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Mechanics of multi walled carbon nanotubes probed by AFM

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Abstract

Using the AFM tip, nanotubes are caught on a raw sample then deposited on a clean surface with an absolute precision better than 500nm. A nanostructured surface made of smooth Germanium dots on flat silicon was used as deposition sample. Nanotube mechanics is probed by AFM tip induced displacement. Nanotubes are shown to be blocked by Ge dots: it is impossible to induce a controlled displacement of the nanotube over a Ge dot when it is pushed against the dot. Elastic energy due to the bending of the nanotube is at the root of that behavior.

Introduction

Carbon nanotubes (CNT) are cylindrical carbon based molecules [1]. Due to their interesting electronic and mechanic properties, they are thought to be key element in nanotechnologies [2-3]. Atomic Force Microscope (AFM) nanomanipulation has already been used to study their mechanical properties [4-6]. Interaction of nanotubes with a nanostructured surface in term of adhesion and friction is reported elsewhere [7-8]. Understanding relevant mechanisms that control movement of nano-objects on a surface is a central issue for further development in the manipulation of biological objects, in developing micro-systems, or in molecular electronics. In this paper, we will focus on the impossibility to induce a continuous displacement of one CNT over one Ge dot by strongly pushing it against the dot.

Experimental

Thin layer of carbon nanotubes (or nanotube carpets) are grown by Hot Filament Chemical Vapor Deposition [9]. AFM and Scanning Electron Microscopy (SEM) experiments show that these carpets are made of entangled nanotubes whose length varies from hundreds of nanometers to several microns. Transmission Electron Microscopy (TEM) experiments show that the nanotubes are multi-walled with a typical diameter of 20 nm. AFM experiments have been performed in air condition at room temperature with a commercial instrument [10]. We used standard Si₃N₄ tips with apex radius of curvature and deflection spring constant respectively given to be around 30nm and 0.06 N.m⁻¹. No attempt was done to check these values. It is however not relevant for the purpose of this paper. Nanostructured surface we used to study the
AFM tip induced displacement of nanotubes are made of Ge dots grown by Molecular Beam Epitaxy (MBE) on oxidized silicon wafer [11]. Ge dots have a spherical cap shape, 50nm in height, 500nm in width, with no significant size distribution. Silicon wafer roughness is well-below nanometer scale. CNT movement is induced by lateral force applied via the AFM tip. In this paper, applied forces are compared in term of load forces. However, we have experimentally checked that, in the force range we explored, lateral forces vary linearly with load.

Results and discussion

As already pointed out, it is possible to catch nanotubes with the AFM tip by performing force curves on nanotube carpets [12]. Once caught, nanotubes can be deposited on a clean and flat Si wafer as a consequence of friction between the tip and the surface while imaging the deposition sample. Deposition process steps are the following: i) choosing a deposition area on the deposition sample (AFM images) ii) catching nanotubes on the raw sample and iii) deposit nanotubes on the deposition sample. Fig 1a is an AFM image of the deposition area before the nanotube deposition. Ge dots (numbered from 1 to 5) define a recognizable landscape. Black cross indicates the exact position where nanotubes are supposed to be deposited. To catch nanotubes with the tip on the nanotube carpet one has to move the tip more than 1 cm away from the chosen deposition area. However, using the AFM XY stage ability to reproduced defined tip displacements, deposition area can be find again after nanotube catching with an precision better than 500nm. Fig 1b is a AFM image of the deposition area after the nanotube deposition. It is clearly the same area as shown of fig 1a since we find again the recognizable landscape defined by the 5 numbered Ge dots. As we can see, the precision achieved is better than 500nm. Using this method, a limited number of nanotubes (usually between 5 an 20) are deposited. In general, deposited nanotubes form ropes. However, it is possible to isolate them into individual nanotubes by strongly press and move the tip against the rope. Thanks to the connected optical system and XY stage, we can change the tip and find again the deposited nanotubes (nano-objects) on the deposition sample (several cm²). Fig 1b AFM image has been recorded with a new tip (tapping mode). That allows one to use all the AFM operating modes and to work with a clean tip.

![AFM images of the deposition area (a) in contact mode before CNT deposition and (b) in tapping mode after CNT deposition. (b inset) blow up of the deposited nanotubes.](image-url)
Deposited nanotubes have further been manipulated with the AFM tip to be placed in contact with Ge dots (see fig 2). By pushing the nanotube against the dot with the tip (with the applied force (1) schematically represented on fig 2a), it is impossible to continuously make it climb over the dot. What happen in such a try is that the nanotube surface contact suddenly breaks and that the nanotube goes away in a totally uncontrolled process (to do that, we have to exert normal forces larger than 100nN). To understand the behavior of nanotubes when they are slowly moved under the force applied by the tip, relevant parameters are nanotube surface friction and elastic forces due to the nanotube bending and/or stretching. We have already shown that friction measured on Ge dots and Silicon wafer is equivalent [7-8]. We have never observed nanotubes with partial sticking to the surface. Then, if we want the nanotube to lie over the dot, it has to follow its profile. In a continuous approximation, we can then estimate the elastic work needed to deform the nanotube [13]:

\[ U = \frac{E I}{2} \int \left( \frac{1}{R} - \frac{1}{R_0} \right)^2 dz \]  

(equ. 1)

where \( E \) is the Young modulus of the nanotube, \( I \) its moment of inertia with respect to its section, \( R_0 \) its radius of curvature at rest and \( R \) the local radius of curvature of the bent nanotube. Applying equ 2 to the CNT [14] leads to an elastic energy \( U \) equals to \( 3 \times 10^{-15} \) J. By equalizing \( U \) to the tip displacement work [15], the lateral force that must be applied to the CNT to follow the dot profile can be calculated to be around 60 nN. For this calculation, neither energy dissipation due to friction nor increased adhesion when the nanotube lies at the border of one dot [7-8] has been considered. Finally, the lateral force that must be applied to the nanotube for it to lie over the dot is much larger than 60 nN. By applying the force (2) on the nanotube (see fig 2a), the nanotube bent around the Ge dot, but once again, it does not climb over it.

If the nanotube ends on the dot, controlled displacement of it over the dot (see fig 3) becomes possible. AFM images (a) and (b) of fig 3 show a CNT pinned between two Ge dots before and after its manipulation. Figures 3 (c) and (d) represent height signal measured in two
opposite directions while nanotube moves (recorded on a nanotube in the same position as the one on fig 3a and b). As we can see, for a load force of about 16.5 nN, signals are perfectly superposed whatever is the scan direction (left to right or right to left). By increasing the load force up to about 24.4 nN, height signals are not superposed anymore (see fig 3d). The nanotube moves under the force applied by the tip and continuously climb over the dot. In that case, the same calculation as the one done above leads to lateral force of about 12 nN (the only change in the calculation is the distance z along which the nanotube is bent and that has been estimated to be around 100 nm). Moreover, increased adhesion when nanotube lies at the border of one dot effect [7-8] is less important than in the case of fig 2 since nanotube dot contact length is shorter.

Conclusion
An experimental method used to deposit CNT with an absolute precision better than 500 nm has been reported. It allows one to deposit a limited number of CNT at a determined place without using wet chemistry (as solvent). Manipulation using the AFM tip of the deposited CNT on a nanostructured surface reveals that CNT can be blocked by Ge dots depending on the nanotube length that has to deform. Calculation done using a very simple model shows that it is a direct consequence of the CNT elastic energy bending due to their bending. These experimental results, obtained for well characterized nanostructured surface and CNT, could be used for more precise simulation of the mechanical and tribological behavior of nanotubes.

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References

[10] Digital Instrument, Inc., 6780 Cortone Drive, Santa Barbara, CA 93117
[14] $I = \pi (D_2 - D_1)^4 / 64$ where $D_2$ and $D_1$ are respectively the external and internal diameter of the CNT estimated from TEM measurement to be around 25nm and 10nm. We used $E = 1$TPa and $R_0 = \infty$. $R$, the local radius of curvature of the bent CNT is chosen to be constant and equal to 675 nm (that is the radius of curvature of a Ge dot). The distance $z$ along which the nanotube is bent is calculated to be around 515 nm.
[15] $U = F_{\text{lat}} \times d$. $F_{\text{lat}}$ is the lateral force and $d$ is the displacement of the tip (equal to 50nm, the height of the dot).