Fabrication of Metal Nanowires by Electroless Plating of DNA*

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For the purpose of the fabrication of nanowires, the metallization of double-stranded DNA by the selective electroless plating method was investigated. Cis-platin was bound to template DNA molecules and reduced to platinum which can catalyze subsequent silver metal deposition. We have found that when DNA-amphiphile polynon 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 clusters 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. 50nm 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. [DOI: 10.1380/ejssnt.2005.82]

Keywords: Biological molecules-nucleic acids; Langmuir-Blodgett films; Nano-wires; Electroless plating; cis-platin

I. INTRODUCTION

The fine electronic circuits embedded in computer chips are fabricated on Si-wafers using the photolithography technique. Fine engraving techniques such as photolithography are known as 'top-down' methods, whereby larger materials are made smaller. The widths of electronic circuits in semiconductor devices can be fabricated under 100nm. However, even finer electronic circuit lines are required for future applications. There are serious difficulties for making them smaller including the physical limitations of the fabrication techniques and enormous manufacturing costs.

Recently, a 'bottom-up' method attracts much attention, whereby 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-range to several millimeters depending on the molecular weight. Stretched DNA molecules have been therefore used as templates for the fabrication of metal nanowires by the bottom-up method [1-7]. Sivan et al. [2] have reported the conductivity of a silver nanowire deposited along a DNA molecule connecting two microelectrodes. Nakao et al. [4] have reported the ordered arrangement of metal particles along DNA molecules stretched and immobilized by a modified 'molecular combing' [8] method on a substrate. Keren et al. [5] have reported selective binding of protein to DNA that allowed for selective metal deposition. However, the number of experimental reports on conductivity measurements of DNA-based nanowires is very limited. In order to prepare fine nanowires using DNA, the metal deposition that occurred only on stretched DNA molecules is a critical requirement.

In this paper, we report 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.

To restrict an electroless plating reaction only along DNA molecules, a catalyst for the electroless plating needs to be bound to the DNA prior to the electroless plating. For this purpose, cis-platin was chosen as the catalyst precursor. 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 [9]. 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 cis-platin bound to the DNA was reduced by dimethylamine boran (DMAB) to platinum metal. Finally, silver electroless plating was enhanced by the platinum deposited on DNA.

We have found that when a DNA-amphiphile polynon 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 [10, 11]. The stretching direction of the DNA molecules is parallel to the lifting direction of the substrate. The LB method does not require any surface modification of the substrate (such as, for example, amino silane coupling), which the 'molecular combing' method requires. In order to utilize DNA as the template of selective electroless plating of silver, DNA combined with reduced cis-platin was stretched and immobilized on a glass substrate by the LB method.

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II. EXPERIMENTAL

A. Preparation of a Lambda DNA-amphiphile polyion complex monolayer

Lambda DNA (Nippon Gene Co., Ltd.) was dissolved with cis-platin in Tris-HCl buffer solution (pH 7.8 at 20°C). The final concentration of Lambda DNA and cis-platin 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 (dihexadecyldimethylammonium bromide (2C_{16}N^+2C_1)), (Sogo pharmaceutical Co., Ltd.) was spread on the surface of the subphase. DNA molecules with the cis-platin formed a polyion complex monolayer at the air-water surface. Ten ml of 25 mM DMAB (Wako Chemical Co., Ltd.) Tris-HCl buffer solution was carefully added to the subphase behind the barrier. After 45 minutes aging, the polyion complex monolayer was compressed at a rate of 0.11 Å^2/molecule/sec until the surface pressure reached 5 mN/m, and then transferred to a glass substrate by the vertical lifting method. 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 using fluorescence microscopy, a fluorescence probe for DNA, YOYO-1 (Molecular Probe Co., Ltd.) was added in the subphase. Pure 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.

B. Silver Electroless Plating Procedure

The glass substrate on which the polyion complex monolayer was transferred was immersed into a silver electroless plating solution [12], which was comprised of 0.03 M silver nitrate, 1.22 M ammonia solution, 0.5 M acetic acid and 0.1 M hydrazine (all reagents were purchased from Wako Pure Chemical Co., Ltd.). After the metal deposition procedure, the glass substrate was washed using the pure water and dried by blowing of nitrogen gas. The surfaces of the samples were observed using FE-SEM (S-5200, HITACHI) and AFM (SPA400/S3800 (SII Co., Ltd)).

III. RESULTS AND DISCUSSION

The fluorescence image of the transferred polyion complex monolayer shows that DNA molecules were stretched, though cis-platin was reduced in the subphase (Fig. 2). The length of a Lambda DNA molecule is estimated to be 16.5m from its base pairs and base pair distance (3.4 Å). A fully stretched DNA molecule could not be observed in obtained fluorescence image (Fig. 2) because the fluorescence emission of YOYO-1 was partially quenched by platinum particles reduced cis-platin. Although the fluorescence emission quenched by the platinum particles was...
FIG. 3: SEM image of a DNA-2C\textsubscript{16}N\textsuperscript{+}2C\textsubscript{1} complex monolayer after silver electroless plating. Inset is a magnified picture. The applied voltage was 1 kV.

invisble by using our CCD camera, some DNA molecules stretched to about 18 \(\mu\)m length could be found by naked eye. Some brighter spots in the fluorescence image indicate that parts of DNA molecules were folded. AFM of the polyion complex monolayer which was transferred to a mica substrate by the horizontal lifting method (the Langmuir-Schäfer method) revealed a pearl necklace like structure (data is not shown here). The height and width of the line was approximate 1 nm and 2 nm respectively, indicating that the line corresponded to the stretched DNA. Dots were arranged on the Lambda DNA at intervals of 50-200 nm. The size of the dots along the DNA reached 2 nm in height and 5 nm in length. The absence of cis-platin in the subphase yielded metallization derived from free silver ions adsorbed to the phosphate group of the matrix DNA could be reduced to metal particles in competition with the electroless plating reaction. However, the phosphate group of the DNA molecule was bound to both the substrate and the cationic amphiphile monolayer. Consequently, silver deposition without the platinum catalyst would be disordered and would proceed slowly. The electroless plating can occur uniformly all over the stretched Lambda DNA molecules, following the scheme shown in Fig. 1.

There was a possibility that silver ions electrically adsorbed to the phosphate group of the matrix DNA could be reduced to metal particles in competition with the electroless plating reaction. However, the phosphate group of the DNA molecule was bound to both the substrate surface and the cationic amphiphile monolayer. Consequently, silver deposition without the platinum catalyst would be disordered and would proceed slowly. The electroless plating experiment without the platinum catalyst yielded metallization derived from free silver ions adsorbing to the phosphate group, indicating inhomogeneous deposition of silver metal, as observed in Fig. 4-b1.

Silver metal deposition on DNA was carried out by immersing the glass substrate on which stretched DNA with platinum particles was immobilized into a silver electroless plating solution. The SEM image (Fig. 3) of the silver-deposited surface shows that DNA molecules were metalized over 10 \(\mu\)m. Inset figure of Fig. 3 shows the height and width of the wire structures was 40-100 nm. Since SEM measurement was carried out without a pretreatment by metal sputtering, the observed wire structures consisted of silver metal. In the case where the electroless plating solution was used without a reducing reagent (hydradzine) 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-a1). The height and half width of the wire at the A-A' cross section (Fig. 4-a2) were 25 nm and 70 nm, respectively. The nucleolus growth of silver occurred dominantly at the platinum bound to the DNA molecule. The wire structures were formed by connecting silver particles grown on platinum particles. Basically the width of the wire structure was depended on the intervals of the platinum particles on DNA. In this experiment, AFM measurements revealed that the intervals of platinum particles on DNA molecule were from 50 to 200 nm. Thus about 100 nm wide wire structures were frequently formed. The AFM image of the electroless plated DNA-amphiphile polyion complex monolayer without cis-platin (Fig. 4-b1) showed that only isolated dots were grown. Although the height of dotted metal structures was c.a. 30 nm, the diameter of the dot (Fig. 4-b2) was two times larger that of the line width of Fig. 4-a2. This indicates that the nucleus growth of silver dots was predominant on pre-deposited silver dots. The DNA molecule could be observed between large aggregations of dots in Fig. 4-b1.

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 arranged. Therefore the reduced platinum particles were also aligned along the DNA molecule. The reaction of silver electroless plating can occur uniformly all over the stretched Lambda DNA molecules, following the scheme shown in Fig. 1.

IV. CONCLUSIONS

The fabrication of silver wire structures on template DNA molecules stretched and immobilized by the LB method was attempted. Cis-platin as a catalyst precursor was preferentially bound to nucleic acid bases of the template DNA and reduced to platinum metal. Platinum clusters derived from cis-platin did not influence stretching of the DNA molecules. Silver deposition on stretched DNA occurred homogeneously and selectively by creating platinum catalysts on the template DNA molecules. We are currently attempting to measurement of electric conductivity of the silver metal nanowires by AFM.

Acknowledgments

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FIG. 4: AFM images of wire-like structures fabricated with a platinum catalyst (a1) and without the platinum catalyst (b1). Cross-sectional profiles at A-A’ in (a1) and (b1) are shown in (a2) and (b2), respectively.

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