (b) Resonance frequency as a function of the mass evaporated on the nanotube.

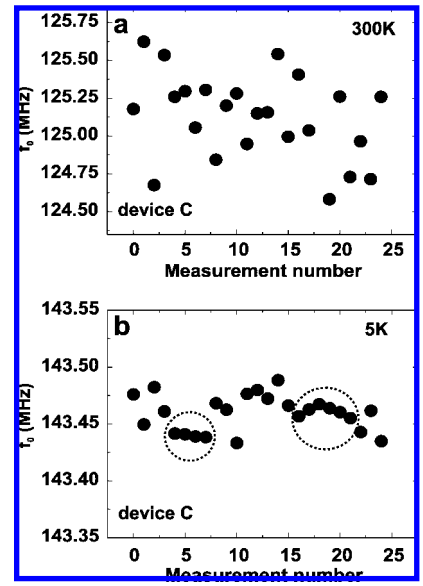

Figure 4. Mass resolution. (a) Resonance frequency measured sequentially at 300 K and ~5 × 10^{-6} mbar in the evaporator. Each f_0 is obtained in 40 s by measuring I_{mix} as a function of frequency, such as in Figure 2c. (b) Resonance frequency measured sequentially at 5 K and ~1 mbar in helium gas in a cryostat. We estimate the motion amplitude to be ~10 nm by comparing on- and off-resonance I_{mix} signals in conjunction with eq 3.[12] $V_g^{ac} = V_{SD} = 7.5$ mV and $V_g^{dc} = 6.8$ V. Notice that f_0 changes with temperature; we speculate that this is due to temperature-induced tension. Q is 865 at 5 K and 50 at 300 K.

The evaporation rate is calibrated by depositing Cr for 120 s onto a structure patterned in PMMA, which is placed at the same location as the nanotube resonator, and by measuring its thickness with an atomic force microscope (1.2 nm). Care is taken to control that the evaporation rate is constant (see Supporting Information).

Figure 3b shows the shift of the resonance frequency as a function of the deposited mass. The slope gives the mass responsivity, $\mathscr{R} = 11$ Hz·yg^{-1}. This is 4 orders of magnitude better than what has been previously reported.[4] This exceptional mass responsivity is attributed to the very low mass of nanotubes. For comparison, the reponsivity can be estimated using $\mathscr{R} = (2m_{eff}/f_0)^{-1}$ and assuming that the resonance corresponds to the fundamental eigenmode of a doubly clamped beam, $m_{eff} = 0.7m_{tube}$ (m_{tube} is the mass of the nanotube). We obtain $\mathscr{R} \simeq 33$ Hz·yg^{-1}, which is quite close to the experimental result. However, we emphasize that estimating the effective mass is tricky. Indeed, m_{eff} depends on the eigenmode, which is unknown,[16] and it can dramatically increase due the presence of contamination, which is extremely difficult to quantify. As a result, the direct measurement of $\mathscr{R}$ is a key point for a proper calibration in mass sensing experiments.

Having demonstrated the excellent properties of nanotube resonators for mass sensing (high $\mathscr{R}$ and high Q), we now look at the mass resolution, which can be obtained by measuring the fluctuations of the resonance frequency. The standard deviation of the resonance frequency $\sigma_{f_0} = \langle(f_0^i - \langle f_0\rangle)^2\rangle^{1/2}$ is 280 kHz (Figure 4a). By use of the above $\mathscr{R}$, this corresponds to a mass resolution of 25 zg. When the nanotube resonator is placed in a cryostat (without the possibility of evaporating a metal), σ_{f_0} is reduced to 15.7 kHz, which corresponds to a resultion of 1.4 zg or about 15 atoms of Cr (Figure 4b).

The mass resolution is likely to be limited by fluctuations in the electric readout circuitry. Indeed, the electrical conductance of nanotubes is known to be quite noisy due to the random motion of nearby charge fluctuators.[20] Figure 2c shows this effect on the mixing current. The fluctuations remain similar independent of the frequency. On the resonance peak, fluctuations of I_{mix} lead to fluctuations in the measurement of f_0 (see Supporting Information). This charge noise is a stochastic process involving multiple charge centers for which the motion can change f_0 to various extents. When the principal charge centers do not move, we can obtain time windows with reduced f_0 fluctuations. This behavior is observed in Figure 3a and 4b. Interestingly, the mass resolution corresponding to the first region indicated in Figure 4b is as low as ~0.1 zg, the mass of one Cr atom. More work will be carried out to reduce this charge noise further.

The mass responsivity and the mass resolution are obtained assuming that every evaporated Cr atom adsorbed onto the nanotube remains on it. Little has been reported on the subject, but the sticking coefficient may be below 1. A lower bound can be given by the sticking coefficient of Au on ultraclean graphite, which is $\gtrsim$0.1.[21] The sticking coefficient of Cr on nanotubes is expected to be significantly higher, because Cr is chemically more reactive than Au and because the adsorption energy is enhanced due to contamination on the surface and due to the nanotube curvature.[22] Overall, the

sticking coefficient may be somewhat below 1. In any case, this would improve the values found for $\mathscr{R}$ and $\delta m_{\min}$. $\mathscr{R}$ would be slightly higher and $\delta m_{\min}$ would be slightly lower.

Nanotube mass sensors have also the ability to be reset by removing the Cr atoms in situ. This process is accomplished by applying a few microamperes of current through the nanotube for several minutes. Adsorbed atoms get removed via heating and/or electromigration.[23−25] As a result, the resonance frequency is reset to its initial value, and the nanotube resonator is ready for new sensing measurements. This reinitialization process has been carried out several times without any loss in sensitivity.

To conclude, we have reported on ultrasensitive mass sensors based on a nanotube. The sensitivity is shown to be limited by the electric readout circuitry. Future work will be devoted to improving the measurement scheme in order to approach the ultimate mass resolution, which is given by the thermal fluctuations of the mechanical motion,

$$\langle z_{\mathrm{th}}{}^2 \rangle = \frac{k_{\mathrm{B}}T}{m_{\mathrm{eff}}(2\pi f_0)^2}$$

Using

$$\sigma_{f_0}{}^2 \simeq \frac{\langle z_{\mathrm{th}}{}^2 \rangle f_0}{z_0{}^2 \, Q} \frac{B}{2\pi}$$

(ref [9]) with $B = 10$ Hz, the measurement bandwidth, and z_0, the motion amplitude in Figure 4b, we obtain a mass resolution of $\sim$1 yg, the mass of about one neutron. Such a mass resolution would open new perspectives for mass spectrometry. It could be possible to weigh large molecules with subatomic precision, which is not possible by means of conventional techniques based, for example, on time of flight. Individual atoms or molecules could also be placed on the nanotube in order to probe the variation of their mass. Chemical reactions in organical or biological molecules could then be monitored in real time, as well as nuclear reactions in individual atoms. In addition, fast mass sensing could be achieved with a bandwidth $>f_0/Q \sim 100$ kHz using radio frequency detection techniques with, e.g., LC tanks.[26] Using methods to align nanotubes on substrates, researchers should be able to fabricate arrays of orientationally ordered resonators for parallel sensing.

After submission of our manuscript, a work was published showing mass sensing with atomic resolution using a nanotube resonator.[27] The detection of the mechanical vibrations is achieved by field emission. In contrast, our device is a nanotube field-effect transistor, a mature and versatile technology offering many possibilities for future applications.

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Supporting Information Available: Description of fluctuations of the mechanical resonance frequency and evaporation of chromium. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Lavrik, N. V.; Datskos, P. G. *Appl. Phys. Lett.* **2003**, *82*, 2697.
(2) Ekinci, K. L.; Huang, X. M. H.; Roukes, M. L. *Appl. Phys. Lett.* **2004**, *84*, 4469.
(3) Verd, J.; Uranga, A.; Abadal, G.; Teva, J.; Torres, F.; Pérez-Murano, F.; Fraxedas, J.; Esteve, J.; Barniol, N. *Appl. Phys. Lett.* **2007**, *91*, 013501.
(4) Yang, Y. T.; Callegari, C.; Feng, X. L.; Ekinci, K. L.; Roukes, M. L. *Nano Lett.* **2006**, *6*, 583.
(5) Ilic, B.; Czaplewski, D.; Neuzil, P.; Campagnolo, C.; Batt, C. *Appl. Phys. Lett.* **2000**, *77*, 450.
(6) Ono, T.; Li, X.; Miyashita, H.; Esashi, M. *Rev. Sci. Instrum.* **2003**, *74*, 1240.
(7) Narine, S. S.; Slavin, A. J. *J. Vac. Sci. Technol.* **1998**, *16*, 1857.
(8) Thundat, T.; Wachter, E. A.; Sharp, S. L.; Warmack, R. J. *Appl. Phys. Lett.* **1995**, *66*, 1695.
(9) Ekinci, K. L.; Yang, Y. T.; Roukes, M. L. *J. Appl. Phys.* **2004**, *95*, 2682.
(10) Reulet, B.; Kasumov, A.; Yu; Kociak, M.; Deblock, R.; Khodos, I. I.; Gorbatov, Yu. B.; Volkov, V. T.; Journet, C.; Bouchiat, H. *Phys. Rev. Lett.* **2000**, *85*, 2829.
(11) Purcell, S. T.; Vincent, P.; Journet, C.; Binh, V. T. *Phys. Rev. Lett.* **2002**, *89*, 276103.
(12) Sazonova, V.; Yaish, Y.; Üstünel, H.; Roundy, D.; Arias, T. A.; McEuen, P. L. *Nature* **2004**, *431*, 284.
(13) Üstünel, H.; Roundy, D.; Arias, A. T. *Nano Lett.* **2005**, *5*, 523.
(14) Witkamp, B.; Poot, M.; van der Zant, H. S. *Nano Lett.* **2006**, *6*, 2904.
(15) Peng, H. B.; Chang, C. W.; Aloni, S.; Yuzvinsky, T. D.; Zettl, A. *Phys. Rev. Lett.* **2006**, *97*, 087203.
(16) Garcia-Sanchez, D.; San Paulo, A.; Esplandiu, M. J.; Perez-Murano, F.; Forró, L.; Aguasca, A.; Bachtold, A. *Phys. Rev. Lett.* **2007**, *99*, 085501.
(17) Eriksson, A.; Lee, S.; Sourab, A. A.; Isacsson, A.; Kaunisto, R.; Kinaret, J. M.; Campbell, E. E. B. *Nano Lett.* **2008**, *8*, 1224.
(18) Poncharal, P.; Wang, Z. L.; Ugarte, D.; Heer, W. A. *Science* **1999**, *283*, 1513.
(19) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. *Nature* **1998**, *395*, 878.
(20) Tobias, D.; Ishigami, M.; Tselev, A.; Barbara, P.; Williams, E. D.; Lobb, C.; Fuhrer, M. S. *Phys. Rev. B* **2008**, *77*, 033407.
(21) Ganz, E.; Sattler, K.; Clarke, J. *Surf. Sci.* **1989**, *219*, 33.
(22) Zhang, Y.; Nathan, F. W.; Chen, R. J.; Dai, H. *Chem. Phys. Lett.* **2000**, *331*, 35.
(23) Moser, J.; Barreiro, A.; Bachtold, A. *Appl. Phys. Lett.* **2007**, *91*, 163513.
(24) Regan, B. C.; Aloni, S.; Ritchie, R. O.; Dahmen, U.; Zettl, A. *Nature* **2004**, *428*, 924.
(25) Chen, Y.-F.; Fuhrer, M. S. *Nano Lett.* **2006**, *6*, 2158.
(26) Schoelkopf, R. J.; Whalgren, P.; Kozhevnikov, A. A.; Delsing, P.; Prober, D. E. *Science* **1998**, *280* (5367), 1238.
(27) Jensen, K.; Kim, K.; Zettl, A. *Nat. Nanotechnol.* **2008**, *3*, 533.

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