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Conductivity of single-stranded and double-stranded deoxyribose nucleic acid under ambient conditions: The dominance of water

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We investigate the conductivity of single-stranded and double-stranded herring deoxyribose nucleic acid (DNA) in buffer solution spotted and dried on Au nanocontacts. We find an exponential increase of the conductivity with increasing humidity that is identical for single- and double-stranded DNA within the measurement accuracy. While the small conductivity of dry DNA is comparable to that of a large band-gap semiconductor, we attribute the increase at high humidity levels to water molecules accumulated at the phosphate backbone. For high humidities we observe s-shaped current-voltage characteristics that can be well explained by the dissociation of water attached to the DNA molecules. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2182027]

The electrical properties of deoxyribose nucleic acid (DNA) remain highly controversial.[1] A large variety of electron transport and conductivity studies have been performed. Different approaches to determine the DNA conductivity included the measurement of single DNA strands fixed between metal contacts,[2,3] the measurement of oriented DNA strands on lipid films,[4] high-frequency loss measurements in resonators,[5] and the measurement of current-voltage (*I-V*) characteristics of unordered DNA on Au nanocontacts.[6,7] Depending on the technique and the experimental conditions, a variety of—sometimes contradictory—results have been obtained. These range from insulating behavior[2] over wide-band-gap semiconducting[3] and ohmic[8] to even metallic behavior at low temperatures.[9] Theoretical models which aim to explain DNA conductivity are based on either tunneling or hopping along coupled π orbitals of the base pairs.[1,10–12]

The electrical properties of DNA are of paramount importance for two visionary technologies: self-assembled nanoelectronics and marker-free gene tests. On one hand, the DNA molecule is considered to be a promising candidate for the realization of molecular electronic devices.[13] Since it forms self-assembled structures it could be used as a template for nanocircuits or as an element of such circuits itself. On the other hand, marker-free bioanalytical methods are highly desired.[14] In this regard the conductivity of DNA could be used to determine its hybridization state. However, for all practical applications it is important that DNA is sufficiently conducting, in particular at room temperature. For gene tests it is also crucial that the conductivity of single-stranded DNA differs from that of double-stranded DNA, in particular under ambient conditions.

Recently Kawai and co-workers studied the conductivity of single-stranded artificial DNA spotted onto nanocontacts,[15] whereas Armitage *et al.* examined DNA in a microwave resonator.[16] In their independent studies both groups measured unordered DNA material for different relative humidities and found the DNA conductivity to increase exponentially with increasing humidity. Their work led to the idea that under ambient conditions the DNA conductivity is dominated by a layer of water molecules accumulated at the DNA backbone. This hypothesis is supported by independent measurements of Jo *et al.*[17] and very recent measurements by Tuukkanen *et al.*[18]

In this letter we study the humidity dependence of the conductivity of herring DNA spotted and dried onto nanocontacts. For the first time we perform *I-V* curve measurements of both single-stranded (denatured) and double-stranded (hybridized) DNA covering nearly the whole humidity range from 10% to 100%. Our measurements reveal an exponentially increasing conductivity with increasing humidity for both kinds of DNA that is identical within the measurement error. At high humidity levels we observe nonlinear *I-V* curve shapes. We clarify here that the nonlinearity results from the hydrolysis of water.

The setup allows for the adjustment of sample temperature, pressure, and gas composition of the atmosphere surrounding the sample during the acquisition of the current-voltage curves. We examine DNA that consists of 120–3000 nucleotides and is solved (10 mg/ml) in a buffer solution of 10 mM tris-HCl, 10 mM NaCl, and 10 mM ethylene diaminetetraacetic acid (EDTA) with *p*H 8. Denatured single-stranded DNA is obtained by heating the solution to 95 °C

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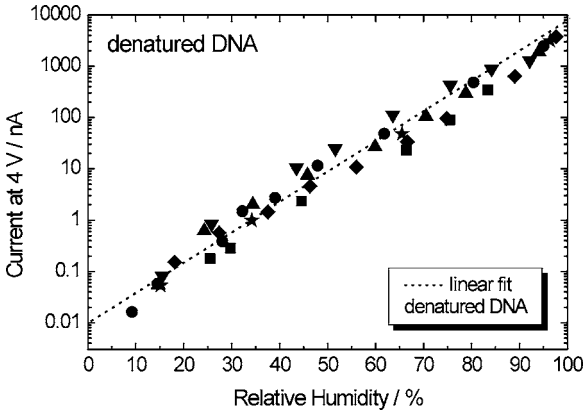

FIG. 1. Current at a voltage of 4 V through nanocontacts with a 100 nm gap covered with spots of denatured DNA. The five different symbols represent measurements obtained with different chips. The humidity has been reduced with a dry nitrogen gas flow starting with an initially saturated atmosphere. The dashed line represents a linear fit of the measurement data.

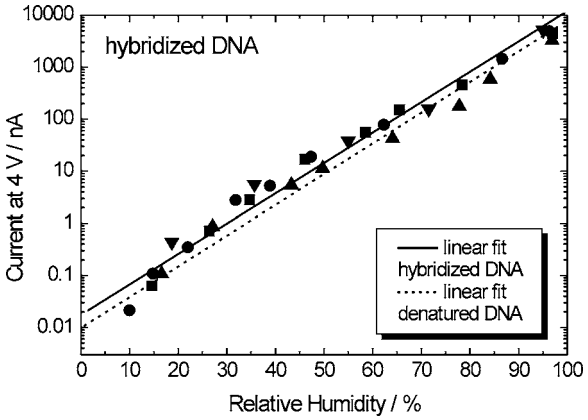

FIG. 2. Current at a voltage of 4 V through nanocontacts with a 100 nm gap covered with spots of hybridized DNA. The four different symbols represent measurements obtained with different chips. The humidity has been reduced with a dry nitrogen gas flow starting with an initially saturated atmosphere. The solid line represents a linear fit of the measurement data. The linear fit for denatured DNA (dashed line) is shown for comparison.

and subsequent shock cooling in ice-water. The Au nanocontacts onto which hybridized and denatured herring DNA is spotted are formed by 100 nm wide metal lines interrupted by a 100 nm gap. They have been deposited on oxidized Si using electron beam lithography techniques. Spotting both types of DNA resulted in layer thicknesses between 100 and 500 nm after drying. Using both finite element simulations as well as a scaled model we are able to show that the layer thickness has no significant influence on the expected current. Different defined relative humidities are either obtained by using saturated salt solutions or by purging the measurement volume with dry nitrogen starting with an atmosphere saturated with water vapor. Using the latter approach we cover almost the whole range from 10% to nearly 100% relative humidity.

Both hybridized and denatured DNA yield resistances between several hundred GΩ and a few MΩ strongly depending on the relative humidity of the atmosphere. In accordance with Kawai and co-workers,[15] we find an exponentially decreasing resistance with increasing relative humidity. Figure 1 shows the current through spots of denatured DNA when a bias voltage of 4 V is applied to the nanocontacts. We find an exponential dependence of the current on the relative humidity as indicated by the linear least-square error fit in the logarithmic plot in Fig. 1. The conductivity varies over 6 orders of magnitude.

Where does the conduction originate from? We note, that Xu *et al.* found convincing evidence for a charge transport via the stacked base pairs for very short strands of artificial DNA (<15 base pairs) in buffer solution.[19] Recently Cuniberti and co-workers[20] suggested that the conduction observed in Ref. 19 could result from a strong perturbation of the electronic system mediated by the dissipative water environment. The perturbation may modify the low-energy electronic structure of the DNA strand and induce new energy states which could induce an increased conduction. Yet, it was shown in Ref. 19 that (i) the DNA conductivity inversely scales with the length of the DNA strands and that (ii) the presence of AT base pairs significantly reduces the conductivity. Since our natural DNA is much longer and has many AT pairs we conclude that the charge transport via the stacked base pairs is not the dominating effect causing the high conduction observed at high humidity. We conclude that for high humidities it is not the DNA itself that provides the leading contribution to the conductivity but that the current mainly flows through the adsorbed water layer (via ionic conduction or the Grotthuss mechanism),[21] the thickness of which grows exponentially with increasing humidity.[16,22] As shown in Fig. 2 basically identical results are also obtained for hybridized DNA. The conductivity of both kinds of DNA increases by a factor of between 3.7 and 3.8 for a 10% increase of relative humidity. Within the measurement accuracy, no difference between the conduction properties of denatured and hybridized DNA can be found, although this would be expected if the conduction occurred along the π orbitals of the base pairs. At humidities below a few percent DNA has only a very small conductance comparable to that of a high band-gap semiconductor.[23]

It is interesting to note that the shape of the *I-V* curves changes as the humidity is increased. Figure 3 shows typical shapes of current-voltage curves for three different humidity values obtained for hybridized DNA. The *I-V* curve develops from a linear ohmic-like behavior for low humidities to a s-shaped curve for high humidities. While Kawai and co-workers[15] have already found deviations from a linear behavior in single-stranded artificial DNA our *I-V* curves are highly reproducible and symmetric.[24] The same s-shaped

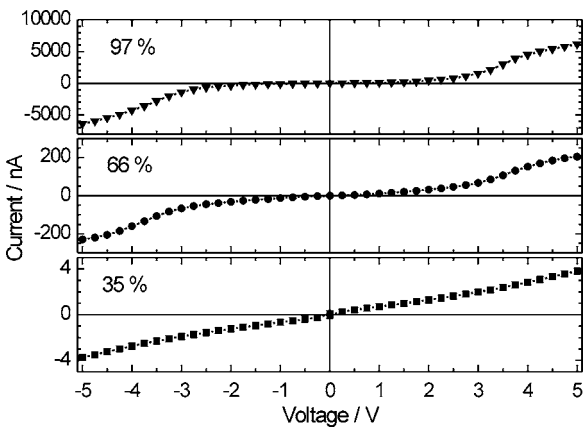

FIG. 3. Current-voltage characteristics measured with hybridized DNA spotted onto nanocontacts with a 100 nm gap spacing. The measured curve changes from linear to s shape with increasing relative humidity.

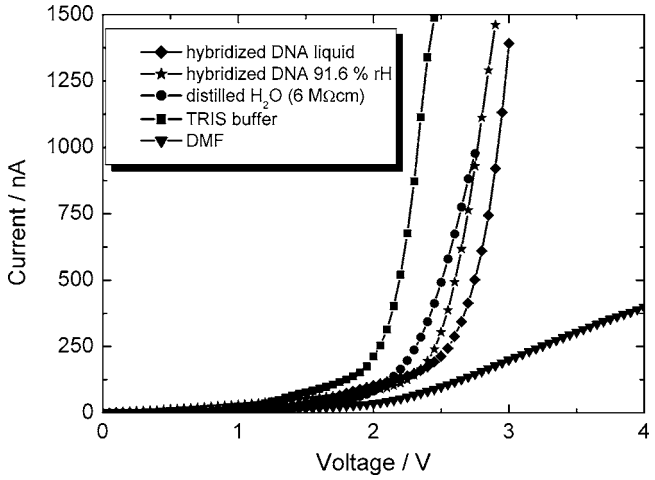

FIG. 4. Current-voltage characteristics for different kinds of samples spotted onto nanocontacts with a 100 nm gap. Liquid hybridized DNA solution as well as hybridized DNA at a very high humidity level of 91.6% have characteristics similar to water. The TRIS buffer with a large ion concentration has an even higher conductivity, the nonpolar solvent DMF a much lower conductivity.

current-voltage characteristics are found for denatured DNA.

As we show in this paragraph the shape of the current-voltage characteristics is dominated by the hydrolysis of the adsorbed water layer. Figure 4 compares the current-voltage characteristics of different samples spotted onto nanocontacts. Liquid hybridized DNA solution as well as hybridized DNA at a very high humidity level of 91.6% have characteristics similar to that of distilled water.[25] They all exhibit a sharp bent in the curve at the water dissociation voltage well known from literature for macroscopic contacts.[26] The dissociation voltage is determined by the electrochemical series from the difference of the redox potentials of the two participant half cells H_2/H_3O^+ (–0.41 V) and OH^-/O_2 (+0.82 V) to 1.23 V. In practice this value is increased by a few hundred mV depending on electrode current density, electrode material, and occurrence of additional ions. For our experimental conditions dissociation voltages between 2 and 2.5 V are expected,[27] in agreement with the experiment. For comparison we also measured TRIS solution and DMF which are part of the buffer solution. The TRIS buffer with a large ion concentration has a somewhat higher conductivity, whereas the nonpolar solvent DMF has a much lower conductivity. For liquid samples, the dissociation process can even be observed under the microscope, as gas bubbles rise from the electrodes for voltages exceeding the dissociation voltage.

In summary, we have shown that dry DNA is a poor conductor. Only at high humidities does DNA show a good conductance. Yet, the current does not flow through the DNA itself but through the water layer adsorbed at the DNA backbone. The amount of adsorbed water molecules increases exponentially with increasing humidity leading to an exponentially increasing conductivity with increasing relative humidity. Denatured and hybridized DNA show an identical behavior within the experimental error. For high humidities we observe an s-shaped current-voltage curve which we show to result from the dissociation of water. On the basis of our results we conclude that native, untreated DNA is neither suited for interelement wiring in nanoelectronic circuits nor for simple marker-free gene tests which are based on DNA conductance.

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[23] We do not want to state here that DNA is a semiconductor. Further investigations on dry DNA would be needed to support such a statement.
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