Selective Growth of Ag Nanowires on Si(111) Surfaces by Electroless Deposition

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Electroless deposition of Ag on atomically flat H-terminated Si(111) surfaces in aqueous alkaline solutions containing Ag ions produced two different sizes of Ag nanowires along atomic step edges: (1) a narrow nanowire of 10 nm in width and 0.5 nm in height and (2) a wide nanowire of 35 nm in width and 11 nm in height. The narrow and wide nanowires were formed by immersion in the solutions containing less than 1 ppb and 8 ppm dissolved-oxygen concentrations, respectively. This result indicates that the dissolved oxygen initiates the formation of Ag nucleation sites and that the fabrication method has a possibility of controlling the size of Ag nanowires.

Nanometer-sized electronic structures are highly desirable for the future miniaturization of electronic devices. Recently, nanowires have attracted a lot of interest because they are required to interconnect functional units in nanoelectronics and molecular electronics in the future and are expected to form the basis for chemical sensors. To achieve them, it is necessary to develop novel methods for preparing metal nanowires on a substrate. The methods should contain a controllability of the wire length, diameter, and composition. The control of the nanowires in a size range of monatomic chains to several tens of nanometers is beyond the size control of conventional photolithographic techniques. Chemical and electrochemical methods are believed to be promising approaches for achieving mass production of nanostructures. Cu and Ni nanowires were formed by controlling the Si potential with the application of an external bias (electrodeposition).[1,2] In addition, it was reported that the electrodeposition of metal (Ni, Cu, Ag, and Au) nanowires was formed along step edges on graphite crystals.[3]

We first reported that long Cu nanowires (>30 μm) could be fabricated on Si(111) surfaces without applying an external bias (electroless deposition).[4] The method consists of two wet processes: (1) flattening of a surface to the atomic level by immersing a Si(111) wafer in ultralow-dissolved-oxygen water (LOW) and (2) the formation of nanowires by immersion

in LOW containing Cu ions. We revealed that the nanowires are constituted of monatomic Cu rows selectively formed at the surface step edges of the Si(111) substrate.[5] However, the size control of the Cu nanowire has not been achieved yet.

In the present study, we investigate a mechanism of Ag adsorption on the H−Si(111) surfaces immersed in aqueous alkaline solutions containing less than 1 ppb and 8 ppm dissolved-oxygen concentrations and report that the electroless deposition of Ag on the Si(111) surfaces produces not only nanowires in the former solution, similar to Cu, but also wider nanowires beaded by nanodots in the latter solution. This is the second example of the unique phenomenon of metal nanowire formation by the electroless deposition method. Additionally, we indicate that the dissolved oxygen initiates the formation of Ag nucleation sites and the fabrication method has the possibility of controlling the size of Ag nanowires.

The samples used in this experiment were p-type Si(111) wafers with a miscut angle of $0.02 \pm 0.02°$ in the $\langle 11\bar{2} \rangle$ direction. All of the Si wafers were etched using LOW with a dissolved-oxygen content of less than 1 ppb in order to form a well-defined step/terrace structure on the Si wafer surfaces, which we will refer to for clarity as the first LOW treatment. LOW is an aqueous solution of ammonium sulfite monohydrates.[6,7] One Si wafer, sample no. 1, and another Si wafer, sample no. 2, were immersed in LOW (DOC < 1 ppb) and saturated-dissolved-oxygen water (SOW; DOC ∼ 8 ppm) containing 10 ppm Ag ions for 10 s at room temperature, respectively. We will refer to the former and latter treatments as the second LOW treatment and the SOW treatment, respectively. Both of the solutions were prepared by adding a Ag standard solution (1000 ppm Ag in 5 wt % HNO_3 solution) to each solution. The SOW was an alkaline solution added to ultrapure water with a small amount of aqueous ammonia

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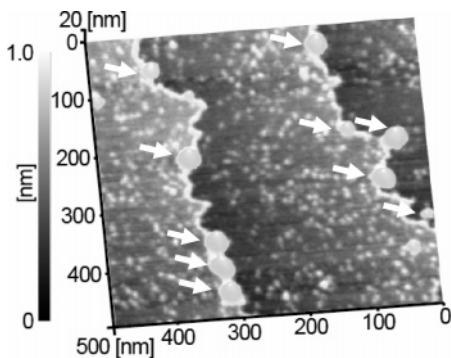**Figure 1.** Topographic AFM image of the Si(111) surface of sample no. 1 after immersion in LOW containing 10 ppm Ag ions for 10 s. The scanning area is 500 nm × 500 nm. The gray contrast indicates a height range of 0−1.0 nm.
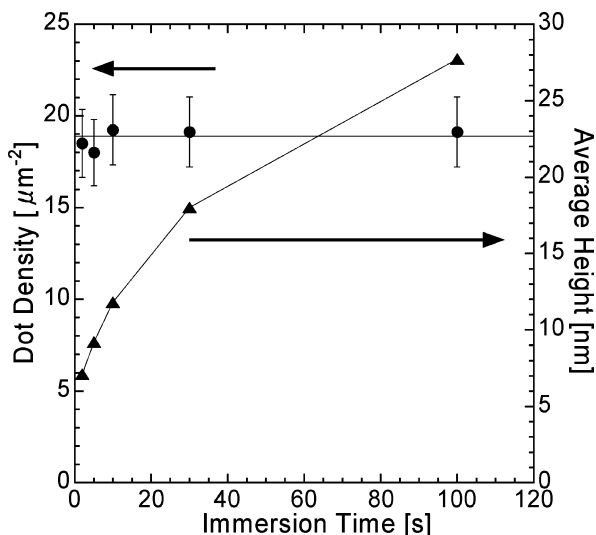

Figure 2. Dot density and average height of Ag dots as functions of immersion time. These data were measured using five AFM images (1 μm × 1 μm).

solution to increase its pH to 9, which was almost the same as that in the LOW. The morphologies of the Si surfaces after the second LOW and SOW treatments were observed by atomic force microscopy (AFM, SII NanoTechnology Inc. SPI3800N + SPA-300HV). The AFM images were obtained in the cyclic mode under ex situ conditions in air. The radius of the Si tips was several nanometers according to the catalog of a production company (NanoWorld).

Figure 1 shows a typical three-dimensional AFM image of the Si(111) surface of sample no. 1 after the second LOW treatment. Continuous wires were selectively formed along the atomic step edges on the surface. The average width and height of the nanowires were 10 and 0.5 nm, respectively. The average height of the nanowires was approximately 0.5 nm even when the immersion time was increased. Additionally, we confirmed by total reflection X-ray fluorescence spectroscopy that Ag was deposited on the surface after the second LOW treatment. These results are consistent with those of Cu nanowires.[4] However, the Ag nanowires should be higher than Cu nanowires because of the atomic radius of Ag. We consider that the difference between the atomic radius of a Ag atom and that of a Cu atom, which is 0.17 Å, is too small to distinguish by our AFM evaluation. On the other hand, 10 dots were formed at the step edges, as shown by arrows. Figure 2 shows the density and average height of the dots as functions of immersion time. The data were measured from five square areas of 1 μm × 1 μm
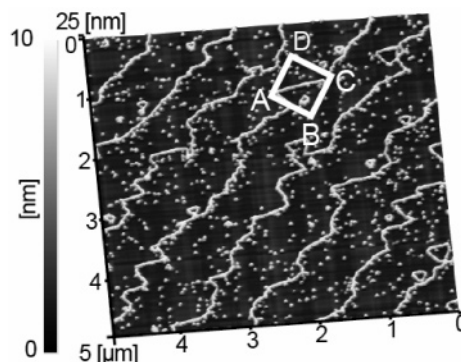

Figure 3. Topographic AFM image of the Si(111) surface of sample no. 2 after immersion in SOW containing 10 ppm Ag ions for 10 s. The scanning area is 5 μm × 5 μm. The gray contrast indicates a height range of 0−10 nm.
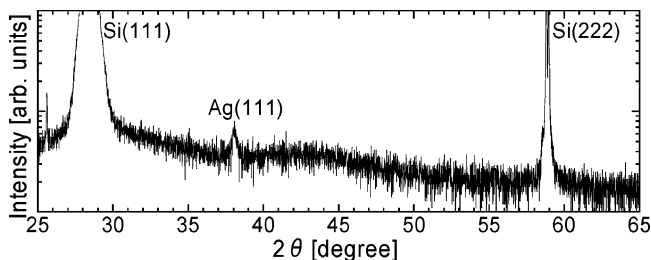

Figure 4. XRD spectrum of a Si(111) substrate after the SOW treatment. The sample was immersed in the SOW containing 10 ppm Ag ions for 100 s.

AFM images. The average height of the dots increases with increasing immersion time, while the area density of the dots is approximately 19 μm^{-2}.

Previously, we showed that no Cu nanowires were formed on the Si(111) surfaces in SOW, which was an aqueous ammonia solution adjusted at pH 11, instead of LOW during the Cu deposition.[8] This is due to the decrease in the density of the reduced Cu atom ($Cu^{2+} + e^- \rightarrow Cu^+$, $Cu^+ + e^- \rightarrow Cu$) caused by a reaction with dissolved oxygen as a superoxide anion radical ($Cu^+ + O_2^{-\bullet} + 2H_2O \rightarrow Cu^{2+} + H_2O_2 + 2OH^-$).[9] On the other hand, we expect that Ag^+ is reduced to a Ag atom even in the SOW because of the single-step reduction reaction ($Ag^+ + e^- \rightarrow Ag$), and Ag nucleation takes place both at the step edges and on the terraces due to Si etching by dissolved oxygen and OH^-. Figure 3 shows a typical AFM image of the Si(111) surface of sample no. 2 after the SOW treatment. As expected, continuous wires were selectively formed along all of the step edges and some dots were formed on the terraces, as shown in this image. This result shows that Ag^+ is reduced to a Ag atom even in the SOW and Ag nucleation takes place both at the step edges and on the terraces. The nanostructures were composed of Ag(111), judging from the X-ray diffraction spectrum of a Si(111) substrate after the SOW treatment, as shown in Figure 4. To evaluate their crystallinity, we prepared a Si(111) sample with a miscut angle of 0.2° after immersion in the SOW containing 10 ppm Ag ions for 100 s. Figure 5 is a magnified AFM image of the square area (ABCD) shown in Figure 3. Two continuous wires and nine dots are observed in this image. Clearly, the nanowires, which were selectively formed along the step edges, were composed of beaded dots, indicating an increase in the density of the dots formed by the dissolved oxygen at the step edges. The average width and height of the wires were 35 and 11 nm, respectively. The average height was almost consistent with that of the dots on the terraces after the SOW treatment and at the step edges after the second
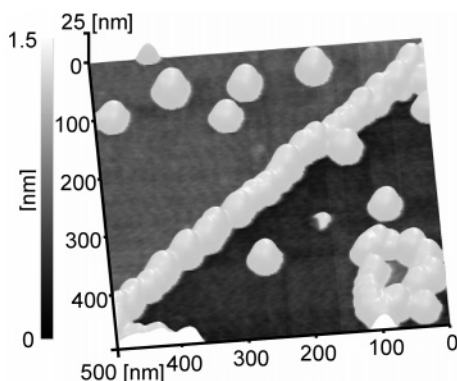
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Figure 5. Topographic AFM image of the Si(111) surface of sample no. 2 after immersion in SOW in the box shown in Figure 4. The scanning area is 500 nm × 500 nm. The gray contrast indicates a height range of 0−1.5 nm.

LOW treatment. The average height of the dots increases with immersion time, as shown in Figure 2. These results indicate that the dissolved oxygen in the solution initiates the formation of the Ag nucleation sites on Si(111) surfaces and the fabrication method has the possibility of controlling the size of Ag nanowires.

Why do the Ag nanowires widen in the SOW? The wide Ag nanowires were composed of Ag nanodots. Such Ag nanodots were also formed on the Si(111) surface after the second LOW treatment, as shown in Figure 1. It is deduced that *the wide Ag nanowires* are obtained when *Ag nanodots* are forced to nucleate with a high linear density at step edges on the Si(111) surface. The density of the Ag nanodots formed in the SOW was higher than that in the LOW. Therefore, the Ag nucleation sites are formed by dissolved oxygen in aqueous alkaline solution. We now propose one possible mechanism. Ag atoms are selectively adsorbed at silicon dangling bonds in an ultrahigh vacuum (UHV).[10] During the Si etching process in solution, it was proposed that some fraction of dissolved oxygen may abstract hydrogen to form silicon dangling bonds.[11] The formation of the dangling bonds would preferentially take place at the step edges than on the terraces. Ag atoms could react with the dangling bonds even in solution. Then, the reaction in which a Ag ion in the solution becomes a metallic atom by capturing electrons can be expressed by the following redox reaction equation.

$$[Ag(NH_3)_2]^+ + e^- = Ag + 2NH_3(aq)$$
$$E° = 0.373 \text{ [V vs NHE]} \quad (1)$$
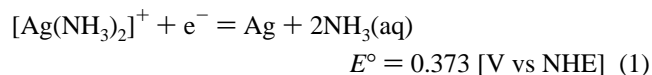
Here, $E°$ is the standard reduction potential (redox potential in a standard state) and NHE is the normal hydrogen electrode. The electron could be released by an oxidation reaction of Si that takes place on the Si surfaces, analyzed by Auger electron spectroscopy. The reaction can be expressed by the following equation.

$$Si + 2H_2O = SiO_2 + 4H^+ + 4e^-$$
$$E° = -0.991 \text{ [V vs NHE]} \quad (2)$$
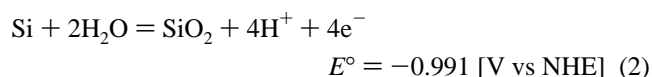
The redox potential of reaction 2, E [V vs NHE], depends on the pH level of the solution. The equilibrium potential of reaction 2 in the SOW (pH 9) is −1.37 V versus NHE. The potential is much more negative than that of the Ag deposition described by reaction 1. Therefore, Ag^+ can take electrons and be reduced to become metallic Ag and thus can deposit at the nucleated Ag sites when the Si atom on the surface is oxidized in the following equation.

$$4[Ag(NH_3)_2]^+ + Si + 2H_2O \rightarrow$$
$$4Ag + SiO_2 + 8NH_3(aq) + 4H^+ \quad (3)$$
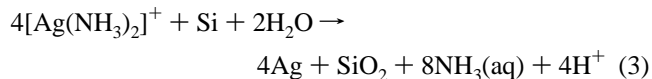
With continued growth, the dense linear array of Ag nuclei evolves into a continuous nanowire, as shown in Figure 3. On the other hand, silicon oxide forms under the narrow Ag nanowires, similarly to the case of Cu.[5] We speculate that the electrons for the reduction of Ag^+ cannot be supplied to the narrow Ag nanowires due to an insulator effect of the silicon oxide.

In summary, the present study has revealed that the electroless deposition of Ag on atomically flat H-terminated Si(111) surfaces in aqueous alkaline solution produces two different sizes of Ag nanowires along the atomic step edges. One is a narrow Ag nanowire 10 nm in width and 0.5 nm in height, and another is a wide Ag(111) nanowire 35 nm in width and 11 nm in height. We revealed that the dissolved oxygen in the solution forms a Ag nucleation site on a Si(111) surface. Our nanowire fabrication method is expected to be a possible solution for controlling the size of Ag and other metal nanowires.

References and Notes

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