Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp1176-1177

G-8-5

Fabrication and Location of 3-nm Pt Wires onto Silicon Surfaces

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1. Introduction

Biological molecules have been found to bring about unexpected chemical reactions. In some cases, a reaction proceeds preferably on a protein surface, resulting in metals or semi-conducting materials molded in the shape of the template molecule. By choosing appropriate molecules or organisms, a desired shape that is conducive to a specific function can be fabricated [1,2]. Furthermore, it has been demonstrated that bio-templated nanoparticles are suitable for use in applications such as memory devices [3, 4]. In addition to nanoparticles, wires with less than 10 nm diameters are indispensable building-blocks for bottom-up fabrication of other nanometer-scaled devices.

In addition to fine control of the size and shape, nanowires need to be selectively placed onto electrodes for a bottom-up fabrication of a device. Biological supramolecules have identical dimensions and their outer-surface can be genetically or chemically modified. The use of a tube-shaped bio-template offers a solution to these requirements.

Tobamovirus (TMV) is a plant virus that has been one of the favored bio-template proteins for making nanowires. The virus is 300 nm in length with outer- and inner-diameter of 18 nm and 4 nm, respectively [5,6]. Utilizing the central channel of TMV, formation of metallic nanowires such as Cu, Ni, Co, Co/Pt, and Fe/Pt have been reported. However, it has been challenging to place them onto a desired position of a silicon surface.

Our ultimate goal is to supply a nanometer-scaled structure for possible applications in constructing electronic and magnetic devices by “biomineralization”.

2. Methods

Pt nanowire formation

First, 1 μl of TMV (1 mg/ml in water; ToMV species[6]), which included Tween 20 (MP Biomedicals, Germany) with the concentration of 1%, was dispersed into 97 μl of potassium tetrachloroplatinate (K_2PtCl_4: Wako Pure Chemical, Osaka) solution (made by mixing 10 μl of 10 mM K_2PtCl_4 and 87 μl of water). After vortex mixing for 2 sec and centrifugation at 13,000 g for 5 sec, the suspension was kept at 25°C for 30 min. Next, 2 μl of freshly prepared 10 mM dimethyl amine borane (DMAB: Wako Pure Chemical, Osaka) was added. About 5 sec later, some black precipitations were observed and the suspension was again mixed using Vortex mixer for 2 sec. The resulting solution was incubated for another 30 min. The final concetrations were 0.01 mg/ml for TMV, 0.01% for Tween 20, 1 mM for K_2PtCl_4 and 0.2 mM for DMAB.

Preparation of nanowires onto a silicon substrate

A silicon substrate was first cleaned with UV/ozone (UV/ozone cleaner UV-1, SAMCO, Kyoto) at 110°C with an oxygen gas flow rate of 0.5 L/min for 10 min.14 Next, 3 μl of TMV/Pt solution was applied and excess solution was removed by a spinner (1H-D2, MIKASA, Tokyo) at 12,000 rpm for 20 seconds, followed by heating at 95°C for 2 min.

3. Results and Discussion

Pt nanowire formation using a TMV template

With our method without ultrasonication, fragmentation of TMV was prevented, resulting in the formation of 300 nm NWs (Figure 1). In some cases, NWs longer than the length of TMV are formed probably because of head-to-tail

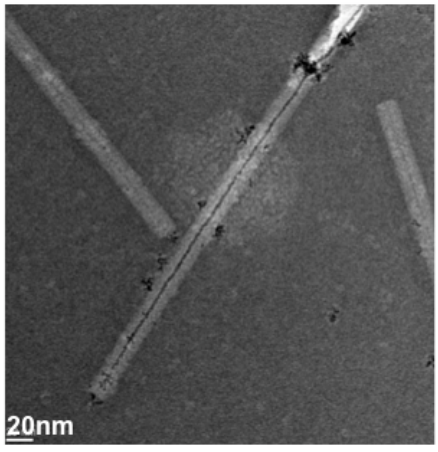

Fig. 1. High aspect ratio 3-nm Pt wires were fabricated using a TMV template. A 300 kV TEM image of 3-nm Pt wire (black line) inside TMV (cloudy white rods). The sample was stained with 3% phosphotungstic acid (PTA). The central channel of the upper TMV is faintly visible due to the presence of PTA.

connection of TMVs. Energy dispersive X-ray spectroscopy (EDS: JED-2200 analyzer, JEOL, Tokyo) confirmed that the wire was made of platinum.

At first, concurrent aggregation of TMV and deposition of large Pt particles outside TMV was a problem. It must be eliminated to meet the demands of future device application. The aggregation of TMV was not observed in the absence of $PtCl^{2-}$ ions suggesting that this aggregation was likely caused by the presence of $PtCl^{2-}$ ions. In fact, using EDS mapping analysis, Pt ion clusters were detected around TMVs in a K_2PtCl_4 solution. This and other results indicated that aggregation of TMV could be mediated by metallic ions, and that aggregation might be prevented if the outer surface of TMV were to become inaccessible to metallic ions. Therefore, we tried to coat the outer surface of TMV to prevent NP formation on the outer surface. We found that the presence of a non-ionic detergent, Tween 20, at concentrations of 0.1-0.01 prevents TMV aggregation (Figure 1). Tween 20 is thought to cover the outer surface of TMV preventing the aggregation of the virus. Lower detergent concentration resulted in TMV aggregation while higher concentration (1%) of the detergent led to micelle formation. Interestingly, in the presence of Tween 20, NW formation inside TMV was not affected and isolated TMVs were observed by high-resolution TEM (JEM-3100FEF, JEOL, Tokyo; Figure 1). The sample was stained with 3% phosphotungstic acid (PTA), which allows clearer visualization of proteins. PTA is known to stain the central channel of TMV as is evident in the faintly stained channel of the lower TMV in Figure 1. The NWs were confirmed to be made of Pt by EDS analysis (data not shown). The percentage of fabricated NWs longer than 100 nm was 5.5% (approximately one per 20 TMV), which was averaged from 600 TMVs observed on a single TEM grid.

Placement of 3-nm Pt wire onto a silicon surface

For future device applications, NWs formed inside TMV must be readily transferred onto silicon surfaces. To achieve this aim, a silicon substrate was cleaned with UV/ozone treatment and TMV/Pt wires are put onto a silicon substrate. Scanning electron microscopy (SEM; JSM-7400F, JEOL, Tokyo) observation revealed that TMV/Pt wires were dispersed onto the silicon substrate (Figure 2a) and after protein elimination, which was achieved by UV/ozone treatment for 30 min, a Pt NW was found at the same position with no migration or defect caused by the treatment (Figure 2b). Although UV/ozone treatment is commonly used to eliminate protein shells [3], detailed analysis using X-ray photoelectron spectroscopy and atomic force microscopy may be necessary before fabricated NWs using a TMV template can be incorporated into nanometer-scaled devices.

4. Conclusions

In conclusion, we succeeded in fabricating and locating high aspect ratio 3-nm Pt wires on a silicon surface, which could not be achieved using conventional lithography. Utilizing the catalytic behavior of Pt, the possibility of fabricating other metal alloy NWs such as Co/Pt or Fe/Pt can now be explored as components for spintronics devices. Nanowires produced in this study are a promising component for bottom-up fabrication of other nanometer-scaled devices.

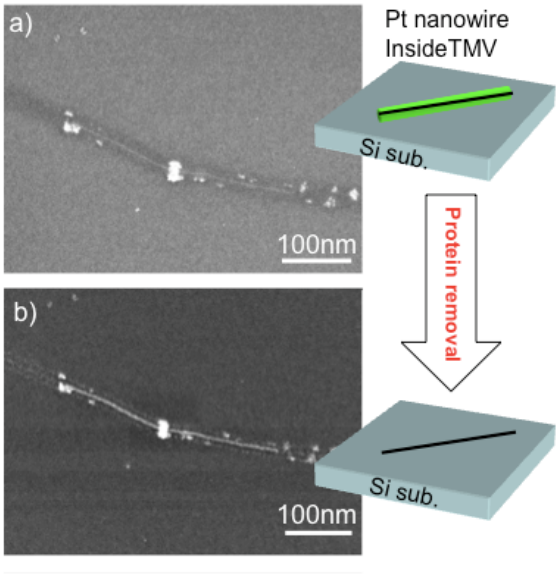

Fig. 2. SEM observation of 3-nm wire fabricated and located on a silicon surface. (a) After spreading TMV/Pt wire onto a silicon surface. (b) A 3-nm line remains after UV/ozone treatment.

Acknowledgements

We would like to express sincere thanks to M. Yamane for her excellent technical assistance. The authors thank S. Fujita for high-resolution TEM and EDS analysis. This study is partially supported by Human Frontier Science Program.

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