Measuring the physical properties of nanostructures and nanowires by field emission

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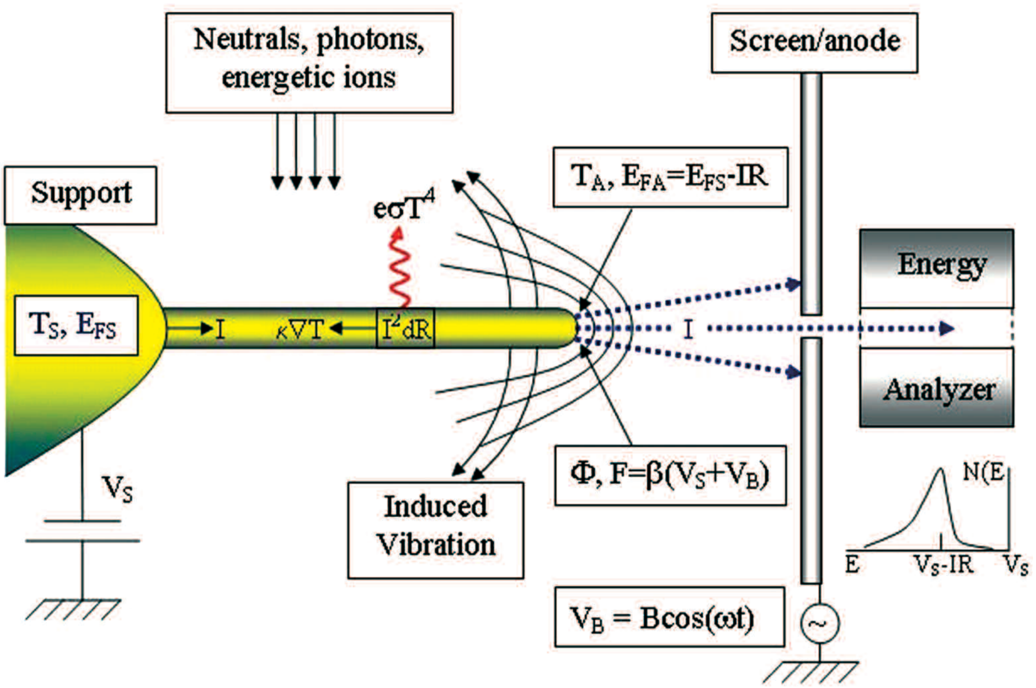
Question : what physical object is currently being investigated for its new possibilities in electronic components (FETs, wiring, memories, optoelectronics, lasers...), nanometric scale sensors (gas and fluid flow, temperature…), mechanical reinforcement (composites, textiles…), energy storage (hydrogen, rechargeable batteries…), near field probes (SNOM, AFM, STM …), electromechanical systems (oscillators, motors…), electron sources (flat screens, xray generators, rf amplifiers…), etc. and etc.? If you answered carbon nanotubes [1] or nanowires [2] or to be more general (N&Ns), pass to the front of the line. One should add that nanotubes have become an excellent testing ground for comparing fine experimental measurements to fundamental molecular dynamics and *ab initio* band-structure studies. This is because of the existence of interesting new phenomena at the nanometer scale, the number of atoms in the real system is tractable by available computing power and techniques have been developed to fabricate, manipulate and measure them individually. N&Ns enjoy a huge advantage over their cluster sisters in that they can be more readily connected to leads for thermal and electrical transport phenomena. The result of all this is that a wide cross–section of physicists, chemists and biologists has now devoted research programme to carbon nanotubes (CNTs), and with increasing vigour to nanowires.

This is a field where the links between basic science and applications are extremely strong and it is simply inconceivable to realise working devices without delving deeply into fundamental studies of these systems. Concretizing the possibilities will depend on understanding and mastering their specific geometrical structure and physical properties such as electrical resistivity, thermal conductivity, optical adsorption and emission, stiffness, surface reactivity, etc. for each application. Currently, independent, specific and often quite elaborate experiments are set up to study each of these properties separately while in fact they are actually strongly correlated, particularly through the important and pervasive role of defects. An important advance would be the development of measurement methods of the different properties on the same individual N&N, in the same experimental setup that would also allow control of temperature, manipulation of defects, controlled adsorption and overlayer deposition, etc. After this long introduction, the point of this article is that good old "field emission" (FE) [3], which is itself one of the leading applications areas for nanotubes, can satisfy this demand because it can give simultaneous access to many N&N properties.

To understand how, consider the classic field emission experiment for an N&N in Fig. 1. A large voltage V_S is applied between the support on which the N&N cathode is attached and an anode/screen. They can be readily attached to support tips by a variety of methods including gluing, capillarity, rubbing and direct growth and they need contact at only one end. The support tips themselves are mounted on tungsten heating loops that allow high temperature heat cleaning. The experiments are generally carried out in ultra high vacuum (UHV - 10^{-10} Torr) to minimise adsorption. When a high enough voltage is applied, a current is emitted from the N&N apex where a high electric field F is created because of the large aspect ratio (length(l)/apex radius(r)). From simple electrostatics $F \cong const \times (l/r) V_S$. This field emission current is due to electrons tunnelling through the surface barrier. The agreement between its predicted and measured current/voltage behaviour was one of the first proofs of quantum theory back in the late 1920's.

The emitted electrons are accelerated by the electric field against the screen/anode giving



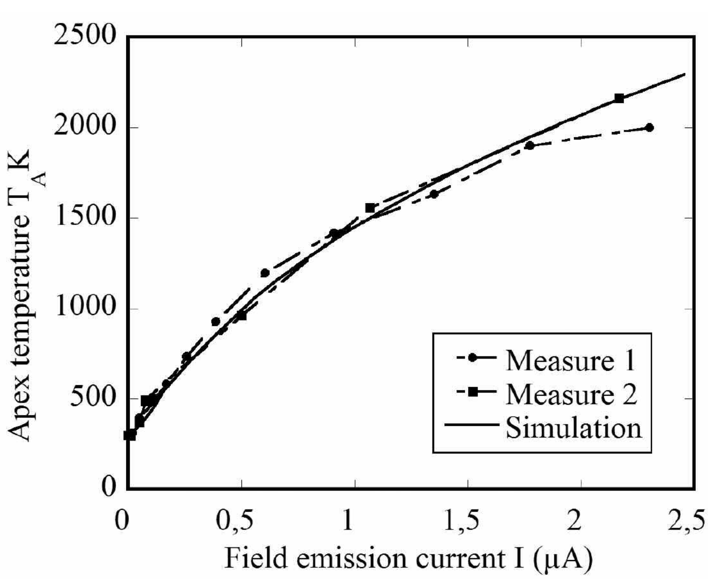
◄ **Fig. 1:** Schematic of the field emission experiment used to measure the physical properties of carbon nanotubes or nanowires.

Article available at http://www.europhysicsnews.org or http://dx.doi.org/10.1051/epn:2006407

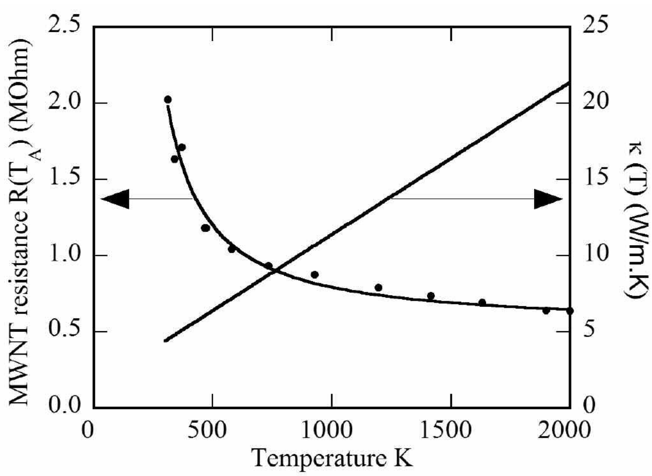
a sort of magnified image of the nanotube apex. This is called FE microscopy. Also the electrons can be projected into an energy analyzer giving rise to FE electron spectroscopy. These are traditionally used to study a tip apex surface – crystal structure, surface diffusion, work function, field enhancement factor and density of states near the Fermi energy. Such studies permit the development of FE cathodes. However, in principle the spectra can be fitted to give the voltage level at the end of the nanotube E_{FA} (Fermi level) and temperature T_A at the tip apex which may be different that those of the support because of a voltage drop IR and Joule heating along the N&N length [4, 5]. The positions of the spectra give directly $R = (E_{FS} - E_{FA})/I$. The high energy side of the spectra is given by the Fermi function and hence is fitted to give T_A.

The physical properties of most tip materials usually come into play only when an emitter is pushed to high currents where it suffers abrupt breakdown due to runaway phenomena linked to resistive heating and surface diffusion. E_{FA} and T_A are not different from the support E_{FS} and T_S because the voltage drop IR is too small to be detected (<μvolt) and if the tip temperature starts to rise the emitter proceeds immediately to breakdown through a catastrophic runaway.

The crucial difference for carbon nanotubes and the semi-conducting nanowires that we are also measuring is that they remain stable even when the current induces high temperatures. This is because of their excellent crystal stability and because the resistivity varies less or even decreases with temperature, in turn restraining runaway heating effects. Consequently large values of T_A and IR are readily created and measured. Temperatures of up to 2000 K [4] (see Fig. 2) and IR = 1.5 Volts have been measured in experiment for a CNT (Fig. 3). We have more recently measured up to 120 Volt for a SiC nanowire. The high temperatures in CNTs are accompanied by light emission visible by eye due to black body radiation whose wavelength dependence was also measured by optical spectroscopy [5, 6] (see Fig. 4). (For the inverse configuration we have recently installed an optical bench for light absorption where the field emitted current will vary and hence probe the optical absorption.)



▲ **Fig. 2:** Temperature at the nanotube apex against field emission current. The high temperatures are induced by Joule heating.

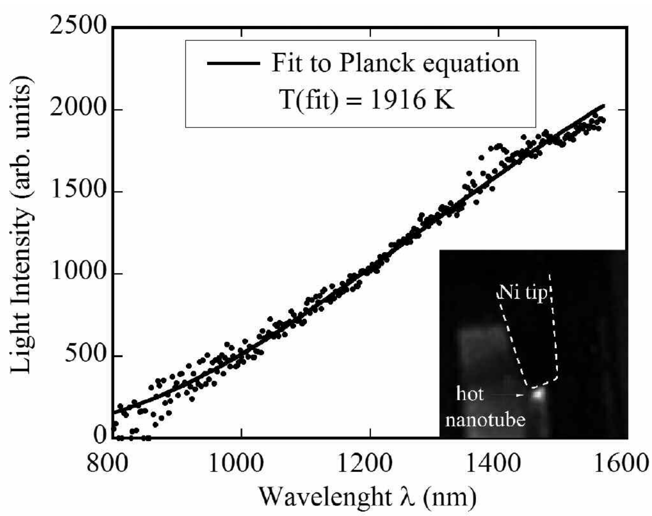


▲ **Fig. 3:** Measured total resistance of the nanotube $R(T_A)$ against apex temperature and the simulated thermal conductivity κ(T) against absolute temperature T, necessary for fitting the experimental curves in Fig. 2 and Fig. 3. ρ(T) is also found in the simulations and is very close to $(\pi r^2/l).R(T_A)$.

To extract the physical parameters from the measurements, simulations of the one dimensional heat transport problem have been carried out to fit the experimental curves which use as inputs the resistivity ρ(T), the thermal conductivity κ(T) and in principle the optical emissivity e(T) [6]. The main elements of the problem are depicted in Fig. 1 where Joule heating, thermal transport to the support and radiation cooling are taken into account. In Fig. 3 we include the rough first results for ρ(T) and κ(T) for our original measurements for CNTs [4, 7], assuming e(T)=1 which is a reasonable value for carbon. Better values must await more extensive measurements and an absolute calibration of the optical system. However it is the first time that the two parameters could be estimated for one nanotube. This can permit a correlation of the mean free paths of phonons and electrons that depend on structural quality of the nanotube.

Another property accessible in this same configuration is the mechanical stiffness or Young's Modulus E(T). This is found by simply applying a sinusoidal voltage to the support or the anode as depicted in Fig. 1 to excite the natural frequencies of the same N&N [8]. When correct frequencies are found the N&N vibrates and the emission pattern is enlarged and the current varies. The frequencies of these resonances give an excellent measure of the N&N stiffness. Actually many series of higher frequency resonances are found by this method (see Fig. 5 for a CNT) and the individual peaks are characterized by jumps and hysteresis. This is because of the non-linear driving of the nanotube in this arrangement. An added bonus in this experiment was that we found that the electric fields pull so strongly on the CNT that it allows a tuning of the resonance frequencies by up to a factor of ten times. Such electrical surface force tuning is a direct consequence of first-year physics principles and to the authors' knowledge had not been demonstrated before. It is unique to N&Ns because it scales with 1/r and is almost negligible for wires thicker than about a micron. It is not difficult to imagine that this tuning and the current variation during resonance are useful tools in future nano-electro-mechanical systems (NEMS) and in fact have already been put to use in several nano-oscillator devices [9, 10].

Now that one can quantify these various properties, it is interesting to study how they vary when an N&N undergoes modifications. In Fig. 1, we point out that many treatments in the



▲ **Fig. 4:** Optical spectrum of a carbon nanotube that heats during field emission.

UHV environment used for FE make it possible to modify these properties. One simple example is the variation of the frequencies of resonance as the nanotube adsorbs gas after a flash heating. We found that even for a large multiwall CNT, the variation of resonances could detect the adsorption of a hundredth of a monolayer of adsorbates. A second example is that we have recently found that SiC nanowires cleaned to high temperatures in UHV can have Q factors as high as 40,000. These two examples emphasize the obvious but often ignored fact that surfaces play a large role in the behaviour of N&Ns. The UHV environment of FE is ideal for studying this.

Before concluding, it must be admitted that this methodology has certain limitations. The apex must be cleaned to high temperature when one wants to avoid measuring adsorption effects and this often causes the loss of glued samples. Getting down to below 20 K is rare in FE studies where many interesting transport phenomenon could be explored. Because of the finite size of the spectra, it is difficult to measure voltage drops of less than about 20 meV and hence electrical resistances <20 kOhms. Separate electron microscopy is still necessary to understand the structure of the N&N. Experiments specific to each physical parameter probably give more reliable and precise results. However, the conclusion of this article is that the FE has two important advantages. Firstly, it is possible to have access to σ, κ, e and E for a single nanotube, or other nanowires, in a single experimental setup under the best UHV conditions and secondly to follow their evolution during any stage of a certain class of controlled modifications. These advantages should make it possible to better understand how the physical parameters are connected in an efficient manner and how they depend on the structural quality of the N&Ns. This should aid in controlling their values and to find new phenomena for future applications. ■

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Current main interests of the team: Nanotubes, nanowires, electron and ion field emission.

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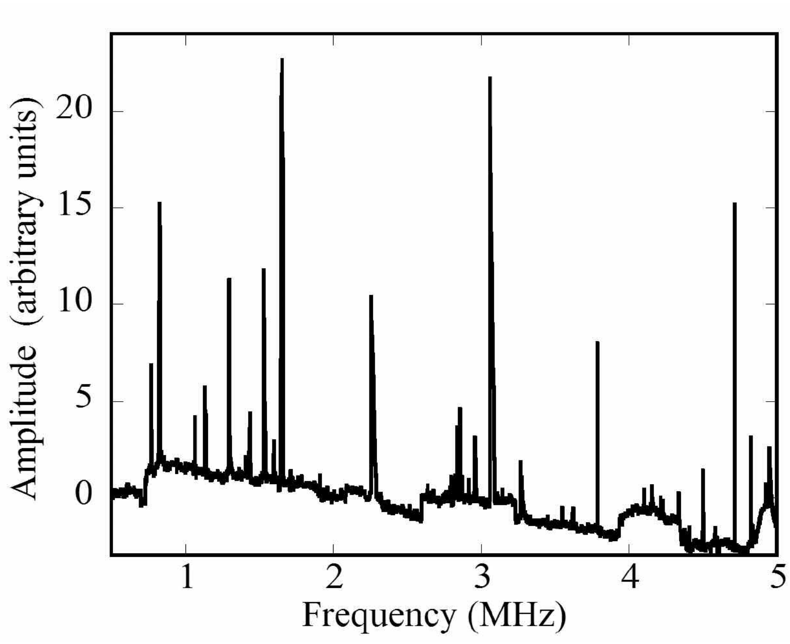

◀ **Fig. 5:** Scan of mechanical resonances of a nanotube in the field emission configuration. The curves are found by measuring the emitted field emission current which varies when the nanotube comes into resonance. The resonances continue to at least to 20 MHz.