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Fabrication of Silver Nanowires based on DNA stretched by the LB Method

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The precise metallization of double-stranded DNA by the selective electroless plating method was investigated for the purpose of the fabrication of nanowires. Cis-platin was bound to template DNA molecules and reduced to platinum which can catalyze following silver metal deposition. We have found that when DNA-amphiphile polyion complex monolayer, which was formed at the air-water interface, was transferred to a glass substrate by using the Langmuir-Blodgett (LB) method, DNA molecules could be immobilized and stretched on the glass substrate. The DNA molecules combined with the platinum particles was also stretched and immobilized on a glass substrate by using the LB method. The electroless plating of the platinum-bound DNA molecules immobilized on the substrate by reduction of silver ion gave uniform silver nanowires (c.a. 50 nm in width and height) along the stretched DNA structures. On the contrary, the electroless plating of DNA molecules without the catalyst provided inhomogeneous silver deposition. Conductive AFM measurement revealed that the obtained silver nanowires as long as several μm had high conductivities.

Key words: DNA, cis-platin, electroless plating, nanowire, Langmuir-Blodgett

1. Introduction

The fine electronic circuits comprising computer chips are manufactured on Si-wafers using the photolithography technique. "Top-down" methods are well known as fine engraving techniques (photolithography), whereby larger materials are made smaller. The widths of electronic circuits in semiconductor devices have been achieved under 100nm. However, finer electronic circuit lines are required for future applications. Making them smaller includes the physical limitations of the fabrication techniques and enormous manufacturing costs will be serious difficulties. Recently, many scientists have been attracted to "bottom-up" methods, where molecular recognition-directed self-assembly and self-organization can be used to construct larger structures from tiny molecules and particles to yield the precise arrangements needed. Therefore the "bottom-up" method is expected to be a strong candidate as a nanoscale manufacturing technology in the future.

A double-stranded DNA molecule is a double helical chain consisting of nucleotides. The diameter of a DNA molecule is 2 nm and the length ranges from the nanometers to several millimeters depending on the molecular weight. Stretched DNA molecules are therefore suitable as templates for the fabrication of metal nanowires.[1-7] Sivan *et al.*[2] have reported the conductivity of a silver nanowire deposited along a DNA molecule connecting two micro-electrodes. Nakao *et al.*[3] have reported the ordered arrangement of metal particles along DNA molecules stretched and immobilized by "molecular combing" [7,8] method on a substrate. Keren *et al.*[4,5] have reported selective binding of protein to DNA that allowed of selective metal deposition. However, the number of experimental reports on conductivity measurements of DNA-based nanowires is limited. It is a critical requirement that the metal deposition occurred only on stretched DNA molecules.

In this report, we describe the fabrication of fine silver nanowires using stretched DNA molecules by using a selective electroless plating method. The electroless plating method is a fundamental technique for the deposition of metal on a specific surface by the reduction of metal ions in the presence of a catalyst.

When DNA is used as a template for the selective electroless plating method, a catalyst for the electroless plating needs to be bound to the DNA prior to the electroless plating. For this purpose, we chose platinum compounds as the catalyst precursor. For example, cis-platin, which has a good success rate for treating cancer, is a platinum compound that forms covalent bonds with the seventh nitrogen atom of such purine bases as adenine and guanine of DNA.[10-12] The selective electroless plating of DNA was carried out as shown in Fig. 1. In the first step, Cis-platin was reacted with and bound to the DNA molecules. Next, the platinum compound bound to the DNA was reduced by dimethylamine boran (DMAB) to platinum metal. Finally, the platinum metal deposited on DNA brings about silver electroless plating. The binding of cis-platin to DNA is strong enough to assist the deposition of silver metal to DNA selectively.

We have found that when a DNA-amphiphile polyion complex monolayer, which is formed at the air-water interface, was transferred to a glass substrate using the Langmuir-Blodgett (LB) method, DNA molecules could be immobilized on the glass substrate in a

stretched configuration.[13] The stretching direction of the DNA molecules is parallel to the lifting direction of the substrate. Because DNA combined with reduced platinum compounds was stretched and immobilized on a glass substrate by LB method, we could utilize the DNA as template to prepare silver nanowires.

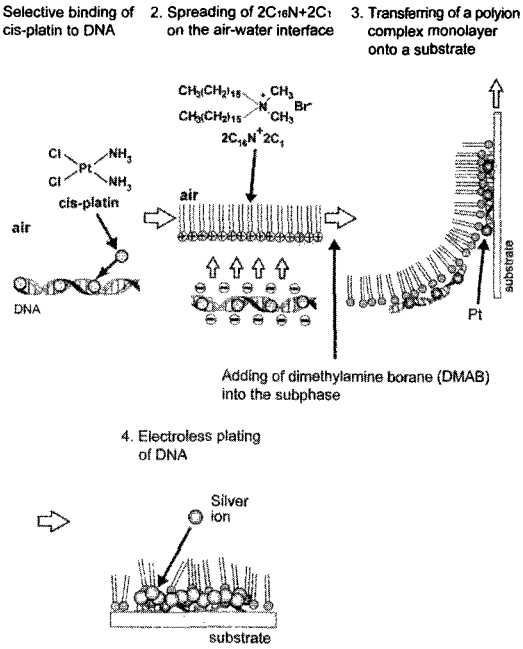

Fig. 1. A scheme for the nucleation of catalysts prepared from cis-platin and for fabricating nanowires along the template DNA molecules by electroless plating.

2. Experimental section

(a) Preparation of a Lambda DNA-amphiphile polyion complex monolayer

Lambda DNA (Nippon Gene Co., Ltd.) was mixed with platinum compounds as catalysts precursors in Tris-HCl buffer (pH7.8 at 20 ℃). The final concentration of Lambda DNA and platinum compounds was 1.0×10^{-8} M (in base pair) and 2.5×10^{-6} M, respectively. This DNA solution was used as the subphase of the Langmuir trough with a Wilhelmy type balancer (FSD-300, USI System). The chloroform solution of 0.68 mM cationic amphiphile (dihexadecyldimethyl ammonium bromide ($2C_{16}N^{+}2C_1$)), (Sogo pharmaceutical Co., Ltd.) was spread on the surface of the subphase. DNA molecules with the platinum compounds formed a polyion complex monolayer at the air-water surface. 10 ml of 25 mM dimethylamine boran (DMAB, Wako Chemical Co., Ltd.) Tris-HCl buffer solution was carefully added to the subphase behind the barrier. After aging for 45 minutes, the polyion complex monolayer was compressed until the surface pressure was 5 mN/m, and then transferred to a glass substrate by vertical dipping. The glass substrate was previously immersed in the subphase and lifted up at a rate of 2 mm/min while being dipped vertically. When the DNA was observed by fluorescent microscopy, it was labeled with YOYO-1 (Molecular Probe Co., Ltd.) in the subphase. Ultrapure water (Milli-Q water, Nihon Millipore Co., Ltd.) was used for sample preparation in all cases and for cleaning the substrates. A fluorescence microscope (E-600, Nikon Co., Ltd.) was used for fluorescence observations. Atomic force microscope (AFM) observations were carried out using a SPA400/S3800 instrument (SII Co., Ltd.).

(b) Silver Electroless Plating Procedure

The polyion complex monolayer on the glass substrate was immersed in the silver electroless plating solution,[14] which was comprised of 0.03M silver nitrate, 1.22M ammonia solution, 0.5M acetic acid and 0.1M hydrazine (all reagents were purchased from Wako Pure Chemical Co., Ltd.). After the metal deposition procedure, the glass substrate was washed using the ultra-pure water and dried by blowing nitrogen gas. The surfaces of the samples were observed using FE-SEM (S-5200, HITACHI) and AFM (SPA400/S3800 (SII Co., Ltd)).

(c) Measurement of the conductivities of metal wires by conductive AFM

A fixed electrode was fabricated on the glass substrate after electroless plating. The fixed electrode was prepared with silver paste (DOTITE, Fujikura Kasei Co., Ltd.). As the silver paste was not sintered, an electrical connection between the fixed electrode and metal wire structures was not assured. To assure the electronic connection, the electroless plating solution was dropped at the boundary of the fixed electrode and reacted for 20 seconds. After the electroless plating solution was removed using filter paper, the glass substrate was washed using the ultra-pure water and dried with nitrogen gas. An Au-coated AFM tip (SI-AF01-A (SII Co., Ltd)) was used as a counter electrode. Topographic images and current mapping images were obtained using conductive AFM (SPA400/S3800 (SII Co., Ltd)).

A D.C. voltage of 1.0 V was applied to the AFM probe while the surface of the glass substrate was scanned. As the conductive AFM measurement needed to be carried out under contact mode, the images obtained were partially crude due to the AFM tip scratching small particles adsorbed on the surface of the glass substrate.

3. Result and Discussion

A DNA-amphiphile polyion complex monolayer was formed by spreading dihexadecyldimethyl ammonium bromide ($2C_{16}N^{+}2C_1$) on an aqueous buffer solution of Lambda DNA, several reagents (cis-platin and platinum group compounds), and YOYO-1. After the reduction of platinum compounds to platinum by the addition of an aqueous DMAB solution into the subphase, the DNA-amphiphile polyion complex monolayer was compressed and transferred to a glass substrate. The fluorescence images (Fig. 2.) of the transferred polyion complex monolayer show that stretching DNA molecules were depended on platinum reagents. Fig. 2(f) indicates the fluorescence microscope image of Lambda DNA-$2C_{16}N^{+}2C_1$ complex without a catalyst precursor as reference. As seen in Fig. 2(c), a similar fluorescence image of the DNA complex was observed only when cis-platin was used as a catalyst precursor. The result suggested that the stretched conformation of the DNA complex was maintained.

To confirm that platinum particles generated by DMAB reduction, TEM observation was carried out (Fig. 3). Because a TEM gird surface is strongly hydrophobic, polyion complex monolayer was hardly transferred onto the TEM grid by vertical lifting method. Horizontal method was used. However, large water droplets brought with the polyion complex monolayer during the transfer disturbed the alignment of stretched DNA molecules due to the hydrophobic surface of the TEM grid.

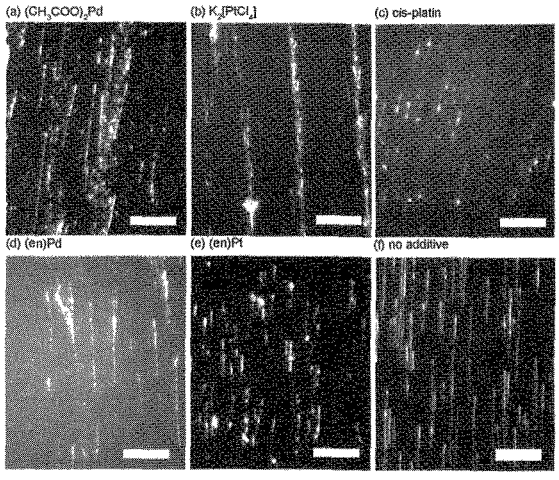

Fig. 2. Fluorescence microscope images of Lambda DNA-$2C_{16}N^+2C_1$ complex monolayers. DNA molecules were reacted with platinum or palladium compounds ((a) palladium acetate, (b) potassium tetrachloroplatinate, (c) cis-platin, (d) ethylenediaminedichloropalladium ((en)Pd), and (e) ethylenediaminedichloroplatinum ((en)Pt); all reagents were purchased from Wako Chemical Co. Ltd.)). The catalyst precursors were reduced by addition of DMAB to the subphase in the Langmuir trough. Platinum or palladium compounds / DNA (in base pair) ratio was 250. Bar equals to 10 micrometers.

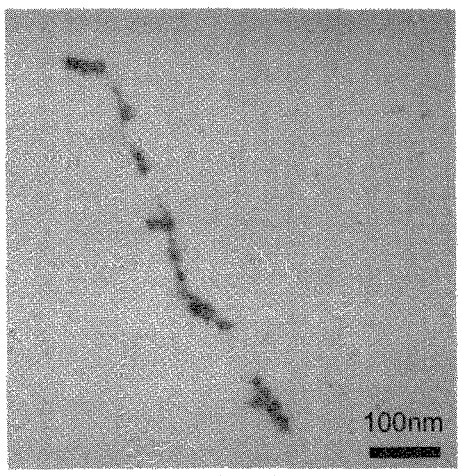

Fig. 3. TEM image of the polyion complex monolayer after reduction of cis-platin in a subphase by adding DMAB

A stripe pattern of many black dots were observed in Fig. 3. Heavy atoms and metal particles are often observed as black dots by TEM observation. On the other hand, DNA is hardly visualized. The TEM image indicated that platinum particles having a diameter of 2~3 nm were formed by the reduction by DMAB. The height of the particles in the pearl-necklace like pattern was the same as the height of the black dots. We confirmed that platinum particles were generated on DNA by reduction of cis-platin.

Silver metal deposition on the stretched DNA with platinum particles was carried out by immersion in a silver electroless plating solution. The SEM image of the silver-deposited surface (Fig. 4(a)) observed without a pretreatment by metal sputtering indicated that wire structures of 40-100 nm wide consisted of silver metal. In the case where the electroless plating solution was used without a reducing reagent (hydrazine) in the silver electroless plating solution, no wire structure could be observed by SEM, indicating that these line structures were composed of deposited silver metal.

AFM measurements of silver deposited DNA showed that the wire structure consisted of a linear cluster of nanoparticles (Fig. 4(b)). The height and half width of the wire at the A-A' cross section (Fig. 4(c)) were 25 nm and 70 nm, respectively. The nucleolus growth of silver occurred dominantly at the platinum bound to the DNA molecule. The AFM image of the electroless plated DNA-amphiphile polyion complex monolayer without cis-platin showed that only isolated dots were grown (data not shown).

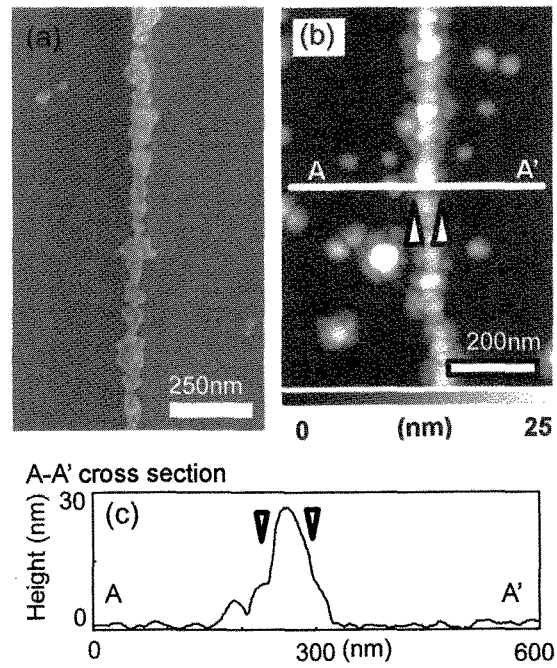

Fig. 4. (a) SEM images of a DNA-$2C_{16}N^+2C_1$ complex monolayer after silver electroless plating. The applied voltage was 1kV. (b) AFM images of wire-like structures fabricated using a platinum catalyst. (c) Cross-sectional profiles at A-A' in (b).

The platinum catalyst was essential for selective silver deposition along the matrix DNA molecule. Since Lambda DNA, which is a natural DNA extracted from a virus, has random base sequences, the reaction points of cis-platin in Lambda DNA is almost randomly

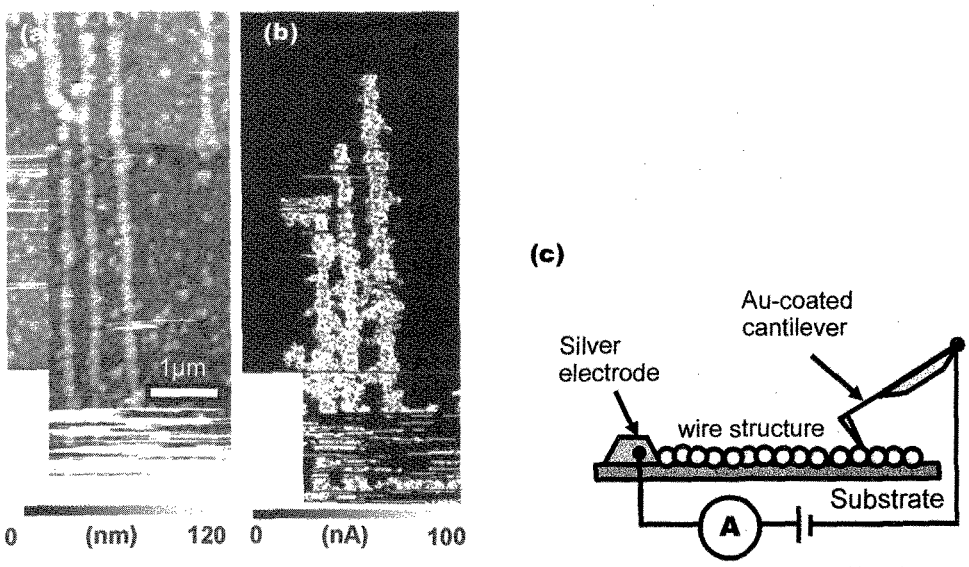

Fig. 5. Conductive AFM images of wire-like structures: (a) Topographic image; (b) Electric current mapping image of (a). The diagram of conductive AFM is shown in (c).

arranged. Therefore, the silver electroless deposition can occur uniformly all over the stretched Lambda DNA molecules, following the scheme as shown in Fig. 1.

The conductivity of a single silver wire was investigated by conductive AFM. The current between an Au-coated AFM tip and a small silver paste electrode placed on the surface through the wire structure were monitored under air as shown in Fig. 5. Conductive AFM employed in this experiment can measure the topographic image as well as yield electric current mapping simultaneously. The topographic image indicates that three parallel wires were connected with a small electrode which was placed at the lower part in Fig. 5(a). Defects such as a grain boundary were hardly observed. In the current mapping, by applying 1 Volt (Fig. 5(b)), the brighter parts corresponded to higher electrically conductive parts between the fixed electrode and the AFM tip. By comparing the conductive AFM image with the topographic image, it was clear that the silver wire structure clearly had a very high conductivity. However, the wires were broken snapped in the middle. These are due to defects such as an invisible grain boundary in the metal particles. The control of the joint between deposited silver nanoparticles is important to obtain straight nanowires without disconnection.

4. Conclusion

In conclusion, the fabrication of silver wire structures on template DNA molecules stretched and immobilized by the LB method is described. Cis-platin as a catalyst precursor was preferentially bound to nucleic acid bases of the template DNA and reduced to platinum metal. Binding of platinum particles onto the DNA molecules did not disturb the stretching of them by the LB method. Silver deposition on stretched DNA occurred homogeneously and selectively by creating platinum catalysts on the template DNA molecules. Conductive AFM measurements revealed that the silver wire structures obtained (<100nm wide) were conductive. We are currently attempting to assemble designed DNA-based metal nanowires for the preparation of nanocircuits.

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