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Direct current electrical characterization of ds-DNA in nanogap junctions

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Measurements of DNA conductivity, hybridization, and melting using electronic means can have wide applications in molecular electronics and biological sensors. We have fabricated nanogap break-junctions by electromigration through thin gold-on-titanium films. 18-mer thiolated ds-DNA molecules were covalently attached between the electrodes and dc electrical measurements were done. The conductance was measured through the molecule before and after a temperature ramp from 300 to 400 K. A dramatic decrease in conductance was observed, analogous to an electrical fuse, possibly attributed to complete or partial denaturing of the ds-DNA molecules bridging the nanogaps. We also show evidence that the dc resistance of dry DNA strands of the same length decreases with increasing guanine-cytosine content in the sequence with values ranging from 10 M Ω to 2 G Ω . These findings can have important consequences in DNA-based molecular electronics and direct label-free detection of DNA hybridization. © 2005 American Institute of Physics. [DOI: 10.1063/1.1900315]

Much work has been carried out on single or small assembly of organic molecules to perform functions analogous to semiconductor devices since the famed description of electronic transport through individual molecule.¹ DNA has also been a candidate for such devices.² Electrical conduction through DNA has been reported earlier,^{3–7} and long range charge transport has been shown to be modulated by intervening sequence⁸ but such effects of sequence or hybridization have not been investigated by electrical measurements. Porath *et al.* used a similar length of DNA as in our experiments but without a thiol group at the end.⁵ Hwang *et al.* physically adsorbed 60-bp DNA on gold electrodes without thiol groups.⁶ Xu *et al.* used a scanning tunneling microscope tip to measure conductance of DNA, showing dependence on the sequence and length.⁷ We report dc measurements of covalently attached thiolated ds-DNA in gold nanogaps to measure the electrical resistance of hybridized and denatured DNA molecules. We also show the conduction dependence on GC content of the DNA sequence.

We fabricated nanoscale gaps in 3 μm wide, 20 nm thick evaporated Au-on-Ti layer on SiO₂ substrate, similar to techniques reported earlier.⁹ Nanoscale gaps were created through electromigration by passing a large current through

the thin Au/Ti line. Figure 1 shows the current voltage characteristic of a metal line before and after the gap was formed. The insets (a) and (b) show a field emission scanning electron microscope (FESEM) image of the metal pattern, before stress and after the gap was formed. The gaps were probed with micromanipulator probes in a dark box on a vibration isolation table. All data was recorded with a Keithley 4200 Semiconductor Parameter Analyzer. The measurements were carried out in a vacuum chamber (MMR Technologies Inc,

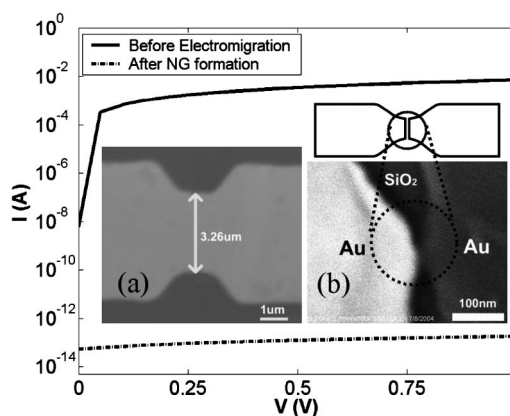


FIG. 1. Current–voltage characteristics of the break-junction before and after the formation of the nanogap. On average, current at 0.5 V dropped from $\sim 3\text{--}5$ mA to less than 0.3 nA after nanogap formation. Devices with leakage current less than 1 nA were considered to be candidate devices for DNA docking. Inset (a) shows SEM images of the break-junction structure before electromigration, and inset (b) shows the sketch and FESEM image of one of the structures where nanogap was formed.

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TABLE I. The three 18-mer DNA sequences and their melting temperatures, used in our experiments.

Sequence name	Sequence	GC-content (%)
Seq-1	SH-CGT ACA TGA TCA TGT ACG (self-complementary)	44.4
Seq-2	SH-CAG TCA GGC AGT CAG TCA	55.6
Seq-3	SH-CGT GCA CGT ACG TGC ACG (self-complementary)	66.7

CA) with a temperature-controlled stage. The gaps were found to be stable, i.e., the current remained the same after repeated temperature ramps from room temperature to 400 K in nitrogen.

Three different 18-mer ds-DNA molecules were purchased and used for the measurements (Integrated DNA Technologies, Coralville IA). The molecules had thiol group attached to the 5' end through a $(\text{CH}_2)_6$ linker, for covalent attachment to the gold electrodes. The sequences differed by their GC content and the corresponding melting temperatures as shown in Table I. The same sequences were also obtained without the thiol groups to serve as control during the incubation. DNA disulfide groups were reduced with 0.1 M DTT, 0.17 M phosphate buffer, pH 8.3 followed by purification using Sep-Pak C18 cartridge (Millipore). The purified DNA was subjected to annealing (90 °C for 10 mins in 10 mM NaCl, 10 mM sodium phosphate buffer, and 0.1 mM EDTA, pH 7.0). Immediately, the DNA attachment on the gold electrodes was done in N_2 ambient by incubating the chips in 600 μL of 12 μM thiolated ds-DNA. Nonthiolated ds-DNA was always used as control. The chips were incubated for 72 h with the addition of 100 μL DTT [dissolved in deionized water] after first 24 h. After incubation, chips were rinsed in 0.3 M phosphate buffered saline (PBS) (pH 7.0) and dried for 12 h in N_2 ambient.

Current–voltage measurements were performed between -1 to $+1$ V. Approximately 15% of the devices showed an increase in current after the incubation step, attributed to the presence of covalently linked ds-DNA molecule in the nanoscale gaps, whereas none of the control samples exhibited increase in current. Figure 2(a) shows the current increase for two typical devices with sequences 1 and 3, as an example, showing about a three order increase in current when compared to the current before incubation and to the control device (i.e., nonthiolated molecule) on a similar device. The devices were then exposed to a temperature ramp to 400 K with a 30 s hold at 5 K increments, and then back

down to room temperature. All the devices that were not exposed to any voltage stress during the temperature ramp, showed a dramatic reduction in current, when measured after the ramp, as shown in Fig. 2(b). The possible explanation for the loss of conduction, which was observed consistently with all different sequences, could be the denaturing of the DNA in the dry state. The melting of the DNA strands in the absence of significant number of counter-ions and water molecules is expected to be easier (reduced or no shielding will make it easier for strands to denature) and should occur within the 100 K temperature ramp that the devices were exposed to. The devices are thus acting as electrical fuses which can be “blown” by a temperature ramp. Two additional points are to be noted. First, at each temperature increment and stabilization during the ramp, we did measure the current–voltage characteristics of two devices (only two could be measured due to availability of four probes in the vacuum chamber) and 50% of these devices did not show a decrease in current, as compared to about 20 devices measured on each die that showed a dramatic decrease in current, after the temperature ramp. The application of a voltage stress during the temperature ramp could reduce the denaturing of the molecule due to charging effects in the ds-DNA, and this interesting phenomenon needs further investigation. Second, after the temperature ramp, the conduction in the devices with DNA was regained in about 10% (2–3 of the 20) devices when reexposed to a PBS buffer and another temperature ramp. It can be postulated that the strands would not re-hybridize unless counter-ions and water molecules are present.¹¹

It is known that guanine (G) and cytosine (C) have a lower energy gap than adenine (A) and thymine (T) and that current conduction through G–C should be higher,^{2,4} but this has not been demonstrated using electrical measurements in dry conditions. We designed DNA sequences such that in the linear dimension, no G and C bases were more than two bases away from each other. We performed dc electrical measurements with the three different sequences and found the resistance around 0 V to increase with decreasing GC content, as shown in Fig. 3. This can be explained by increased hole hopping between the hydrogen bonds in the guanine-cytosine pair.¹⁰ As the ionization potential of guanine is the lowest ($G < A < C < T$), it is considered the easiest path for conduction of holes.¹¹ This results in less resistance to the charge flow in the sequence containing higher G–C pairs and we measured a decrease in resistance between Seq-1 and Seq-3 by an order of magnitude. The resistances from the linear region of the I – V curves closer to 0 V and the calculated resistivities are shown in Fig. 3. Previously reported resistivities values are $0.025 \Omega \text{ cm}$ [DNA diameter assumed to be 10 nm, length 1.7 to 2.9 μm (5000–8600 bp)] and $1 \Omega \text{ cm}$ for poly(dG)–poly(dC) (average resistance value

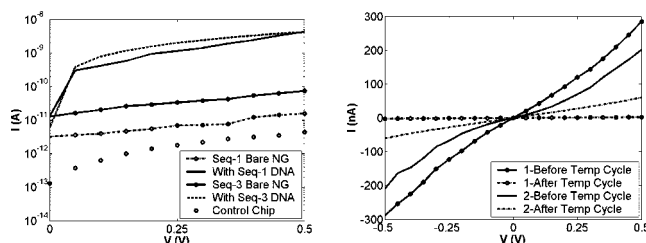


FIG. 2. (a) Comparison of current–voltage characteristics of conduction through bare nanogaps, with DNA docked in it for Sequences 1 and 3, and for the control chip after incubation in nonthiolated Sequence 1, where no conduction was observed. (b) Two representative I – V plots for Sequence 1 show decrease in conduction after temperature cycling. Conduction was restored after reincubation and temperature cycling step.

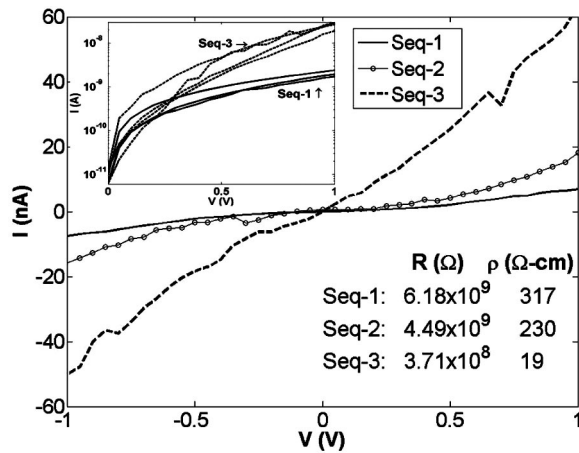


FIG. 3. Current–voltage plots of the three DNA sequences. Close to 0 voltage, the resistance decreases with increasing GC content. The resistivity values assume a single molecule, 6.7 nm long and 2 nm in diameter. Inset shows a number of I – V plots for Sequences 1 and 3, all measured on different devices.

of 50 nm of self-assembled DNA networks),¹² 0.41 Ω cm for λ -DNA (DNA diameter assumed to be 2 nm and the conductivity was evaluated from the measured loss of highly sensitive resonant cavities operating at 12 and 100 GHz),² and 1 m Ω cm for 600 nm long DNA (diameter \sim 2 nm).³ Otsuka *et al.* plotted resistance values from 10^9 to 10^6 with increasing relative humidity from 30 to 100% in 1 kb to over 35 kb long molecules, indicating the dependence of resistance on water molecules in the ambient.¹⁰ The calculated values shown in Fig. 3, assuming one ds-DNA chain of 2 nm diameter and 6.72 nm length, are an upper limit on the resistivity, as there can be more than one DNA molecule bridging the gap.

In summary, we have electrically detected the denaturing of DNA when the conduction through the molecule is lost after a temperature ramp. The conduction is regained by providing appropriate conditions to the molecule. The ds-DNA molecule can be thought of as a fuse that can “blow” at higher temperature. In addition, we have shown the dependence of electrical conduction through the DNA on its sequence, especially the GC content. These findings can have consequences in DNA-based molecular electronics and direct label-free detection of DNA hybridization.

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