# FORMATION OF A SINGLE METALLIZED DNA NANOWIRE IN A NANOCHANNEL

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# ABSTRACT

We present a novel fabrication process of a single silver nanowire using metallization of a DNA molecule. First, we introduced a single  $\lambda$ DNA molecule into a nanochannel by capillary force. Then, the  $\lambda$ DNA molecule was stretched and immobilized by applying an AC voltage between two electrodes that were placed 15 µm apart. Next, naphthalene diimide molecules labeled with reducing groups were intercalated into the  $\lambda$ DNA so that the reducing groups were arrayed along the  $\lambda$ DNA strand. Finally, the  $\lambda$ DNA was metallized with silver using treatment with Tollens' reagent and reduction of silver ions along the  $\lambda$ DNA, which resulted in formation of silver nanowires. The electrical property of the fabricated nanowire was evaluated with the complex impedance plot. As a result, an equivalent circuit for the nanowire was found to be expressed as the series connection of a resistance and several parallel RC circuits.

## **KEYWORDS**

Nanowire, DNA, Nanochannel, Metallization, Intercalator

## INTRODUCTION

Many research groups have already reported about metallized DNA nanowires for nanoelectronic components [1, 2]. However, their fabrication processes required complicated pretreatment such as modification of DNA molecules before their immobilization and metallization. Moreover, their processes were poorly-reproducible and low-yield due to unreliable immobilization techniques. In order to solve these problems, we previously reported a metallization technique of unmodified DNA molecules using intercalator molecules, which sequentially follows electrical immobilization of the DNA molecules between two electrodes in a microchannel [3]. However, because this process had difficulty in placing only a single DNA molecule between two electrodes, it was impossible to evaluate electrical properties of an individual nanowire. In this study, we present a novel fabrication process of a single nanowire using a nanochannel which is a powerful tool in manipulation and analysis of DNA at single molecule level [4]. This permits simple, highly-reproducible, high-yield formation of a single nanowire, which will be very helpful for accurate analysis of its electrical properties.

## METHODOLOGY

Figure 1 shows the procedure of nanowire formation. A device for nanowire formation consists of a microchannel, several nanochannels, and two gold electrodes. First, when a solution including  $\lambda$ DNA molecules of 16µm in length is injected into the microchannel (Fig. 1(a)), each single  $\lambda$ DNA molecule is introduced into a nanochannel by capillary force (Fig. 1(b)). Then, the  $\lambda$ DNA molecule is stretched and immobilized between the electrodes by applying an AC voltage of 1 MHz and 20 V<sub>p-p</sub> [5] (Fig. 1(c)). Next, when a solution of naphthalene diimide molecules labeled with



*Figure 1. Procedure of formation of a single metallized DNA nanowire (a-f) and structural formula of reducing group-labeled intercalator (g).* 

reducing groups, galactoses, as shown in Fig. 1(g) is introduced into the microchannel, the naphthalene diimide molecules diffuse into the nanochannel and are intercalated into the double strand of  $\lambda$ DNA so that the galactoses are arrayed along the  $\lambda$ DNA (Fig. 1(e)). Finally, when Tollens' reagent including silver ions is injected into the microchannel, silver ions diffuse into the nanochannel, and the  $\lambda$ DNA is metallized with silver because aldehyde groups of the galactoses reduce silver ions along the  $\lambda$ DNA (Fig. 1(f)).

#### **EXPERIMENTAL RESULTES**

Figure 2 shows the schematic of a micro/nano fluidic device for nanowire formation. The microchannel measuring 50  $\mu$ m in depth was made of PDMS (polydimethylsiloxane). The nanochannels measuring 500 nm in width and 500 nm in depth were fabricated on a silicon wafer using a FIB (focused ion beam) technique. The two gold electrodes were patterned 15 $\mu$ m apart using a lift-off process after the wafer surface was insulated by a thermal oxidation process. Figure 3(a) shows a photograph of the fabricated device. The SEM image of the fabricated nanochannels is shown in Fig. 3(b), and the cross-sectional SEM image of the fabricated nanochannel is shown in Fig. 3(c).



Figure 2. Schematic of a micro/nano fluidic device for nanowire formation.

Figure 3. Photographs of the fabricated device and SEM image of the nanochannel.

The fluorescence image of the stretched and immobilized  $\lambda$ DNA which were preliminarily labeled with the fluorescent dyes (Hoechst 33258) is shown in Fig. 4. Also, the SEM images of the silver nanowire formed by  $\lambda$ DNA metallization are shown in Fig. 5. The fabricated nanowire had a linear chain conformation of silver clusters, and its average width was about 30 nm.







Figure 5. SEM images of the metallized  $\lambda$ DNA nanowire.

Figure 6 shows the impedance spectrum of the nanowire formed between a pair of electrodes in the nanochannel. The impedance was maintained at an almost constant value in the frequency lower than 100 kHz, and decreased rapidly in the range of 100 kHz to 5 MHz. Figure 7(a) shows the complex impedance plot obtained from the nanowire in the frequency

range of 4 Hz to 5 MHz. In our analyses, the equivalent circuit for the nanowire was given by the series connection of a resistance and several parallel RC circuits (Fig. 7(b)). Probably the circular arc was mainly attributed to the resistances  $(R_n)$  and capacitances  $(C_n)$  at the contact faces between adjacent silver clusters. Also, the bulk resistance of silver clusters  $(R_0)$  was much smaller than  $R_n$ .

100



(a)(b) Imaginary part of impedance [Ω] 80 60 40 20 0 **`** 20 40 60 80 100 120 140 160 Real part of impedance  $[\Omega]$ (b)  $R_{c}$  $C_1$  $C_{\gamma}$ 

Figure 6. Impedance spectrum of the metallized  $\lambda DNA$ nanowire.

Figure 7. Complex impedance plot and an equivalent circuit of the metallized  $\lambda DNA$  nanowire.

#### CONCLUSIONS

We fabricated a silver nanowire using metallization of a single  $\lambda$ DNA molecule after its straight stretch and immobilization between the two microelectrodes which were placed 15 µm apart in a nanochannel. The fabricated nanowire had a linear chain conformation of silver clusters, and its average width was about 30 nm. Also, an equivalent circuit of the nanowire was estimated using an electrical impedance analysis. Naphthalene diimide molecules labeled with reducing groups that were used for DNA metallization in this study can be intercalated into double-stranded DNA, but cannot be into single-stranded DNA. In the near future, in order to give molecular recognition property to metallized DNA nanowires, we will make non-metallized portion on the nanowires using partial metallization of DNA complexes consisting of single strands and double strands.

## **ACKNOWLEDGEMENTS**

This work was partly supported by the Grant-in-Aid for Scientific Research (B) of the MEXT (Ministry of Education, Culture, Sports, Science and Technology) in Japan.

#### REFERENCES

- [1] E. Braun, et al., DNA-templated assembly and electrode attachment of a conducting silver wire, Nature, 391, pp. 775-778 (1998)
- [2] M. Fischler, et al., Formation of bimetallic Ag-Au nanowires by metallization of artificial DNA duplexes, Small, 3, pp. 1049-1055 (2007)
- [3] T. Himuro, et al., Nanowire formation using metallization of extended and immobilized DNA, Proc. µTAS 2011, pp.1101-1103 (2011)
- [4] E. Angeli, et al., DNA manipulation with elastomeric nanostructures fabricated by soft-moulding of a FIB-patterned stamp, Lab on a Chip, 11, pp. 2625-2629 (2011)
- [5] M. Kumemura, et al., Single DNA molecule isolation and trapping in a microfluidic device, ChemPhysChem, 8, pp. 1875-1880 (2007)

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