NANO LETTERS

2003
Vol. 3, No. 3
359−363

DNA-Templated Construction of Copper Nanowires

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Received January 9, 2003; Revised Manuscript Received January 23, 2003

ABSTRACT

We have developed a method to deposit Cu metal onto surface-attached DNA, forming nanowirelike structures that are ~3 nm tall. DNA is first aligned on a silicon surface and then treated with aqueous $Cu(NO_3)_2$. After the copper(II) has electrostatically associated with the DNA, it is reduced by ascorbic acid to form a metallic copper sheath around the DNA. The resulting nanostructures have been observed and characterized by atomic force microscopy. A more complete coating can be obtained by repeating the Cu(II) and ascorbic acid treatment. Control experiments involving treatments with aqueous solutions containing either NO_3^- or the divalent cation Mg^{2+} show no change in DNA height upon ascorbic acid exposure. These experiments indicate that copper nanowires, which may be valuable as interconnects in nanoscale integrated circuitry, can be readily generated from DNA molecules on surfaces.

Over the past few decades, the size of features on integrated circuits has rapidly decreased, principally because of improvements in the lithographic materials and techniques used to create microstructures. As the size of the smallest circuit components passes below 100 nm, the use of optical patterning techniques becomes much more complicated primarily because of the ambient absorption of hard ultraviolet radiation.[1] Other lithographic techniques are being developed, including scanning probe lithography[2] and electron beam lithography,[3] but these are both more expensive than optical approaches and presently lack scalability to high throughput. Thus, alternative methods of creating miniaturized circuit components are being investigated. Particularly appealing are "bottom-up" strategies, which involve the creation of a structural base and then the assembly and creation of the circuit components directly on the base with relatively little human intervention. One potential bottom-up method involves using DNA to arrange and bind circuit components to a surface, taking advantage of the specificity with which DNA base pairs interact. Although this approach offers an attractive method for the bottom-up spatial localization of components, surface-adsorbed DNA has been observed to have low intrinsic conductivity,[4] and thus techniques must be developed to provide conductive electrical connections between assembled components on the DNA template.

The deposition of silver,[5] gold,[6] platinum,[7,8] and palladium[9,10] metal on DNA has been investigated as a potential approach for creating conductive nanowires. Indeed, Braun et al. recently reported not only making conducting gold and silver nanowires from DNA templates but also protecting specific regions of DNA molecules from metal deposition by associating proteins along sections of the DNA.[6] The ability to control metallization spatially provides an important step toward the bottom-up assembly of functional nanocircuits.

Interestingly, although copper is a metal presently used to create connecting wires in integrated circuits,[11] the DNA-directed fabrication of metallic copper nanostructures has remained elusive. The lack of experimentation with copper may be partially due to observations that some Cu(II) complexes can cleave DNA molecules.[12,13] However, the ability to generate copper nanowires from DNA templates could ease the transition from top-down lithographic fabrication techniques, which presently use copper, to bottom-up techniques. This capability could be a significant advance for nanoscale integrated circuit manufacturing. In this paper, we report the metallization of surface-attached DNA with copper to create nanowire structures that are up to 10 nm tall and average around 3 nm in height.

A section of a polished silicon (100) wafer (TTI Silicon, Sunnyvale, CA) was rinsed three times in water from a Barnstead (Dubuque, IA) purification system and then treated with 45 μL of 1 ppm poly-L-lysine diluted in water from a 0.1% stock solution (Ted Pella, Redding, CA). The poly-L-lysine interacts with the silanol groups on the silicon surface and presents a positive charge to bind electrostatically the phosphate groups on DNA. After 2−3 min, the poly-L-lysine solution was removed, and the surface was again rinsed three times with water. DNA was then aligned on the surface using a previously developed method.[14] Briefly, a 1-μL droplet of a 2 ng/μL λ double-stranded DNA solution (New England Biolabs, Beverly, MA) was pipetted onto the surface, held in place by surface tension between a microscope slide cover slip and the substrate, and then linearly moved across the surface using a three-axis translation stage. After the droplet

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10.1021/nl034016+ CCC: $25.00
Published on Web 02/14/2003

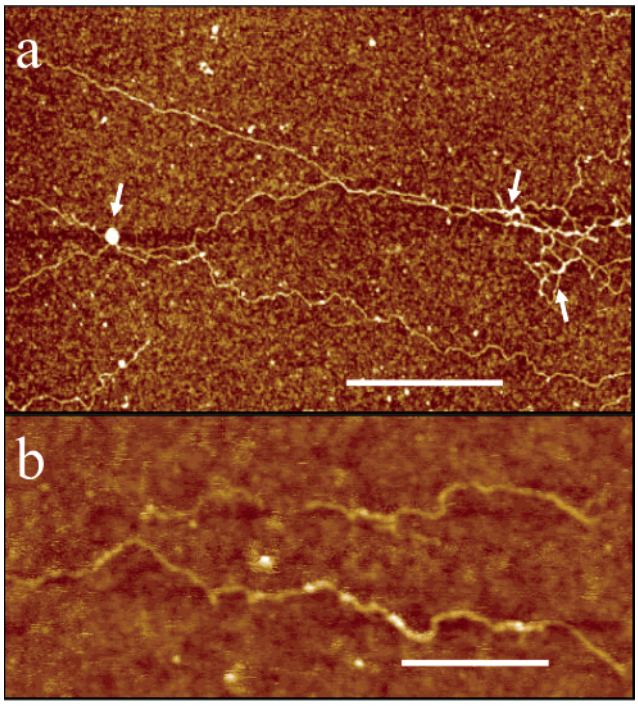

Figure 1. AFM height images of λ DNA deposited on silicon. (a) Image of a larger area showing several long, continuous strands of DNA. Arrows indicate slightly raised features on the DNA. Scale bar is 1 μm. (b) Image of a smaller area. Scale bar is 250 nm. In both images, the height scale is 5 nm.

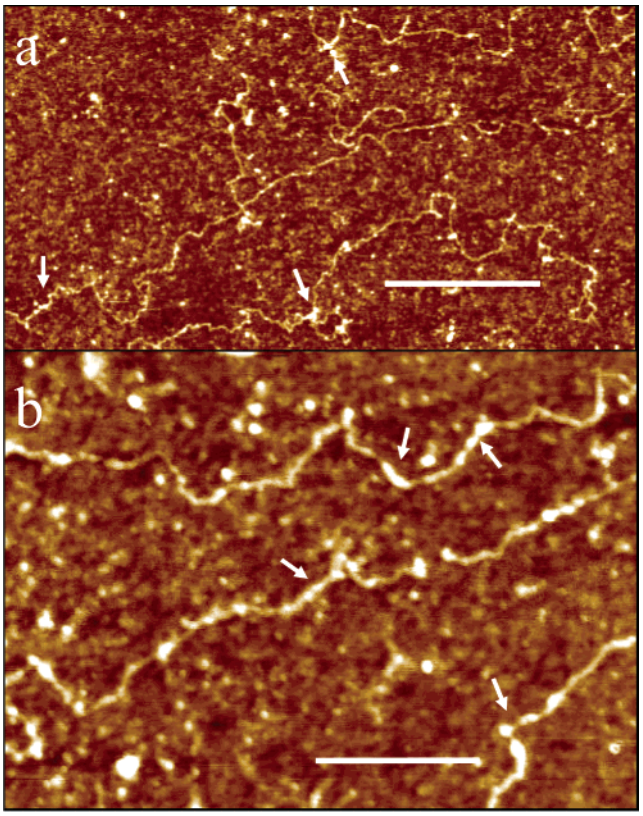

Figure 2. AFM height images of λ DNA deposited on silicon and treated once with copper(II) nitrate followed by ascorbic acid. (a) Image of a larger area. The raised areas, some of which are indicated by arrows, correspond to specific copper deposition on the DNA templates. Scale bar is 1 μm. (b) Smaller-scale image. Regions where Cu has deposited (see arrows) have an increased height compared to the image in Figure 1b. Scale bar is 250 nm. In both images, the height scale is 5 nm.

was translated across the surface, we removed the droplet and rinsed the surface to dislodge any unbound DNA. The surface was then analyzed using an atomic force microscope (AFM)[15] equipped with a carbon nanotube-modified tip.[16−19] Processed AFM images were used to determine the average height of the aligned surface structures.[20] Nanostructure heights rather than widths were measured because observed heights are not affected by variations in tip radius.

The surface with aligned DNA was treated with 35−45 μL of 0.1 M aqueous $Cu(NO_3)_2$ (Mallinckrodt Baker, Paris, KY) for 3−5 min in a darkened room. During incubation, the positively charged copper ions associated with the negatively charged DNA phosphate groups. The electrostatic association of DNA and divalent cations has been reported previously,[21] and the association of Cu(II) ions with surface DNA should be similar in nature. After the incubation time had elapsed, 35−45 μL of 0.1 M ascorbic acid (Fisher Scientific, Fair Lawn, NJ) was added to reduce the Cu(II) ions to metallic Cu^0. This reaction was allowed to proceed in the dark for 5−8 min, and then the combined solutions were removed from the surface. We observed that longer ascorbic acid treatment times (15 min or greater) caused increased amounts of nonspecific Cu^0 reduction. The surface was rinsed three times with water and imaged using AFM, and the heights of the resulting DNA/Cu^0 nanostructures were measured. In some instances, the $Cu(NO_3)_2$ and ascorbic acid treatments were repeated, and further Cu^0 deposition was profiled by AFM.

Before treatment with Cu(II), the DNA height appeared uniform, with a few small regions that were slightly raised, indicated by arrows as shown in Figure 1. These raised regions in the untreated DNA likely correspond to overlapping DNA strands, contaminant particles on the surface, or localized secondary structure in the DNA. After treatment with $Cu(NO_3)_2$ and ascorbic acid, the surface DNA had numerous sections with raised height, which we attribute to Cu^0 deposition, as well as some sections that were unaffected, as shown in Figure 2. The elevated features in these images represent areas where copper associated with the surface DNA was reduced and then the Cu^0 acted as a nucleation site for further metallization. These raised areas both increased in height and covered more extensive portions of the surface DNA upon subsequent copper(II) nitrate treatment and ascorbic acid reduction, as shown in Figures 3 and 4. Nonspecific Cu^0 deposition also occurred, as can be seen in Figures 2 and 3, because of Cu(II) in solution being reduced by ascorbic acid and presumably falling to the surface. Reduction times of ~5 min were used to minimize this nonspecific deposition; however, the building up of nonspecifically deposited Cu^0 limited to around two the number of treatments that could be performed before nonspecific Cu^0 deposition obscured the DNA. These results suggest the feasibility of creating Cu nanowires with ~10 nm diameters along surface DNA molecules by performing multiple Cu(II) treatments followed by ascorbic acid reductions.

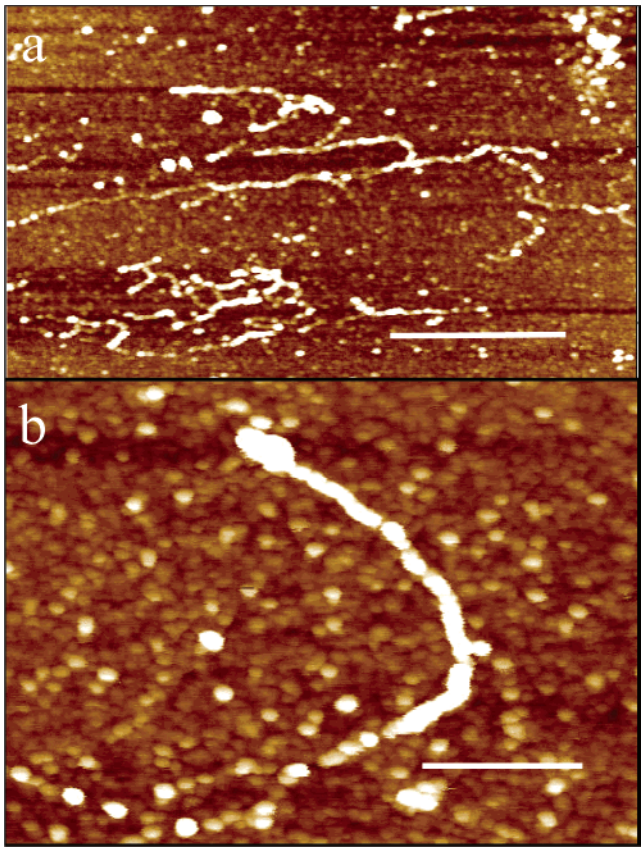

Figure 3. AFM height images of λ DNA deposited on silicon and treated twice with copper(II) nitrate and ascorbic acid. (a) Image of a larger area. After two treatments, the raised features covered more extensive areas of the DNA (cf. Figure 2a). Scale bar is 1 μm. (b) Smaller-scale image. The copper deposition has become more even in this area, but unprotected sections of DNA are also vulnerable to cleavage, as is seen in the lower left area of the image. The scale bar is 250 nm. In both images, the height scale is 5 nm.

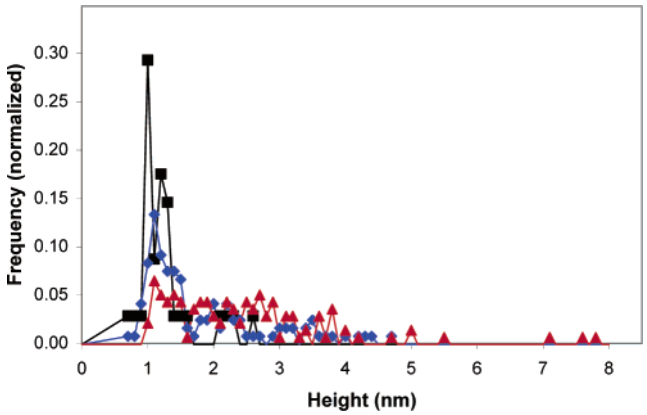

Figure 4. Relative frequency of DNA heights, normalized and sorted by increments of 0.1 nm. The untreated DNA (■) appears in two clusters: <1.6 nm and >2 nm. The heights that are <1.6 nm correspond to unmodified double-stranded DNA. The larger height observations may be due to areas of secondary structure within a double-stranded DNA segment or multiple DNA strands that overlap. After one (♦) and two (▲) $Cu(NO_3)_2$ and ascorbic acid treatments, the frequency of observed heights below 1.6 nm becomes successively smaller, whereas the frequency of >2 nm height observations greatly increases. The zero frequency points have been omitted from the plot for clarity. Roughness measurements of an atomically flat mica substrate indicate that the noise level in measuring AFM heights under these conditions is below 0.05 nm, or half the bin size.

Some DNA segments did not have noticeable metal deposition even after two treatments. This is evident in Figures 3a and b and 5b and c, which show surfaces that were treated with cupric nitrate and ascorbic acid for the second time several days after their first treatment. Interestingly, sections of DNA that had no protecting layer of copper metal were cleaved (Figure 5b), whereas segments protected by deposited metallic Cu were not fragmented (Figure 5c). Copper(II) complexes have previously been reported to cleave DNA under specific conditions;[12,13] in our experiments, a combination of oxidation from oxygen in the air or some ambient contaminant is likely involved in the copper(II) cleavage of DNA. This phenomenon can be useful in determining the degree to which the DNA has been coated with copper and also indicates that the uniform metallic coatings both cover the DNA and protect it from cleavage. Cu(II)-induced DNA cleavage might also be valuable for removing unneeded DNA from the surface after metallization.

Treating surface-adsorbed DNA with copper(II) nitrate and ascorbic acid resulted in a significant increase in the observed height of localized regions on the DNA. In subsequent treatments, not only did the height increase but the copper also covered more extensive regions on the surface DNA. On the basis of images taken from three different samples, 10−25% of the length of the DNA showed significant copper deposition (denoted by a total height >2 nm) after one treatment. For DNA that had been treated with copper twice, the areas of surface DNA showing significant deposition increased to 30−50%. Typically, after two depositions, enough time had passed that any further attempted reactions cleaved unprotected DNA instead of resulting in a more extensive metal coating. The horizontal dimensions of the AFM tip limited the ability of this approach to determine whether the coating formed a continuous metallic wire or if it was particulate in nature; experiments to elaborate the structure further are ongoing. A summary of the height data obtained is shown in Table 1. Control experiments using either nitrate or divalent magnesium ion treatments, followed by ascorbic acid exposure, were performed under conditions identical to those used in the Cu(II) treatment and ascorbic acid reduction. These experiments showed no surface DNA height increase and no DNA cleavage, confirming that both of these phenomena are due to the presence of Cu(II).

Upon treating surface DNA with copper(II) nitrate and ascorbic acid, a significant height increase was observed along as much as 50% of the DNA because of the deposition of copper metal around the DNA. The degree to which this process occurs can be controlled somewhat by the number of copper(II) nitrate/ascorbic acid treatments to which the DNA is subjected. Presently, the average thickness of the Cu metal deposited on top of the surface DNA using this method is around 20 Å. Future research on the effects of the copper metallization of DNA will include the optimization of the treatment process such that conductivity measure-

Table 1. Height of DNA after Various Treatments

		one Cu(II) treatment		two Cu(II) treatments	
	untreated DNA	metallized[a]	unaffected[b]	metallized[a]	unaffected[b]
average height (nm)	1.22	3.03	1.18	3.15[c]	1.36
std dev (nm)	0.43	0.69	0.24	0.73	0.28
% of DNA	100	10−25	75−90	30−50	50−70
surface roughness (nm)[d]	0.20	0.22		0.25	

[a] Defined as regions >2 nm high. [b] Defined as regions <2 nm high. [c] As shown in Figure 4, much taller metal deposits were seen in DNA treated twice with Cu(II) and ascorbic acid than after a single treatment. However, the growth (in previously uncoated regions) of more extensive metal deposits that were just over 2 nm high resulted in only a slightly greater average overall height. [d] Surface roughness was measured in areas lacking DNA on the surface; the increase in roughness after treatment is an approximate measure of the extent of nonspecific Cu deposition.

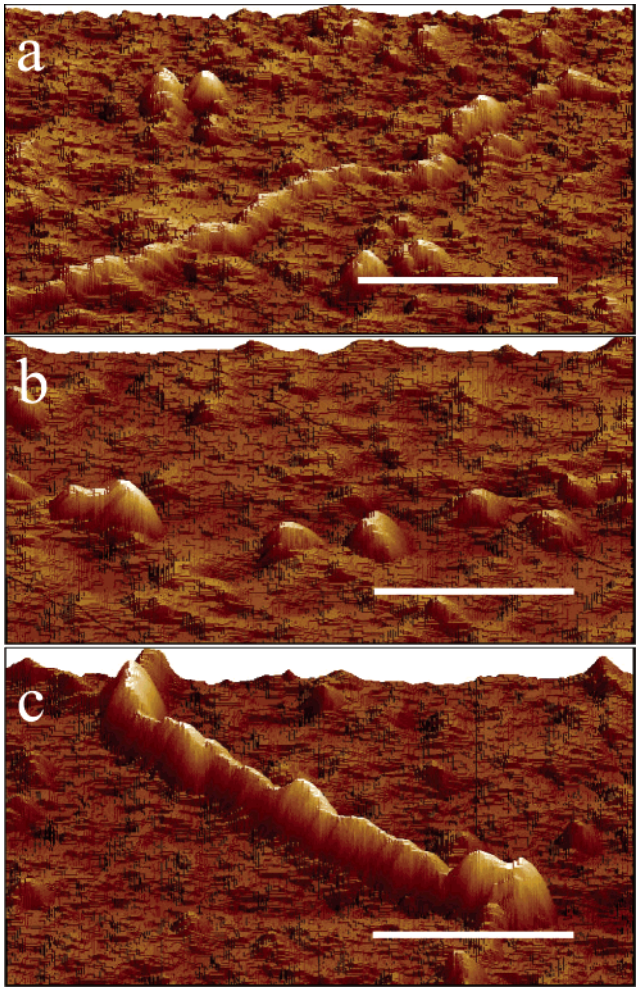

Figure 5. Processed, 3D-view AFM image of λ DNA deposited on silicon. (a) Untreated DNA; scale bar is 100 nm. (b) Area with cleaved DNA on a surface treated twice with copper(II) nitrate and ascorbic acid. The DNA appears to be broken into smaller fragments, which have about the same height as the untreated DNA seen in a. Scale bar is 100 nm. (c) DNA treated twice with copper-(II) nitrate and ascorbic acid. The elevated region is significantly higher than the unmodified DNA segment shown in a. Scale bar is 100 nm. Height scale is 6 nm for all three images.

ments can be performed on the synthesized nanowires. The DNA-templated generation of copper nanowires is a valuable advance in nanometer-scale science and an important step toward the formation of functional nanodevices from surface DNA segments linked to molecules or molecular assemblies that can function as switches, diodes, and so forth.

Acknowledgment. We thank Dr. Jason H. Hafner and Prof. Charles M. Lieber for providing Si substrates with single-walled nanotubes for attachment to AFM tips. Supported in part by startup funds from Brigham Young University. This material is based upon work supported in part by the U.S. Army Research Laboratory and the U.S. Army Research Office under grant number DAAD19-02-1-0353. We also acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. C.F.M. was supported in part by an Undergraduate Research Award of the College of Physical and Mathematical Sciences, Brigham Young University.

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(15) Images were obtained using a Multimode IIIa AFM and microfabricated Si cantilever tips (Digital Instruments, Santa Barbara, CA). Vibrational noise was reduced by using an active isolation system (MOD1-M, Halcyonics, Goettingen, Germany). During imaging, parameter settings were (i) resonant frequencies, 60−80 kHz; (ii) free oscillation amplitude, 0.5−1.0 V; (iii) setpoint, 0.3−0.7 V; and (iv) scan rate, 1.0−1.8 Hz.

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(19) To affix a nanotube to an AFM tip, the tip was used to image a silicon surface on which single-walled carbon nanotubes had been grown as described in ref 16. The Si surface with nanotubes was kindly provided by Professor Charles Lieber's group at Harvard University. When the tip contacted a nanotube that was vertically oriented, the nanotube occasionally detached from the surface and associated with the tip, resulting in an apparent change in the height of the image. When this type of abrupt jump in height was detected, the tip was checked for the presence of a protruding nanotube by using the force calibration mode to have the tip approach, contact, and retract from the surface. Nanotube protrusion was confirmed when elastic buckling was observed as a transient decrease in tip amplitude with no corresponding increase in tip deflection.
(20) To determine the height of a segment of DNA, the AFM image was first flattened to remove any tilt in the surface. A section profile was taken across the DNA segment of interest, and the height of the DNA relative to its surroundings was measured using software included with the AFM.
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