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## Thickness and low-temperature conductivity of DNA molecules

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We argue that interaction between molecules and substrate is a key parameter which determines the conducting or insulating behavior of DNA molecules. In this letter, we show that strongly deformed DNA molecules deposited on a substrate, whose thickness is less than half the native thickness of the molecule, are insulating, whereas molecules keeping their native thickness are conducting down to very low temperature with a non-ohmic behavior characteristic of a 1D conductor with repulsive electron–electron interactions. © 2004 American Institute of Physics. [DOI: 10.1063/1.1644909]

Conductor or insulator? The debate about the conductivity of DNA have been recently revived due to contradictory results of transport measurements on a small number of molecules deposited on a substrate and connected to metallic electrodes, and an answer to this question is important for DNA based molecular electronics. In several works it was observed that double-stranded (ds) DNA molecules are conducting (either metallic or semiconducting).<sup>1–6</sup> However in other works<sup>7</sup> DNA was found to be insulating, even when the molecules had perfectly ordered base pairs.

In this letter we emphasize the importance of the interaction of the molecules with the underlying substrate. For most commonly used substrates like mica or silicon oxide the interaction between the molecule and the surface is very strong and induces a very large compression deformation of deposited DNAs. The thickness of such compressed DNAs is 2–4 times less than the diameter (about 2 nm) of native Watson-Crick B-DNA.<sup>7</sup> Here we confirm the insulating character of DNA on such substrates. On the other hand when the substrate is treated (functionalized) so that deposited molecules keep their original thickness, we find that they are conductors, both from conducting AFM and transport measurements on molecules connected to platinum electrodes. This conductivity persists down to very low temperature (0.1 K) where it exhibits a non-ohmic behavior with a power law singularity in the bias dependence of the differential resistance typical of one-dimensional conductors with Coulomb interactions between electrical carriers.

$\lambda$  DNA molecules were deposited on mica substrates partially covered by a Pt film with thickness of 3 nm.<sup>8</sup> Using an AFM microscope operating both in standard and spreading resistance (SRM) modes<sup>9</sup> it was possible to measure simultaneously the height and conductivity of the same mol-

ecules, crossing the edge of the Pt film. In the SRM, the conducting tip of the AFM is pressed on the molecule, and the current which goes through the tip-DNA junction is recorded for a given voltage difference. In the absence of any treatment of the mica+Pt substrate we measure a typical height of the DNAs of about 1 nm and no contrast in the SRM mode indicating insulating molecules in agreement with previous observations [Figs. 1(a) and 1(b)]. In contrast, very different results are obtained if prior to deposition of molecules, a thin (about 0.5 nm) layer of discontinuous polymer film is sputtered on the surface of both Pt and mica by glow discharge of pentylamine vapor, as was done in our previous experiments.<sup>4</sup> This film is mainly constituted of ionized  $\text{NH}_3^+$  molecules on which the negative phosphate groups of the DNA molecules get attached. The thickness of observed DNA molecules was then measured to be of the order of 2 nm and they were clearly visible in SRM [Figs. 1(c) and 1(d)], indicating a conducting behavior.

We interpret these results in the following way: the deposition of the polymer film decreases hydrophilicity of mica and thus its interaction with DNAs. The average thickness of DNA molecules on the substrates treated by pentylamine is 2.4 nm (with a dispersion of 0.5 nm for 64 measurements on different molecules) this value is very close to the native thickness. For DNAs on the clean substrate the thickness is 1.1 nm (with a dispersion of 0.2 nm for 57 measurements). Careful studies in AFM have shown that the hugely reduced thickness of DNAs on clean mica and silicon substrates is indeed a real effect and not an artifact of microscopy.<sup>10</sup> We have additionally confirmed the reduced thickness by transmission electron microscopy replica method without use of AFM (Fig. 2). Concerning SRM measurements, DNAs on the clean untreated surface have the same contrast as mica, which indicates that they are insulators. On the Pt surface some of DNAs are seen in negative contrast [Fig. 1(b)]. Such a contrast was already observed by scanning tunneling microscopy (STM) and interpreted as proof of the insulating behavior of DNAs.<sup>11</sup> In contrast,

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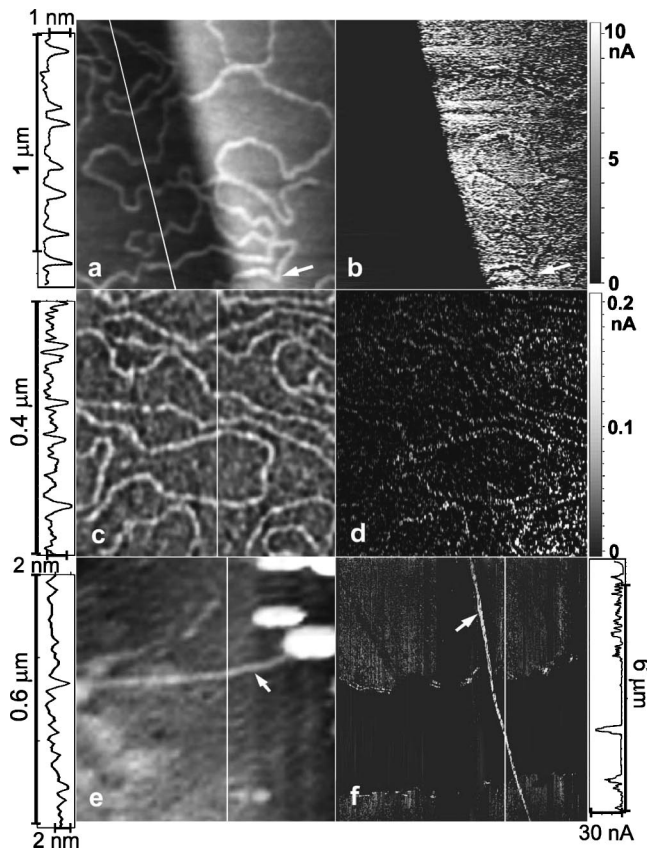


FIG. 1. AFM (left) and SRM (right) images of DNAs: (a) AFM image of DNAs on the clean substrate without pentylamine; (b) SRM image of the same molecules (right bright part of a and b images is Pt); (c) AFM picture of DNAs on the substrate treated by pentylamine; (d) SRM image of the same molecules, Pt electrode is outside of the image; (e) AFM image of a DNA combed (as in Ref. 4) across the slit between Re/C electrodes on mica; (f) SRM image of a rope of DNAs combed (as in Ref. 4) between Pt electrodes on mica. On the left- and right-hand sides of the image there are profiles of DNAs and current scales of SRM (voltage was up to 0.23 V) images, respectively. Note that when (b) is plotted on the same current scale as (d), the DNA molecules on the mica still appear as black as the mica substrate.

DNAs on the pentylamine-functionalized mica surface are visible by SRM in positive contrast [Figs. 1(d) and 1(f)]. Thus they are conductors. We believe that the conductivity of DNA stems from the native, regular stacking of the base pairs in the molecules.<sup>12</sup> It is well known that mechanical stretching deformation can lead to denaturation of DNAs.<sup>13</sup> Likewise compressing deformation may be able to destroy the regular stacking of pair bases. Compressed DNA with thickness 2–4 times less than B-DNA probably consists in

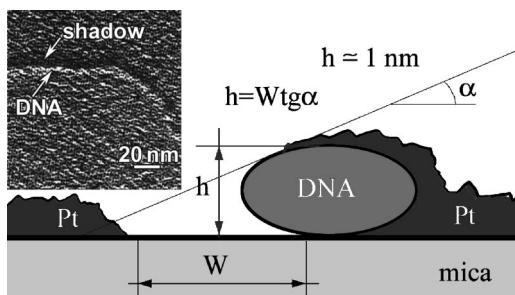


FIG. 2. Schematic image of shadow evaporation technique. Inset: Transmission electron microscopy image (negative) of Pt/C DNA replica from untreated mica shadowed at  $6^\circ$ , indicating a thickness of 1 nm.

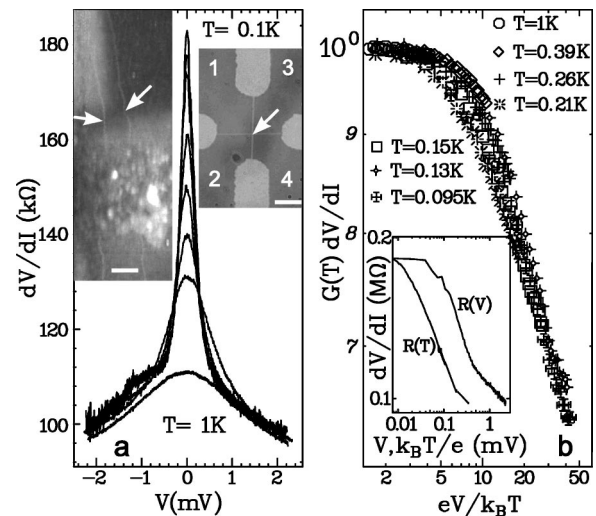


FIG. 3. (a) Bias dependence of the differential resistance for different temperatures between 0.1 and 1 K. Note the asymmetry of the curves above 0.4 mV. The excitation current is 0.1 nA. Right inset: optical image of the slits etched in the 3 nm thick Pt film on mica. The wide part of the slits were etched using a focused laser beam, the narrow submicron part was etched using a focused ion beam. Scale bar is 20  $\mu\text{m}$ . Left inset: AFM picture of DNA molecules combed across the slit. Two molecules are clearly visible (shown by arrows) on the Pt contacts (dark) but not on the etched mica because of the rough surface state impedes good visualization of the molecules. Scale bar is 250 nm. (b) Scaling behavior of the differential resistance in the temperature range between 0.1 and 1 K and voltage range between 0.02 and 0.4 mV. Inset: Temperature dependence of the resistance of sample depicted on the insets compared to the bias dependence measured at 0.1 K on a log-log scale indicating a power law increase of the resistance at low temperature and low bias.

two independent, chaotically intersecting strands. Single-stranded DNAs definitely are insulators.<sup>1</sup>

Previous work on DNA<sup>1–6</sup> is compatible with this statement that DNAs are conductors if their thickness is the native thickness of about 2 nm (in this case it makes more sense to call it diameter). Conductivity was indeed observed for suspended DNAs<sup>2,3,5</sup> and DNA films<sup>1</sup> where there is no interaction with a surface, and the diameter of molecules should be close to native. For thick ropes of DNAs<sup>6</sup> the molecules inside the rope are also expected to keep their native diameter and to contribute to their conductivity.

We previously showed<sup>4</sup> that DNA molecules on rhenium/carbon bilayer contacts, prepared on a pentylamine-functionalized substrate, like depicted in Fig. 1(e), exhibit a resistance of the order of 100 k $\Omega$  per molecule and remain metallic down to milli-Kelvin temperature. We have even observed proximity induced superconductivity below the superconducting transition temperature of Re/C, indicating low temperature phase coherent transport at the micron scale. We present in the following low temperature transport measurements performed on DNA molecules connected to 3-nm-thick platinum electrodes on mica separated by a 200–500-nm-wide slit made using a focused ion beam [see Fig. 3(a), insets]. After the substrate with platinum electrodes was treated with pentylamine, the molecules were deposited using the combing method with a continuous flow of DNA solution previously described.<sup>8</sup> The estimated number of connected molecules is between 1 and 5. Figure 3(b) (inset) shows the low temperature transport measurements of one of these samples measured below 4 K. The resistance was equal

to 55 k $\Omega$  at room temperature, and increased moderately to 95 k $\Omega$  as the temperature decreased to 4 K. These values are of the same order of magnitude as what was found for the previously measured molecules mounted on Re/C contacts. This indicates that there is no major difference between the quality of contacts realized with Pt films compared to contacts made of Re/C bilayers.

We now focus on the very low temperature transport, both linear and nonlinear, which could be accurately characterized below 1 K. In contrast to the case of the previously investigated Re/C contacts which were superconducting, in the present case the Pt electrodes are not superconductors, and, as expected, we find no sign of superconductivity. The resistance in the linear response regime was measured with a low frequency 10 Hz excitation ac current with an amplitude below 1 nA. It decreases monotonously between 0.1 and 1 K like a power law:  $R(T) \propto T^{-x_T}$  with  $x_T = 0.27 \pm 0.03$ . We have also investigated nonlinear transport in the same device, by measuring the differential resistance with a dc current superimposed to the ac one. The differential resistance decreases with the voltage bias as shown on Fig. 3(a), and presents a peak centered at zero bias which gets sharper with decreasing temperature. This peak is not a symmetrical function of the voltage drop through the sample, an asymmetry we attribute to the contacts which are certainly not identical. Above a threshold value which increases with temperature, the differential resistance function of the dc voltage through the samples, decreases as a power law [see Fig. 3(b) (inset)]. The exponent  $x_V = 0.29 \pm 0.03$  is nearly identical to  $x_T$ . Deviations are observed when the dc voltage drop through the sample exceeds 0.4 mV.

In this range of temperature between 0.1 and 1 K and bias voltage between  $10^{-5}$  and  $4 \times 10^{-4}$  V it is possible to describe the data by a single scaling function:  $R(T, V) = R(T, 0)f(eV/k_B T)$  as shown on Fig. 3(b) where the function verifies  $\lim_{y \rightarrow 0} f(y) = 1$  and  $\lim_{y \rightarrow \infty} f(y) = y^{-x}$ . This behavior is very similar to what is observed in carbon nanotubes mounted on tunnel contacts in the range of voltage and temperature where there is no Coulomb blockade. It can be attributed to the existence of rather strong unscreened Coulomb interactions in DNA molecules which behave as 1D conductors. Such power law scaling of differential resistance with similar values for the exponents has been interpreted in single wall carbon nanotubes as a signature of a Luttinger liquid in these systems.<sup>14</sup> (The measured value of the exponent is known to strongly depend on the transparency of the contacts when their transmission is of the order or smaller than the resistance quantum  $h/e^2$ , with no temperature dependence in the case of perfectly transmitting contacts.)<sup>15</sup> A more general explanation in terms of dynamical Coulomb blockade or quantum wires with a small number of channels in multiwall carbon nanotubes in which electronic transport is diffusive.<sup>16</sup> It is interesting to observe a similar behavior in DNA.

The above results are the confirmation that we are able to prepare DNA molecules which are conducting even at very low temperature (which thereby excludes the possibility of parasitic ionic conduction). Conductivity of DNA molecules is however expected to depend on many other factors

than the one which has been clearly identified here, in particular:

The structure of the molecule: Different types of kinks and bendings decrease conductivity. SRM and conductivity measurements indicate that straight DNAs [Figs. 1(e) and 1(f) and 3(a)] are more conductive than curved ones [Fig. 1(d)]. The molecule can also be overstretched by combing, which leads to reduced base to base electronic transfer.

The chemical environment of the molecules: It determines the presence of ions and water molecules attached to the DNA molecules. A very dry environment is expected to induce structural transitions from standard form B of the molecule to the form A.

The contacts: They are inevitably at the origin of a kink in the molecules which is important when the contacts are too thick.<sup>17</sup> They can also have a crucial role in acting as strong electron or hole dopants. They could provide a sufficient number of carriers delocalized along the molecular wire because of the quasi-absence of electrostatic screening in one dimension.<sup>18</sup>

All these factors need to be precisely investigated in the future.

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<sup>8</sup> A drop of 10–15  $\mu$ l of DNA solution of concentration 1–3  $\mu$ g/ml in a buffer containing 10–30 mM of ammonium acetate and 7–9 mM of magnesium chloride. The samples were incubated for 5–10 min. The mica was then washed with water, blotted with filter paper, and dried with argon.

<sup>9</sup> SRM images were acquired with the scanning probe microscope Solver P47-Bio (NT-MDT Company, Moscow, Russia) in the contact mode using Pt–C coated silicon cantilevers (NT-MDT Company, Moscow, Russia). About SRM method see: P. De Wolf, M. Geva, T. Hantschel, W. Vanderhorst, and R. B. Bylisma, *Appl. Phys. Lett.* **73**, 2155 (1998).

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