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Nanomanipulation by atomic force microscopy of carbon nanotubes on a nanostructured surface

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We have investigated atomic force microscopy (AFM) induced displacement of carbon nanotubes (CNT) on a nanostructured surface. Evidence is given that nano-dots act as pinning centers for CNT. We show that adhesion between nano-objects and mechanical properties of nanotubes are the basic mechanisms that control the interaction of mobile and deformable nano-objects with static nano-dots under the mechanical constraint applied by the AFM tip.

Keywords: Atomic force microscopy; Carbon; Adhesion; Physical adsorption; Sticking; Tribology

1. Introduction

Single-walled carbon nanotubes (CNT) are made of one graphite sheet wrapped into a cylinder while multi-walled ones are concentric shells of these sheets [1,2]. Using the tip of an atomic force microscope (AFM) as a tiny plow, manipulation of CNT has been used to study their tribological

and mechanical [3–6] or electrical [7,8] properties. Detailed understanding of the relevant mechanisms that control the movement of nano-objects on a surface (e.g. adhesion or friction) is indeed a central issue for further development in the manipulation of biological objects or in molecular electronics. Description of object movements based on classical friction and contact laws, absence of intrinsic adhesion, gravity or inertia become new fields of research when transferred at the nanometer scale. A drastic consequence of the scale reduction is the change in relevant interactions. As pointed out by Persson [9], Van der Waals interaction gradually overcomes gravity below a typical size of about 1 μm . Inertia is no

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more a relevant parameter as friction overdamps all movements at the surface. Friction and adhesion at the nanometer scale are not simply determined by macroscopic scale laws [9–12]. Energy dissipation in elementary excitations is experimentally addressed [13–16].

CNT exhibit specific mechanical properties. As an example, their original shape can be reversibly recovered after repeated large bending [17,18]. Moreover, their friction behavior when moved on a surface remains an open question since they exhibit continuous contact with surfaces (i.e. apparent and real contact areas are the same). When CNT are moved on a surface, all the aforementioned mechanisms combine to determine their behavior. Using the AFM tip, we have moved CNT on a nanostructured surface made of germanium (Ge) dots on an oxidized silicon substrate. Ge dots are shown to block CNT (though strongly pushed against dot, CNT does not climb over it) and to act as pinning centers for CNT (we have to exert a large force to push the CNT away from the dot). On the contrary, CNT are extremely mobile on the flat silicon surface. These main results are discussed in this paper giving a better understanding of the basic mechanisms that govern the manipulation of objects at the nanometer scale.

2. Experimental

Carpets of CNT have been produced by hot filament chemical vapor deposition (HFCVD) technique. The experimental setup, originally built for diamond film synthesis [19], is now used for carbon nanostructures synthesis [20,21]. Transmission electron microscopy (TEM) and Raman spectroscopy experiments show that CNTs are multi-walled with a typical diameter of 20 nm are structurally good. Their length, measured by scanning electron microscopy (SEM) and AFM, can be as long as a few micrometers. Using the AFM tip as a nanofishing rod, we can catch CNT on the raw sample and deposit them on a clean surface with an absolute precision on about 500 nm [22,23]. We can also change the tip after the deposition process and find again the deposited nanotubes. That allows one to be sure to work

with a clean (non-contaminated by CNT) tip and to be able to use all the AFM operating modes.

Experiments have been performed using a Digital Dimension 3100 AFM in air and dry nitrogen condition at room temperature and on baked samples (100 °C during 1 h in dry atmosphere). We used Si_3N_4 contact tips with radius of curvature at the apex and deflection spring constant given to be around 20 nm and 0.06 N m^{-1} respectively. No attempt has been done to check these values. It is however not relevant for the purpose of this paper. Experimentally, the parameter that we control for the displacement of nano-objects is the load force (normal force that is exerted by the AFM tip on the surface and deduced from force curve measurements). However, nano-object displacement is caused by the lateral force (force in the plane of the surface that is used to push the nano-objects). We experimentally checked that, in the range we explored, the lateral force varies linearly with the load force. Then, comparing load forces is equivalent to compare lateral forces.

The nanostructured surface is composed of Ge dots grown by Molecular Beam Epitaxy on a heated silicon wafer covered by a very thin silicon oxide layer [24]. The dots have a spherical cap shape, about 500 nm wide and 50 nm high, with no significant size distribution. The typical distance between randomly distributed dots is about 500 nm. Silicon wafer roughness is well below the nanometer scale. This nanostructured surface then represents a model system where a very flat silicon area surrounds smooth germanium dots. Using the AFM tip, CNT have been deposited in the vicinity of these dots. Then, with a new tip, they have been manipulated in order to study their interaction with the Ge dots.

3. Results and discussion

Major results presented in this paper are shown in the AFM images of Fig. 1. The CNT has been previously manipulated with the tip to be placed exactly in this position. First, Ge dots act as pinning centers for CNT since the CNT is not pushed away from dots A and B under the constraint

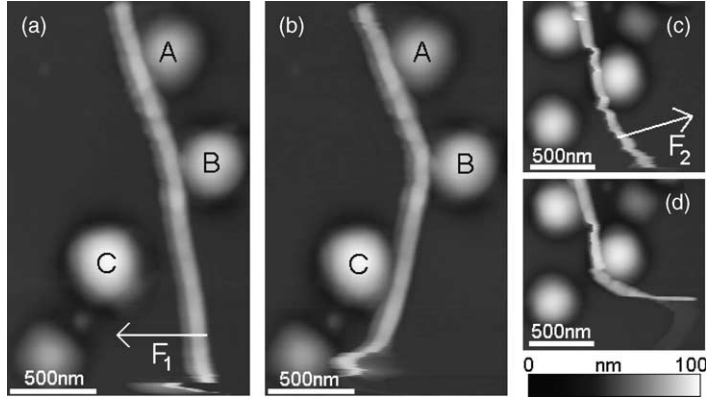


Fig. 1. Contact mode AFM images of a nanotube deposited on the nanostructured surface recorded with a load force of 34 nN (a) before and (b) after the CNT displacement induced by the tip. The load force F_1 used to move the nanotube is equal to 54 nN. (c) Initial configuration of one CNT pinned to Ge dots and (d) its configuration after displacement both recorded with a load force of 30 nN. Load force F_2 used to move the CNT is equal to 45 nN.

applied by the scanning tip (Fig. 1a and b). On the contrary, when deposited on flat surfaces (mica or silicon), CNT are easily moved while imaging, so that images in contact mode are almost impossible to obtain. The blurring CNT bottom end in Fig. 1a and b reveals that the CNT is moved at its free end (i.e. its part that is not in contact with a Ge dot) while imaged. The pinning center phenomenon is made evident by the curvature of the CNT at dot B in Fig. 1b. The Force F_1 (shown in Fig. 1a) has been applied to the nanotube in order to push it away from dot B. Rather than (i) staying in its initial straight position and pivoting on dot A or (ii) rolling or sliding on the surface, the CNT is bent at dot B. This bending is due to a force that acts against a straightening force. CNT adhesion force on dot C is large enough to counterbalance the elastic force due to its deformation (using tapping mode, we have already seen CNT on a flat surface snapping back to their straight rest position under their own elastic force after their manipulation). Once pinned on dot C, it is possible to push the CNT away from it. However, the force that must be applied to the CNT (in the opposite direction to F_1) is much more greater than F_1 .

To understand the pinning center phenomenon, we have to consider the forces that can pin a CNT to a Ge dot. In these experimental conditions, all present surfaces are chemically inert. Experimental observations remain the same in air and in con-

trolled dry nitrogen condition, the sample been baked or not. Relevant parameters to understand the static behavior of CNT are their elastic forces and their interactions with the nanostructured surface, which are here dominated by Van der Waals interactions (we experimentally checked by electrostatic force measurements (EFM) that there was no specific electrostatic contribution from the Ge dots with respect to the substrate). Force curve mapping measurements performed on a CNT pinned to two Ge dots is shown in Fig. 2. In Fig. 2a, the CNT appears darker than the Ge dots or silicon wafer (compare also the jump off contact on individual force curves of Fig. 2c). This lower adherence force behavior is discussed elsewhere [25]. We notice that adherence force is the same for Ge dots and silicon wafer. There is a large increase of the adherence force measured when the tip is at the border of either a Ge dot or the CNT. These results are the same whatever the experimental conditions (air or dry nitrogen atmosphere, the sample being baked or not). That increase in adherence force is due to the particular tip geometry with respect to the one of the nano-objects (CNT or Ge dot). For CNT and Ge dots, the tip radius of curvature is such that when the tip is at their border, it is in contact both with the substrate and the nano-object. Then, in a Van der Waals scheme, atoms of both the nano-object and the substrate contribute to the adhesion. Notice that the

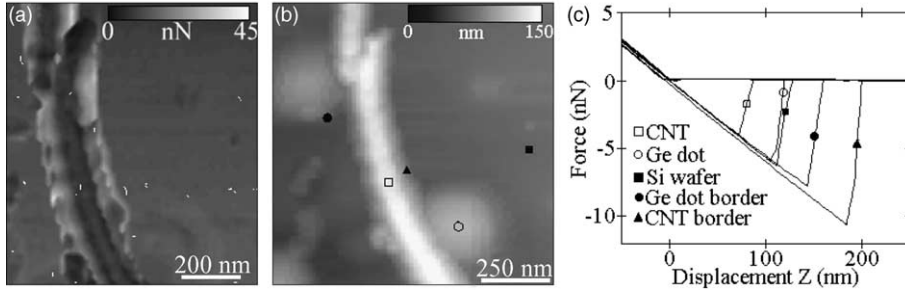


Fig. 2. (a) Adherence force mapping measured on one CNT pinned to two Ge dots, (b) corresponding height image. (c) Individual force curves used to construct the image (a) measured at specific locations indicated on (b).

tip-CNT border adherence force is greater than the tip-dot border one (see Fig. 2c). This behavior is expected since, considering the geometry of the tip with respect to the one of the Ge dot or CNT, tip-CNT contact area (then adherence force) is greater than tip-dot one when the tip lies at the CNT or dot border respectively. If the CNT lies at the border of one Ge dot, it interacts both with the dot and the substrate. That results in an increase of its interaction force with the sample, as it is the case for the tip whose diameter is comparable. Pinning center phenomenon is due to the increase of Van der Waals interaction when the CNT lies at the border of one dot.

Second, CNT is blocked by Ge dot. If the force F_2 is applied via the AFM tip on the CNT (Fig. 1c), the CNT does not climb on the Ge dot but bends around it (Fig. 1d). Anywhere the force is applied to the CNT, it is impossible to continuously push it over a dot. Within such an attempt it appears that (i) the CNT bends around the dot (see Fig. 1d) or (ii) the CNT goes away in a totally uncontrolled process. At the nanometer scale, no potential energy has to be considered. Higher friction on dot than on silicon could prevent CNT to be pushed on dots. However, friction measurements in air or dry nitrogen condition show that the friction on Ge dots is equivalent to the one on the silicon wafer. When lying on one dot, CNT is bent which leads to the increase of its elastic energy. Considering the geometry of one dot (50 nm in height, 500 nm in diameter), the CNT bending (i.e. the CNT elastic force) is higher if the CNT is bent around the dot (Fig. 1d) than if it lies over the dot. Then the CNT should prefer to lie over the

dot rather than to be bent around it. Moreover, the number of neighboring atoms is much higher if the CNT is bent around the dot rather than lying on it, thus leading to a strong increase of the CNT-sample adhesion force. As for the pinning center phenomenon, Van der Waals interaction is at the root of the blocking of CNT by Ge dots.

We can estimate both the elastic and adherence forces, when the CNT is bent around the dot. In a continuous medium frame, the elastic energy of a deflected beam can be roughly estimated [26]:

$$U_{\text{elastic}} = \frac{EI}{2} \int \left(\frac{1}{R(z)} - \frac{1}{R_0} \right)^2 dz \quad (1)$$

where E is the Young modulus of the beam, I its quadratic momentum with respect to its section, R_0 its radius of curvature at rest and $R(z)$ the local radius of curvature of the bent beam. Applying Eq. (1) to the CNT² leads to an elastic energy U_{elastic} equals to 3×10^{-13} J. The bending energy of a CNT in contact with a silicon wafer, that characterizes the interaction energy due to Van der Waals force, varies as [27]:

$$E_{\text{Bending}}(\text{eV}) = (0.086 \times d - 0.053) \times L \quad (2)$$

² $I = \pi(D_2 - D_1)^4/64$ where D_2 and D_1 are respectively the external and internal diameter of the CNT estimated from TEM measurements to be around 25 and 10 nm. We used $E = 600$ Gpa (mean value measured in Ref. [4]) and $R_0 = \infty$. R , the local radius of curvature of the bent CNT is chosen to be constant and equal to 250 nm (that is the dot radius). Z , the distance along which the nanotube is bent is measured to be around 520 nm (1/3 of the dot perimeter).

where d is the CNT diameter and L its length (both in Å). Applying Eq. (2) to the case of the CNT of Fig. 1d ($d = 25$ nm, $L = 5$ μm), we find $E_{\text{Bending}} = 1.7 \times 10^{-13}$ J. The CNT elastic and bending energies are of the same order of magnitude. However, in the calculation of the bending energy, the contribution of the Ge dots to which the CNT is pinned has not been considered. The CNT bending energy is then higher than 1.7×10^{-13} J. These simple calculations show that the adhesion force due to Van der Waals interaction is large enough to counterbalance the CNT elastic force.

Fig. 3a and b show two configurations of a CNT pinned to two Ge dots. When manipulated with the tip, the CNT has two equilibrium positions. For both of them, it lies at the border of the dots (we did not manage to position the CNT over the dot). Changing the load force allows one to switch the CNT from one configuration to the other one. In Fig. 3c, trace and retrace height profiles are perfectly superposed: for a load force of about 16 nN, the CNT is not moved. On the contrary, the CNT switches from one side to the other side of the dot if the load force is increased to about 25 nN (see Fig. 3d). Lying on the dot or being bent around it is equivalent for the CNT of Fig. 3 in term of elastic energy. In term of adher-

ence, it is of course better for the CNT to lie at the border of the dot. This measurement is very consistent with our analysis of the increase of Van der Waals interaction when a CNT lies at the border of one dot.

4. Conclusion

Ge dots are shown to act as strong pinning centers for CNT. They also block CNT when pushed by the AFM tip. These two phenomena originate from the increase of the adhesion force when the CNT is at the border of a Ge dot. In a Van der Waals scheme, that effect is due to an increase of the number of neighboring atoms that contribute to the CNT-sample interaction. Our measurements provide direct evidence that nano-dots dramatically affect the CNT displacement over a surface. These observations have been rationalized using a continuum description and a macroscopic model of elastic deformation. This model, extended to nano-objects, has been shown to provide useful orders of magnitude that are directly comparable to the one provided by Van der Waals interaction forces. In the framework of molecular electronics, these measurements

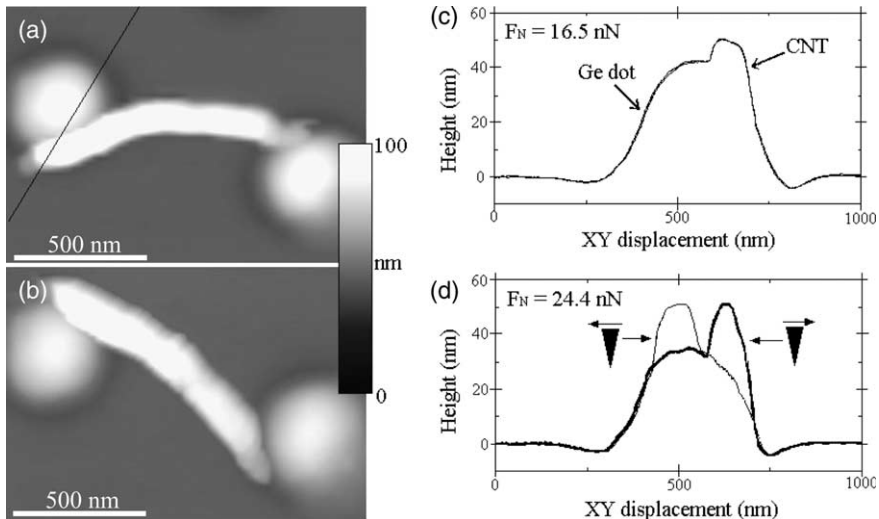


Fig. 3. (a) and (b) Contact mode AFM images of a CNT that switches from one side of a Ge dot to the other. (c) Trace and (d) retrace height profiles of the dot and the nanotube (measured along the line indicated on (a)) recorded with load forces respectively equal to 16.5 and 24.4 nN.

describe the stability of artificial 2D configuration in the absence of glue due to chemical interaction. This is such an effect that has been used to position single wall nanotubes before conductance experiments related to the detailed nanotube shape [28].

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