

Optimized fabrication and electrical analysis of silver nanowires templated on DNA molecules

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We report on the electrical conductivity measurement of silver nanowires templated on native λ -bacteriophage and synthetic double-stranded DNA molecules. After an electroless chemical deposition, the metallized DNA wires have a diameter down to 15 nm and are among the thinnest metallic nanowires available to date. Two-terminal I - V measurements demonstrating various conduction behaviors are presented. DNA templated functional nanowires may, in the near future, be targeted to connect at specific locations on larger-scale circuits and represent a potential breakthrough in the self-assembly of nanometer-scale structures for electronics layout. © 2006 American Institute of Physics. [DOI: 10.1063/1.2234282]

Recent developments in DNA-based nanotechnology have shown the suitability of this novel assembly method for constructing useful nanostructures.^{1,2} DNA molecules can serve as precisely controllable and programmable scaffolds for organizing functional nanomaterials^{3,4} in the design, fabrication, and characterization of nanometer scale electronic devices and sensors.⁵ DNA templated metallic nanowires are an example of the capability of DNA scaffolds and have been considered an interesting research subject since 1998, when first reported by Braun *et al.*⁶ Since then, DNA has been metallized with silver,⁷ gold,⁸ palladium,⁹ platinum,¹⁰ and copper.¹¹ Up to this point most templates for fabricating nanowires have used *native* bacteriophage λ -DNA molecules. Recently we proposed to use complex self-assembled superstructures composed of DNA “tiles”^{1,2} as scaffolds for templating functional nanoelectronic devices.¹² Specifically, we have reported on three distinct self-assembled one-dimensional DNA nanostructures: cross-tile nanoribbons,¹³ triple-crossover nanotubes,¹⁴ and three-helix nanobundles¹⁵ and successfully demonstrated the use of these artificially designed DNA nanostructures as nanowire scaffolds. In this letter, we present the base sequence design of synthetic double-stranded DNA (dsDNA) and fabrication of metallic silver nanowires templated on both synthetic dsDNA and bacteriophage λ -DNA molecules. We also demonstrate the electrical conductivity of our metallized nanowires. While nonmetallized DNA molecules do not appear to be highly conductive,¹⁶ the DNA templated metallic nanowires promise to become useful as programmable interconnects in bio-electronic devices.

The DNA base sequence of the synthetic unit dsDNA tile was designed to minimize the chance of sequence symmetry and undesired associations.¹⁷ The strand sequence for the molecules used here is given in Fig. 1. A unit dsDNA molecule consists of 50 nucleotides (nts), has length ~ 16.2 nm, and was designed to concatenate and form long double-helical DNA. Synthetic oligonucleotides were purchased from Integrated DNA Technology Inc. and purified by poly-

acrylamide gel electrophoresis (PAGE). Complexes were formed by mixing a stoichiometric quantity of each strand in standard buffer, $1\times$ TAE/Mg⁺⁺ [40 mM Tris acetate (pH 8.0), 2 mM EDTA, and 12.5 mM magnesium acetate]. Oligo mixtures were cooled slowly from 95 to 20 °C in 2 l of boiled water in a styrofoam box for two days to facilitate hybridization. Incubation of annealed samples at 4 °C overnight prior to examination by atomic force microscopy (AFM) improved the quality of the imaging data.

Native λ -DNA (Promega Inc.), about 50 000 base pairs in length, with a concentration of 1.6 nM and synthetic dsDNA molecules of 1.0 μ M were visualized by tapping mode AFM in air and under buffer, respectively. For AFM imaging in air, samples were prepared by pipetting λ -DNA solution (~ 20 μ l) onto a mica substrate, they were allowed to adhere for 5 min, rinsed gently by doming a drop of water onto the mica, then dried under a stream of nitrogen. For AFM imaging in liquid phase, ~ 5 μ l sample was spotted on mica and left to adsorb to the surface for 5 min. Then, 30 μ l of buffer was placed onto the mica and another 30 μ l of buffer was pipetted onto the AFM tip. Imaging was performed under buffer in a tapping mode fluid cell on a Multimode NanoScope IIIa (Digital Instruments) using NP-S tips (Veeco Inc.). Figure 2(a) is an AFM image of λ -DNA and (b), synthetic DNA. From the inset in Fig. 2(b), we see the helical pitch of the DNA molecules with a peak-to-peak distance of 3.4 ± 0.3 nm, in good agreement with the known distance of ~ 3.4 nm. The length of the synthetic dsDNA varies from a

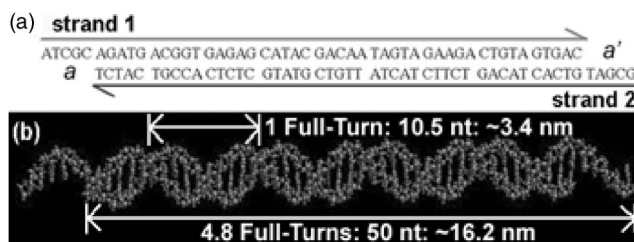


FIG. 1. (a) DNA base sequences of synthetic dsDNA molecules. The arrows indicate simplified strands running from 5' to 3'. The complementary sticky end of *a* is *a'*. (b) An atomic-resolution cartoon of a unit dsDNA molecule which consists of 50 base pairs with 46% CG content.

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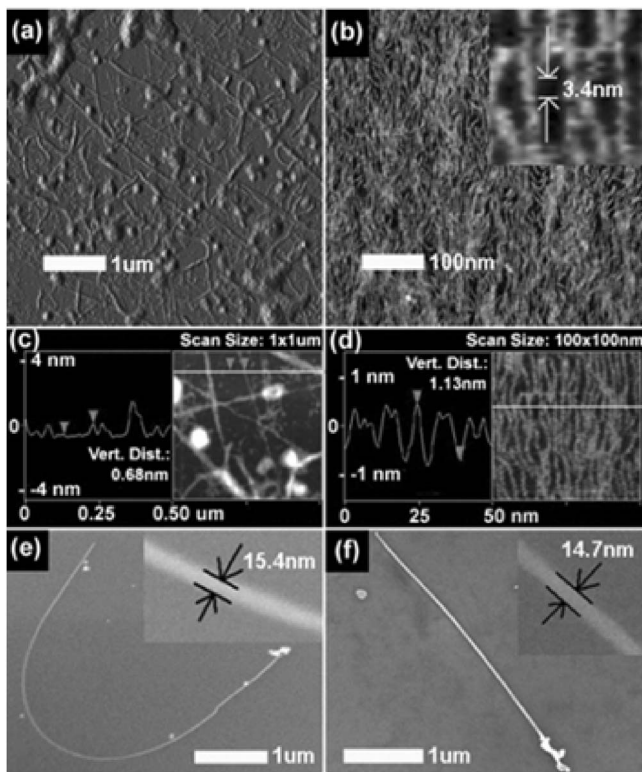


FIG. 2. (a) AFM image of λ -DNA in air. (b) AFM image of synthetic dsDNA in liquid phase. (Inset) In a high resolution AFM image with a periodic bump pattern on the dsDNA. (c) and (d) are height measurements of single λ -DNA (~ 0.7 nm) in air and synthetic dsDNA (~ 1.1 nm) molecules under buffer. (e) and (f) are SEM images of λ - and synthetic-dsDNA after two-step silver metallization process.

few hundreds of nanometers to several microns with average length of $\sim 5 \mu\text{m}$. Representative section profiles of single λ -DNA height of ~ 0.7 nm and synthetic dsDNA of ~ 1.1 nm are shown in Figs. 2(c) and 2(d). Empirically, we noticed that the tapping mode AFM height of single layer duplex DNA molecules were 0.6 ± 0.2 nm in air¹⁸ and 1.2 ± 0.2 nm under buffer where the known diameter of the double-helix DNA molecules was ~ 2 nm. These heights are in good agreement with the ones measured previously under similar conditions.

We applied a two-step metallization process¹⁹ to coat λ -DNA and synthetic dsDNA molecules in silver. Study of lengths and diameters of silver nanowires, formed on dsDNA, had shown their dependence upon the times of incubation of the DNA with glutaraldehyde treatment both at room temperature and on ice, time of dialysis, and time of incubation of DNA with the initiator AgNO_3 . We have found that the optimal conditions yielding nanowires with average lengths of $3 \mu\text{m}$ and average widths of 35 nm can be obtained from the following parameter values; DNA sample was incubated with 0.2% glutaraldehyde in $1 \times \text{TAE}/\text{Mg}^{++}$ buffer on ice for 30 min, then at room temperature for 20 min, then DNA sample was loaded into a Slide-A-Lyzer Mini Dialysis unit, and dialyzed for 15 h at 4°C in 1 l of $1 \times \text{TAE}/\text{Mg}^{++}$ buffer (we describe the complete procedure in Ref. 19). Figures 2(e) and 2(f) are scanning electron microscopy (SEM) images of λ - and synthetic-dsDNA templated silver nanowires. The metallized nanowires display widths down to 15 nm and lengths up to $7 \mu\text{m}$. We observed that the nanowires width (as measured by SEM) and height

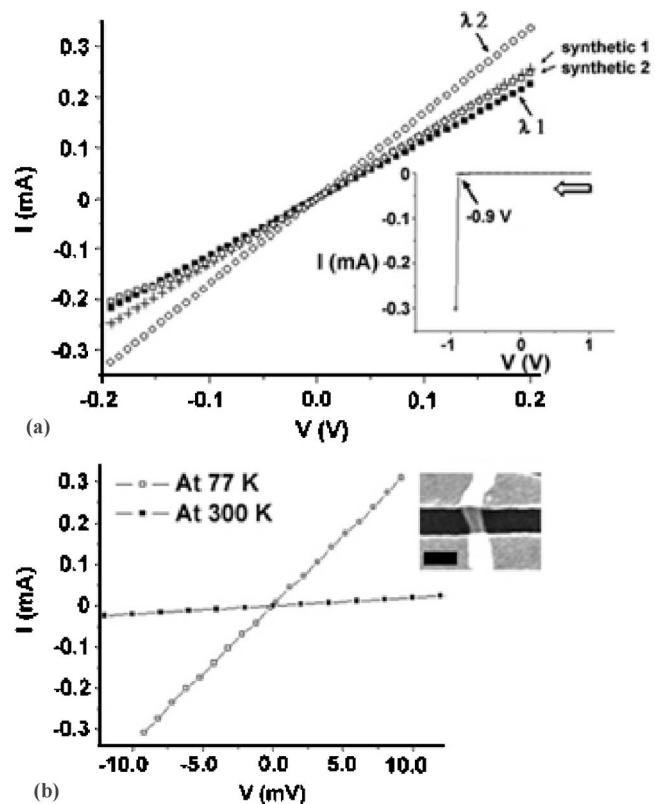


FIG. 3. (a) Linear two-terminal I - V characteristics of silver nanowires. (Inset) Initial high resistance can be reduced by applying bias voltage. The white arrow indicates voltage sweep direction. After the first few sweeps of bias voltages, current dramatically changes at a certain critical voltage V_c (here, $V_c = -0.9$ V). (b) The I - V curves of a silver nanowire measured at two different temperatures, 300 and 77 K. (Inset) SEM image of an actual device with scale bar, 100 nm. Cr-Au double layer electrodes, with 5 nm of Cr followed by 25 nm of Au, were patterned by electron beam lithography onto the nanowires on the silicon substrate.

(as measured by AFM) agree with one another within $\sim 10\%$.

We next performed two-terminal I - V measurements of the silver nanowires templated on both λ - and synthetic-dsDNA molecules. In many samples, the as-prepared wire resistance was very high and dramatically decreased following several voltage sweeps in the range of about ± 3 V [inset of Fig. 3(a)]. Most probably the initial high resistance is caused by an oxide or contamination layer covering the nanowire, which prevents formation of an adequate contact between the nanowire and the metal leads. No visible granularity was observed in the SEM [Figs. 2(e) and 2(f)], so a weak coupling between grains along the length of the wires seems to be an unlikely explanation for the initial highly resistive state. The oxide or contamination layer is evidently destroyed upon application of a large enough source-drain voltage V_c . The magnitude of V_c in different nanowires varies from a few millivolts to roughly 3 V. The two-terminal I - V curves of about 30 (out of 70) samples in the low-resistance state show mostly linear behavior. The samples presented in Fig. 3(a) demonstrate resistances of 895 Ω for a first λ -DNA templated nanowire ($\lambda 1$), 597 Ω for a second sample ($\lambda 2$), 798 Ω for a first synthetic dsDNA templated nanowire (synthetic 1), and 784 Ω for a synthetic 2 measured at 0.1 V. These numbers correspond roughly to bulk resistivities (ρ) of $\sim 20, 10, 5, 4 \times 10^{-6} \Omega \text{ m}$ for $\lambda 1, \lambda 2$, synthetic 1, and synthetic 2, respectively. The resistivity of bulk silver is $1.6 \times 10^{-8} \Omega \text{ m}$. We observed that larger V_c typically

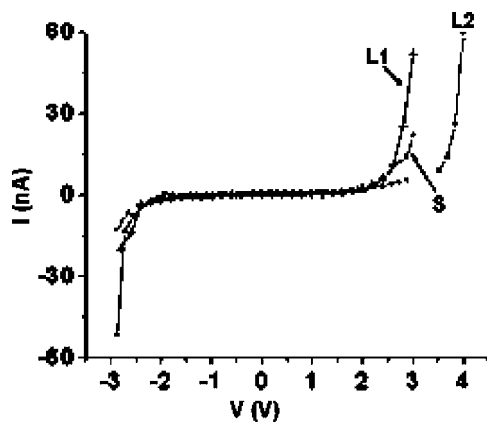


FIG. 4. Nonlinear two-terminal I - V characteristics of silver nanowires. About 15% of total number of measured nanowires are non-Ohmic and may have slightly asymmetrical $I(V)$ with respect to zero bias. Among them, three data sets, two from λ indicated L1 and L2 and the other S from synthetic-dsDNA templated wires, are shown.

resulted in larger resistance (R) after the increase in conductance that followed the application of high current. Finally, Fig. 3(b) shows I - V curves of the ~ 35 nm width nanowire with ~ 110 nm between electrodes and shows R of ~ 500 Ω at 300 K and ~ 30 Ω at 77 K. This change of resistance (~ 17 -fold for a change in temperature of about 4-fold) is unexpectedly large, compared to the available data on nanostructured silver films of a significantly higher conductivity.²⁰

We also note that about 10 nanowires out of 70 showed non-Ohmic $I(V)$ behavior after the initial increase in conductance. In these cases, the oxide/contamination layers between electrodes and nanowires might not be removed thoroughly during applying bias voltages even at voltages higher than V_c . After applying voltages higher than 5 V, most nanowires were damaged severely and become disconnected. The range of biases where the conductance was suppressed varied from a few millivolts to ~ 6 V. Three typical I - V nonlinearities are shown in Fig. 4.

In conclusion, we have presented a method for fabrication of metallic silver nanowires, templated on λ -DNA and synthetic dsDNA molecules, which have been formed by a two-step chemical deposition of silver. The nanowires display uniform widths down to ~ 15 nm and lengths up to 7 μm ; these results are easily reproducible. We have also demonstrated two-terminal I - V curves of silver nanowires. Understanding of the mechanism limiting the preinitialized conductance of the wires is necessary before these DNA templated wires can be reliably used as interconnects in bioelectronic nanodevices.

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