Analysis of Scattering of Conduction Electrons in Highly Conducting Bamboolike DNA-Templated Gold Nanowires

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Over the past decade the field of nanoelectronics has emerged as an active area of research in an effort to provide a bottom-up approach to the directed assembly of nanoscale electronic device components. This is proposed as an alternative to the top-down approach of conventional device fabrication, which is expected to reach fundamental limits within the next 10 to 15 years, when alternative fabrication techniques applied to the production of novel devices for data processing and storage will be required.

Within this new paradigm, the ability of DNA to act as a template for the self-assembly of nanoscale components into complex device structures could play an important role. Already, DNA has been proven to be a versatile template for metal nanowires, which are of considerable interest to nanoelectronics because of their potential use as interconnects,[1,2] unidirectional heat sinks, sensors,[3] or integral device components.[4] It is well-known that as the dimensions of a conductor shrink, the resistivity increases due to increased scattering of the conduction electrons by the surface of the conductor[5] and by internal grain boundaries[6] whose dimensions often scale with the external dimensions of the conductor. A key issue for nanotechnology is how significantly this increased scattering affects the transport properties of nanowires.

DNA has been exploited as a template for the fabrication of nanowires of a range of materials such as silver,[7] gold,[8−10] palladium,[11,12] and cobalt,[13] although gold is of particular interest because of its high intrinsic conductivity and resistance to oxidation under ambient experimental conditions. Electrical measurements on DNA-templated gold nanowires have generally shown an enhanced resistivity compared to the bulk value, but even the work that has demonstrated the most highly conducting DNA-templated gold nanowires to date has not been able to quantitatively account for the enhanced resistivity.[9,10] Increased scattering due to impurities or other defects associated with a bottom-up approach and/or a high contact resistance may also play a role.

Here we report electrical measurements on highly conducting, bamboolike, DNA-templated gold nanowires that show that the enhanced resistivity can be adequately explained by scattering of conduction electrons by the grain boundaries with perhaps a minor contribution from surface scattering.

The nanowires are produced according to the following four step approach: (i) immobilization of the DNA template, (ii) partial metallization of the DNA by exposure to a solution of suitably charged gold nanoparticles, (iii) full metallization by electroless plating of these nanoparticles to produce continuous nanowires, and (iv) integration of the nanowires into a circuit for electrical characterization. Earlier work using this broad approach resulted in poorly conducting gold nanowire devices.[14]

Key changes to this approach have been made. First, polystyrene-coated silicon wafers are used, instead of plasma-treated oxide-coated wafers, so that the DNA can be stretched straight by molecular combing.[15,16] A single linearly elongated drop of DNA solution is dragged across the wafer surface resulting in a high degree of alignment of DNA in a predictable manner across large areas of the wafer. The polystyrene layer is carefully removed from underneath after nanowire fabrication so that the nanowires are deposited on the underlying oxide-coated wafer without disturbing their orientation.

Second, a major advance in this report is the use of a hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and tetrachloroauric acid ($HAuCl_4$) mixture, for the electroless plating of gold onto the nanoparticles templated by the DNA to enlarge and enjoin the nanoparticles to form continuous nanowires. Hydroxylamine has been used as a reducing agent in electroless deposition by a number of researchers. Williams et al. reported the formation of iron oxide/gold core/shell nanoparticles,[17] and Natan et al. have used hydroxylamine to enlarge gold nanoparticles in solution[18,19] and form

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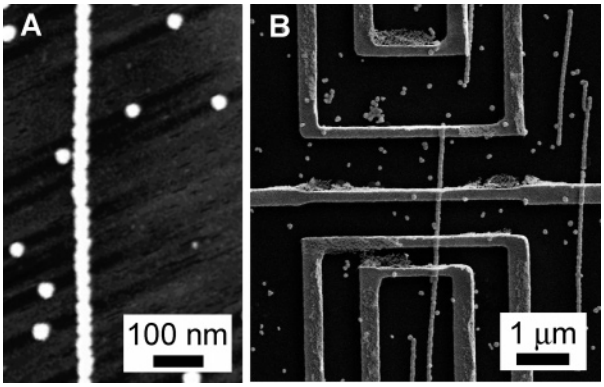

Figure 1. (A) AFM tapping mode image of DNA-templated gold nanowire. (B) SEM image of a typical sample of track and electrode chip layout deposited on top of DNA-templated gold nanowires. Collinear orientation of nanowires and tracks avoids short circuits across the tracks.

conductive gold films from particles immobilized on a substrate.[20] Figure 1A shows an atomic force microscopy (AFM) image of a DNA-templated gold nanowire. The bamboolike structure is clearly visible here and in the scanning electron microscopy (SEM) images in Figure 4 below. The height of the nanowire from Figure 1A was determined to be 21 nm. SEM analysis of nanowires from the same region of the wafer resulted in average diameter measurements of 44 nm, thus indicating a semi-cylindrical structure. The nanowires are robust and well-distributed with the result that it is easy to find correctly oriented nanowires across macroscopic areas of the wafer. This is illustrated in Figure S2 in Supporting Information.

Third, electrical contact to the nanowires is made through a track and electrode layout that is patterned on top of the nanowires. This approach should result in a low contact resistance.[8,10,21] The layout is designed so that the tracks are collinear with the nanowires to avoid the nanowires spanning two or more tracks and causing a short circuit; the electrodes are perpendicular to the tracks at the center of each chip where the nanowires are contacted, as illustrated in Figure 1B. Full details of procedures for the nanowire fabrication and lithographic deposition of electrodes can be found in Supporting Information.

Four-terminal two-probe resistance measurements were carried out on segments of nanowires of a range of lengths and average diameter of 79 nm as shown in Figure 2. The resistance data is plotted against L/A in Figure 3, and the slope of the best fit of a straight line to this data yields a resistivity value of $3.9 \pm 0.3 \times 10^{-8}$ Ω m. The contact resistance was determined to be 0.8 ± 0.9 Ω, confirming good contact between the electrodes and the nanowires. The quoted uncertainties were returned by the software used to carry out the best fit to the data. It is important to note that despite the resistivity being close to the bulk value for gold, the bulk value lies outside the range of uncertainty so that we can say with confidence that the measured resistivity is

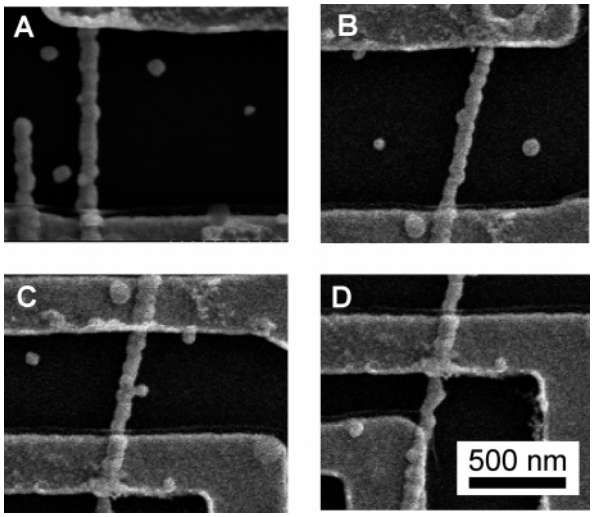

Figure 2. SEM images of four DNA-templated gold nanowire segments for resistance measurements. Average diameter = 79 nm, height = 40 nm, lengths = (A) 883 nm, (B) 918 nm, (C) 573 nm, and (D) 353 nm.

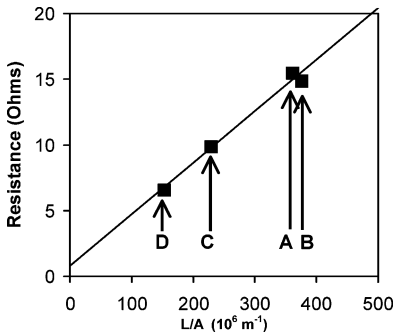

Figure 3. Plot of measured values of resistance for nanowire segments from Figure 2 against L/A (squares) and best fit of a straight line to these data points, the slope of which is the resistivity of the nanowires (solid line).

higher than that of bulk gold. This can be explained by considering the effects of surface and grain boundary scattering.

Durkan and Welland have shown for gold that only when the dimensions of nanowires decrease below about 25 nm does surface scattering significantly affect the resistivity.[22]

Therefore, for now, we shall only consider the effects of grain boundary scattering on the resistivity. Assuming that Matthiessen's rule holds, we can apply the Mayadas−Shatzkes model for grain boundary scattering:[6,23]

$$\rho = \rho_0\left[1 - \frac{3\alpha}{2} + 3\alpha^2 - 3\alpha^3 \log_e\left(1 + \frac{1}{\alpha}\right)\right]^{-1} \qquad \alpha = \frac{\lambda}{D}\frac{R}{1-R}$$

where λ is the mean free path of electrons in the bulk material, D is the average distance between grain boundaries, and ρ_0 is the resistivity of the bulk material. An analysis of a high-resolution SEM image of the nanowire segment from Figure 2C has determined the average grain boundary separation to be approximately 57 nm (see Figure 4). Thus we can determine a value for R, the grain boundary reflectivity parameter. The mean free path, λ, is taken to be 40 nm.[22] Using these parameters, the resistivity is plotted as a function of R in Figure 5. The value of R that gives the

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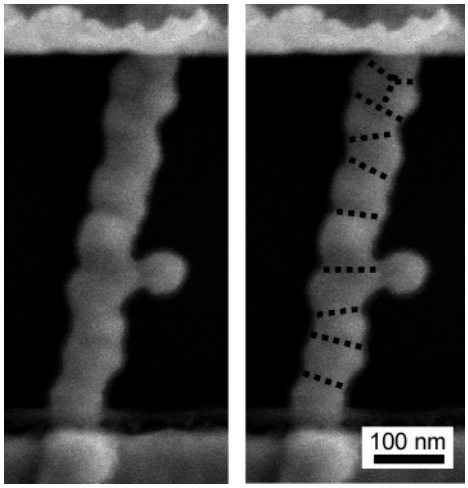

Figure 4. (Left) High-resolution SEM image of the nanowire segment from Figure 2C. The bamboolike morphology of the nanowire is clearly visible. (Right) Grain boundaries in the nanowire segment are identified and marked in the image as dashed lines. There is an average grain boundary separation of 57 nm along the length of the nanowire.

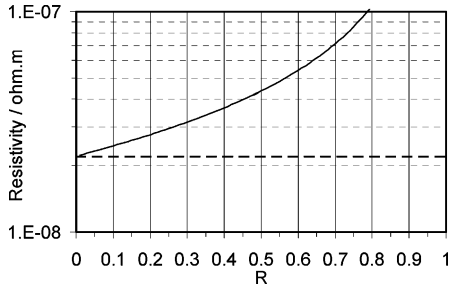

Figure 5. Plot of enhanced resistivity for gold (solid line), as predicted by the Mayadas−Shatzkes model, compared to the bulk value (dashed line) as a function of *R*, the reflectivity parameter for the grain boundaries. $\lambda =$ 40 nm, $D = 57$ nm.

closest value of ρ to the experimental value can now be read off and was determined to be 0.44. Considering the 0.3×10^{-8} Ω m uncertainty in the resistivity, *R* has a range from 0.39 to 0.48.

A value of 0.35 ± 0.05 has been determined from resistivity measurements of thin gold films of various thickness and temperature,[24] although values as low as 0.295 ± 0.02[25] and as high as 0.45[26] have also been obtained.

In contrast, some very large values for *R* have been determined by scanning tunneling potentiometry (STP) of individual grain boundaries to be in the range of 0.7 to 0.9.[27] This discrepancy was resolved by conducting AFM experiments by Bietsch and Michel[28] on lithographically patterned gold nanowire structures. Their work determined the resistance of several individual grain boundaries, from which *R* could be estimated, and their results showed that there is a wide range of *R* values for different grain boundaries within any given sample, from less than 0.2 up to 0.8 (a value similar to that determined from STP). This suggests that although some grain boundaries are highly reflective, an average value for *R* from a statistical sample of grain boundaries would be in the range of 0.1 to 0.4, consistent with the lower values obtained from resistivity measurements on thin films of gold and with the value for *R* obtained here, even though the nanowire here represents a statistically small sample size of grain boundaries.

The value for *R* obtained from the nanowire is clearly at the higher end of the range of *R* values obtained from thin gold films, and quite possibly this results from an overestimation of the contribution that grain boundary scattering makes to the resistivity. A contribution from surface scattering to the resistivity can be roughly estimated by considering *R* to be 0.35 as obtained by the work on thin films by de Vries.[24] From the plot in Figure 5, a value of 0.35 for *R* would lead to a resistivity of 3.4×10^{-8} Ω m, leaving in a balance of 0.5×10^{-8} Ω m as an estimate of the contribution from surface scattering to the resistivity, that is, about a 25% increase in resistivity above the bulk value. This is consistent with an approximately 35% increase for singly twinned silver nanobeams of the same cross-sectional area.[29]

The ability of DNA to template nanowires that are almost as highly conducting as the bulk material represents a crucial step in realizing the nanoscale integration of nanoelectronic devices. The results presented here show that a bottom-up assembly approach can be employed for the fabrication of nanoscale conductors that are as highly conducting as can be expected once surface and grain boundary scattering effects on the resistivity are taken into account. There is no erroneous increase resistivity that needs to be accounted for by considering additional contributions to scattering from impurities or from defects arising from poor wire quality.

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Supporting Information Available: Detailed description of materials and methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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