Electrical characterization of DNA in mechanically controlled break-junctions

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Abstract. Electrical characterization of DNA molecules using the mechanically controlled break-junction technique is presented. The main advantage of the technique is the control over the electrode distance during the measurement. This can be used to stretch the DNA and search for the influence of the conformation on the conduction process. The DNA is characterized in liquid and dry environments. From our data, we conclude that only a small number of molecules are contacted in each measurement.

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1. Introduction

The conductance of DNA is of great fundamental and technological interest. On the one hand, self-repair mechanisms are apparently based on the ability of DNA to move charge along its backbone [1]. On the other hand, the enormous potential offered by the self-organization of DNA molecules makes it a possible candidate for building large molecule-based electronic circuits [2]. Initial conductance measurements on DNA yielded a wide range of results [3]. In many experiments, insulating behavior was observed, while other groups reported semiconducting or even metallic behavior [4]. It soon became obvious that details of the contacts, the environment and the sequence of the DNA are important in the definition of the properties of the measured structure.

Specifically, the recent experiments by Kasumov et al [5] show that the interaction between DNA molecules and the substrate is a key parameter that determines the conducting or insulating behavior of DNA molecules. The surface force field, strongly deforming the DNA molecule, may be a reason for blocking the current along the molecule. Another important characteristic of the DNA molecule is its remarkable expansibility due to the conformational change from the B conformation to the S conformation. It is assumed from measuring force–distance curves on DNA that it undergoes a conformational change when it is stretched. The influence of this conformational change on the conducting properties of the DNA has been theoretically investigated [12]. Therefore, a controllable method combining control of mechanical stress of the DNA molecule and electrical measurement is essential for studying the mechanism of charge transfer through DNA. In addition, it is important that new contacting methods allow the control of as many parameters as possible. Measurements of DNA using scanning tunneling microscopy (STM) [6], for example, have already shown remarkable stability of the measured results. If, in such a configuration, one end of a thiol-functionalized double-stranded (ds) DNA is connected to a gold surface in a self assembled monolayer (SAM) of single-stranded (ss) DNA molecules and the other end to a gold nanoparticle, stable ‘s-type’ current–voltage ($I–V$) curves can be measured [7]. Test measurements on either unfunctionalized ds-DNA, ss-DNA or bare gold surfaces show quite a different behavior [8]. Sequence-dependent statistical information on short (8 basepairs long) double-stranded oligomers reveals higher conductance values for guanine (G)-rich species obtained by repeatedly contacting the molecules with an STM tip [9]. It is, however, mandatory to compare results from different techniques in order to exclude all possible artifacts coming from a single contacting method.

In this work, we report on measurements of the conductance through a single or a small number of DNA molecules contacted using mechanically controllable break-junctions (MCBs). This technique has been used to characterize atom-sized metallic contacts [10] as well as current transport through single organic molecules [11]. The main advantage of this technique in the current context is the possibility of adjusting the separation of the metallic contacts at a precision of fractions of 1 Å. This allows one to change the length of the contacted molecule in a very controlled way and to measure the conductance of the structure simultaneously.

The DNA molecules in our experiments are terminated with thiol endgroups attached to the 5′ end of the first base. During chemisorption on the Au electrodes, the H atom is expected to be cleaved off. This chemisorption ensures good mechanical coupling of the molecules to the contacts, and thus mechanical stretching of the molecule is possible before the molecule–metal bond breaks.
Figure 1. Sketch of the measurement technique using MCBs. (a) A nanometre-scaled suspended bridge is fabricated using e-beam lithography and reactive ion etching on a flexible substrate. The substrate can be bent by pushing at the central support rod. This causes the bridge to break into two well-defined metal contacts. (b) A molecule can bind through the thiol linker groups to the metal contacts.

2. Experimental

The characterized DNA molecules are double-stranded short pieces of a complex sequence (5′ thiol-dG-GGC GGC GAC CTT CCC GCA GCT GGT ACG GAC). After pairing, the thiol groups are situated on both ends. The 10 nm size is adequate to span two closely spaced nano-electrodes as a linear, almost stiff structure, so that the trapped DNA molecules are suspended above the substrate and keep their original thickness, avoiding the effect of the surface field.

The working principle of metal–molecule junctions with the MCB technique is shown in figure 1. Using standard lithography and etching techniques, a narrow metal bridge is formed. This bridge can be broken by bending the substrate with precise control of the breaking mechanism. Using this technique two atom-sized metal contacts form, which are separated only by a few Ångstroms. This procedure can be performed in vacuum, under ambient conditions or in the presence of a solvent. In all cases, the characteristic conductance steps as a function of the distance of gold atomic-size contacts [13] can be seen before the two contacts separate. Once a gap between the metal contacts arises, the conductance decreases exponentially with the distance of the electrodes. This exponential decrease changes in the presence of a solvent [14]. It can, in principle, be used to determine the displacement, i.e. changes of the distance between the electrodes, accurately. However, for small changes of the electrode distance it is not known whether on the atomic (molecular, respectively) scale the motion of the apex atoms follows linearly the motion induced by the motion of the bending beam. Furthermore, the origin of the distance scale, i.e. the point where the electrodes separate or come into contact, is in general not known because of the so-called ‘jump to contact’ [13]. In what follows, we therefore distinguish between, on the one hand, the notions ‘distance’ and ‘changes of distance’ when changing the position of the support rod by a large amount and thereby indeed inducing a distance change of the electrodes on a large scale and, on the other hand, ‘displacement’ when we change the...
position by a small amount only. Strictly speaking, the motion of the bending beam displaces the anchor points of the bridge, but it is unknown whether on the subatomic scale the motion of the bending beam is linearly related to a distance change of the electrode’s apex atoms.

In the experiments presented here, we open, under atmospheric conditions, the contacts by approximately the length of the molecules. In the next step, a droplet of the molecular solution (1 µl of a 25 pmol µl⁻¹ solution) is applied to the contacts and dried in air or a stream of dry N₂. During the drying, an ac voltage of ±4 V was applied at frequencies of 100–1000 Hz to the junction in order to trap and align the molecules effectively between the electrodes. It has to be mentioned that later experiments indicate that voltages in this size range can change the electric behavior of the DNA irreversibly.

3. Results and discussion

The behavior of the junction as a function of time can be seen in figure 2. Initially the resistance is given by tunneling between the two contacts in dry conditions \((R > 10^{10} \Omega)\). After deposition of the droplet, the resistance immediately decreases. It can be seen that the resistance for pure water \((R \approx 10^9 \Omega)\) is three orders of magnitude higher than the resistance in the case of a DNA solution \((R \approx 10^8 \Omega)\). The time for the droplet to dry is approximately 20 min. During this time the resistance remains almost constant in both cases, because the central gap is fully covered by the liquid. During the final stages of the drying, we observe a sharp rise in resistance again. In the case of the pure water droplet, the resistance recovers to its initial value, indicating that we did not damage the metal electrodes by depositing the water droplet nor leave any residue on the contacts. After drying of the DNA solution, however, the junction resistance remains lower than the initial value \((R \approx 10^8 \Omega)\). These two facts, the lower resistance of the junction in the presence of the DNA solution and after drying compared to test samples using pure water, indicate that indeed DNA molecules are connected to both the metal contacts and dominate the conduction behavior after our processing. We will now
Figure 3. Resistance versus displacement curves taken after the formation of a molecular junction. Arrows indicate the direction of the sweep; the junction is opened from left to right. The abrupt steps indicate the rupture and formation of a molecular bond.

discuss the behavior of such junctions under different environmental conditions (in liquid, under atmospheric conditions and in vacuum) and the response to changes in electrode displacement. These measurements were done at a bias voltage of 100 mV, the current being limited to 1 µA.

Figure 3 shows the behavior of a junction after creation of the molecular layer upon electrode displacement in vacuum conditions. The behavior deviates clearly from the exponential behavior known from bare metal junctions (shown in the inset of figure 4(b)). The resistance remains nearly constant over a large range of displacement values. Further stretching the junction leads to an abrupt rupture of the structure, resulting in a step-like increase in resistance. Consecutive closing (i.e. reducing the curvature of the bending beam again) of the same junction leads to an inverse behavior: the resistance remains high and constant, until it drops abruptly, indicating a relinking of the structure. This behavior can be reproduced in a subsequent opening and closing of the structure, showing similar resistance values for the ‘open’ and ‘closed’ states. Thus, instead of breaking and linking metallic contacts, it is likely that the contact to a molecule or an ensemble of molecules is opened and closed. This is an additional evidence for the fact that we are able to produce molecular junctions using our contacting technique. The highest stable resistance which we observed (in the closed state) is about 10 GΩ (not shown here), the second highest about 5 GΩ, suggesting that a single, well-contacted molecule would have a typical resistance of 10 GΩ [9, 13], while the contacts with $R = 5$ GΩ would correspond to two molecules in parallel. We conclude that the discrete resistance values in the ‘low-resistance’ regime indicate that a small number of molecules contribute to the conductance.

Once a molecular junction with resistance in the GΩ range has been established, it can be carefully pushed further together or stretched apart. This treatment reveals an interesting behavior, examples of which are represented in figure 4. The resistance shows characteristic
Figure 4. Resistance of the metal–DNA–metal junctions as a function of electrode displacement. The resistance shows clear steps in all represented curves, unlike the very smooth exponential behavior observed in a clean junction (inset of (b)).

jumps as a function of the electrode displacement. The amplitude of these steps is smaller than amplitudes observed upon breaking the link between the molecules and metal (as represented in figure 3). Here, we observe typical jumps of about 4 GΩ at a total resistance of 10 GΩ as opposed to jumps from 1–5 GΩ to 100 GΩ. Possible explanations for the smaller jumps are configuration changes of the molecule(s) or a change in the number of conducting molecules in the junction. The fact that a change in configuration can lead to a change in conductance has been pointed out based on calculations [12]. The overlap of the conducting π-orbitals changes due to a conformational change, if the DNA is overstretched. However, the amount by which the resistance of our molecules is expected to change is not easy to estimate from the theoretical considerations. Also a fluctuation of the number of molecules would induce a change in the observed order, i.e. of the overall resistance, if the number of molecules is small. The strength of the thiol–gold bond makes fluctuations of this bond highly unlikely. It has been shown that gold–gold bonds are more likely to break than the metal–molecule bond [15]. In the following, we propose several mechanisms that might be at the origin of the observed jumps in the resistance versus displacement data. The fact that we observe jumps to higher as well as to lower resistance while closing the junction can be understood by the geometry of the electrodes on the atomic scale and the motion behavior of the gold atoms: on this length scale, the electrodes form rather rough and wide tips with several possible narrowest gaps to the counter-electrodes. As mentioned above, the molecules form rather stiff rods which are only able to chemisorb and thus to contribute considerably to the transport if the spacing between the electrodes is suitable. Furthermore, the arrangement of the atoms determines the force on the molecules and thus either the configuration or the number of molecules solidly attached to the electrodes. This arrangement does not necessarily vary monotonously with the separation of the electrodes. When stretching the contact, one of the few molecules may undergo a conformational change to its stretched ‘S’ conformation which is assumed to be less conductive. Further stretching may break one of the contacts of the molecule to the electrodes. If this happens the force on the atoms and molecules is released such that the molecule can flip back to its initial conformation. It is very likely that upon closing the electrodes, the distance of a particular pair of atoms contacting...
Figure 5. $I$–$V$ curves measured before and after deposition of molecules in the MCB. (a) Before deposition of molecules the $I$–$V$ curves show linear characteristics, typical of a tunneling contact in the low-bias regime. Different resistance values correspond to different electrode distances. (b) $I$–$V$ curves taken after deposition of the molecules show a clear deviation from linear behavior (indicated by the solid black line, corresponding to a resistance of $\approx 500 \, \text{M}\Omega$). Such a behavior can be expected from transport through a single DNA molecule and has been reported in different measurement techniques.

one molecule will fall below the length of the molecule. If this happens one of the contacts of the molecule to the electrodes might break, and this conduction path will vanish. Consequently, the atoms as well as the molecules may rearrange in such a manner that another molecular junction can be formed or relaxed to the high-conducting state upon further closing the bridge. Typically, 2–5 jumps are observed before the contact either completely breaks or totally closes.

In figure 5, we compare current–voltage characteristics ($I$–$V$ curves) taken at ambient conditions with and without molecules deposited. Without molecules the $I$–$V$ curves are linear and the resistance is in the high G$\Omega$ range. After deposition of the molecules, the resistance drops and deviations from the linear behavior can be seen at source-drain voltages of about 400 mV. Such a nonlinear behavior has been reported for a number of molecules, e.g. for DNA molecules measured in an STM configuration [16]. It can be attributed to activated transport through the organic conductor. At $T = 0$ a conductance gap is expected due to the energetic misalignment between the Fermi energy $E_F$ of the contacting metals and the charge-carrying molecular orbital. For elevated temperatures, transport in the gap can be assisted by thermal fluctuations, thus a softening of the gap can be expected, leading to the ‘S-shaped’ $I$–$V$ curve observed in our experiments. The conductance in our systems is only weakly suppressed for a range of about $\pm 400$ mV (‘conductance gap’). Experimental results in different configurations [7] and theoretical calculations [17] report strong conductance gaps of more than 1 V. This apparent difference can be due to the different coupling to the electrodes and the environment in our experiments. The highest resistances for which we were able to detect reproducible $I$–$V$ curves are in the order of $500 \, \text{M}\Omega$ to $2 \, \text{G}\Omega$, thus comprising a small number of molecules again.

At ambient conditions, however, several parallel conductance paths cannot be excluded. For example, tiny amounts of residual water in the DNA can lead to ionic conduction along
Figure 6. $I-V$ curves measured in water. $V_{sd}$ is continuously swept from $-6$ to $+6$ V. The system degrades from the initial state (red and green curves) to a less conductive state, until conductance vanishes completely, with time (see development of blue curves, which were taken after the recording of the red and green curves).

4. Conclusion

To summarize, we have shown measurements of single or a few DNA molecules in a MCB configuration. The behavior of the resistance during deposition of the molecules clearly
indicates that we are able to deposit and characterize molecular ensembles. Displacement-dependent measurements of the resistance show a behavior different from the one known from purely metallic contacts. We see sharp resistance steps of the order of the overall resistance for a small variation of the displacement and a sharp increase in resistance once the electrode distance exceeds a certain value. Both facts further support our assumption that we indeed observe transport through small molecular ensembles.

The conductance behavior of the junctions in the dry state is comparable to previous measurements on DNA in different geometries [16]. It shows the typical ‘S-shape’, which can be expected for such systems from the alignment of the molecular energy levels and the Fermi energy of the metals. The dependence of the conductance on the electrode displacement can be understood as an effect of the conformational change of the DNA. Measurements on the junctions in liquid environments reveal a strong increase in conductance at large bias voltages. In future experiments these effects will be investigated in DNA molecules with a better electronic coupling of the π-electrons to the leads.

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