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Area-selective electroless deposition of
gold nanostructures on silicon

Hiroki Itasaka

2016
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General Introduction

Nanosized metal is a promising material for electronic, photonic, and magnetic applications owing to its unique properties that are dramatically different from those for bulk metal. One of the remarkable properties is localized surface plasmon resonance (LSPR), a coherent oscillation of the conductive electrons in the metal nanostructure excited by an incident electromagnetic field with a particular resonant frequency. Figure 1 schematically illustrates the interaction between the collective oscillation of conductive electrons in metal nanostructures and the incident electromagnetic field. As the result of LSPR, metal nanostructures intensely absorb and scatter light when the wavelength of the light well matches the resonant frequency of the nanostructures. This property opened up a new field of optics, called “plasmonics”, and has been explored for applications such as surface enhanced Raman scattering (SERS), biosensing, plasmon waveguides, and metamaterials. Although LSPR is theoretically able to be observed for any metal that has a large negative real dielectric constant and a small positive imaginary dielectric constant, gold, silver and copper are commonly used for these applications owing to their resonant frequencies of LSPR in the visible to near infrared range. Since the resonant frequency of metal nanostructures strongly depends on their size, shape and configuration, controlling such parameters is essential to effectively use their plasmonic properties. In the light of practical application of
Figure 1. Scheme of interaction between electric field and collective oscillation of conductive electrons of metal nanospheres.
the plasmonic properties, fabrication of precisely-patterned metal nanostructures, especially on semiconductor surfaces, is a key technique.

In this context, there are a wide variety of approaches to fabricate patterned metal nanostructures on semiconductor. Lithography combined with metal deposition using sputtering and vacuum evaporation is a popular option for nanosized patterning of metal nanostructures on semiconductor substrates. Several lithographic techniques achieved the nanoscale patterning resolution beyond the diffraction limit of light: UV,\(^7\) X-ray,\(^8\) electron beam,\(^9\) focused ion beam (FIB),\(^10\) scanning probe microscopy (SPM),\(^11\) and nanosphere\(^12\) lithographic techniques, for example. These lithographic techniques, however, require many steps due to their use of resist films for temporary-mask fabrication and most of them are only applicable to flat substrates.

To overcome these limitations in the lithographic techniques, some researchers reported maskless and resistless methods using selective electrodeposition and electroless deposition of metal on semiconductor. P. Schmuki et al. demonstrated micro-patterning of gold nanostructures on silicon substrates.\(^13\) In the method, gold nanostructures selectively grow on the FIB-irradiated silicon surface by electrodeposition. L. Santinacci et al. reported another selective electrodeposition, in which copper nanostructures selectively grow on the silicon surface mechanically scratched by using an atomic force microscopy (AFM).\(^14\) In these cases, FIB irradiation and AFM scratching locally removed the insulating oxide layer on silicon substrates and
resulted in local current flow on the processed silicon surface. On the other hand, Y. Zhang et al. demonstrated selective electroless deposition of copper nanostructures on silicon surfaces scratched by using an AFM.\textsuperscript{15) At nearly the same time, N. Kubo et al. also reported fabrication of copper nanopattern on silicon substrate by a maskless and electroless method using AFM scratching,\textsuperscript{16) and they later applied their method to fabrication of gold, silver and cobalt nanopatterns.\textsuperscript{17) Selective electroless deposition is also applicable to fabrication of gold nanoparticles on the particular face of silicon nanowires as S. Y. Sayed et al. reported.\textsuperscript{18) These electroless deposition methods are based on galvanic displacement assisted by hydrofluoric acid (HF) described as follows:\textsuperscript{19)\textsuperscript{19}}}

\begin{align*}
M^{z+} + ze^{-} & \rightarrow M^{0} & \text{(1)} \\
\text{Si} + 6\text{HF} & \rightarrow \text{SiF}_6^{-} + 6\text{H}^{+} + 6e^{-} & \text{(2)}
\end{align*}

where M represents a metal species.

In our laboratory, T. Matsuoka et al. previously reported HF-free electroless deposition of gold nanostructures on crystalline silicon.\textsuperscript{20,21) They demonstrated that gold nanostructures selectively grow on the localized silicon surface (as shown in figure 2 (a)), which was preliminary irradiated by using a femtosecond pulsed laser or a FIB, from an Au ion-containing solution. Figure 2 (b) illustrates the processes of the method: a tetrachloroauric acid (HAuCl$_4$) aqueous solution was reacted with 3-mercaptopropyltrimethoxysilane (MPTMS) at 100 °C. The product solution was
Figure 2. (a) An SEM image of gold nanostructures grown on the FIB-irradiated silicon surface and (b) procedure of electroless deposition method reported in ref. 20.
dropped onto a silicon substrate surface that was preprocessed with FIB- or femtosecond pulsed laser-irradiation in selected areas, followed by drying at 80 °C in an electric furnace. Since this method used no HF throughout all processes, the growth mechanism of gold should be different from the galvanic displacement described as the equations 1 and 2. In order to investigate the mechanism of the selective growth of gold, they carried out Raman measurement and revealed that amorphization of silicon induced by FIB or femtosecond laser irradiation is essential for the gold growth on the irradiated area. As a consequence, they concluded that Au (III) ions were reduced to Au (I) ions in the solution by the reaction with MPTMS, which did not work a coupling agent in this system, and then Au (I) ions were finally reduced to Au (0) by electrons from the amorphized silicon surfaces. However, the details of the mechanism have still remained unclear. Detailed understanding of this growth mechanism is important to achieve the further controllability of the size and shape of the nanostructures for this nano-fabrication method and can provide fundamental insights to electrochemical deposition of metal on semiconductor.

In present work, I investigated the mechanism of selective growth of gold nanostructures on the amorphized silicon focusing on the following points: (1) where electrons reducing Au ions come from and (2) how Au ions are reduced. In order to clarify these points, surface analysis for silicon before and after the gold growth and quantitative evaluation of the amount of gold nanostructures were carried out by using
X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, FIB, and field emission scanning electron microscopy (FE-SEM). In addition to the investigation of the growth mechanism, the electroless method was applied to a silicon AFM probe to fabricate the nanotips with gold nanostructures at their apexes. Such a tip can be utilized for tip-enhanced Raman spectroscopy (TERS), an analytical technique combining Raman spectroscopy and scanning probe microscopy, because of the strong enhancement of electric fields of incident and scattered light in the visible range originated from the LSPR of the gold nanostructures at the tip apex. The outline of this work is summarized in the next pages.
Summary of each chapter

Chapter 1: First, I added a new rinse step to our previous method in order to investigate the cause of the reduction of Au ions on the amorphized silicon. The result reveals that Au ions in the solution are reduced by electrons from the amorphized silicon. Furthermore, the addition of the rinse step enables our method to fabricate gold nanostructures from a pure HAuCl$_4$ aqueous solution without thiol compounds. Second, from investigation of the correlation between the oxidation degree of amorphous and crystalline silicon surfaces and the number density of gold nanostructures, I found that silicon dangling bond defects are an electron source for the reduction of Au ions.

Chapter 2: For the further understanding of the reduction of Au ions by dangling bond defects, I investigate the role of solvent molecules in the reductive reaction by using protic and aprotic solvents for preparing the HAuCl$_4$ solutions and dropping them on the FIB-irradiated silicon surface. Gold nanostructures successively grew on the FIB-irradiated silicon from the solution using protic solvents, while no gold growth was observed for the solution using the aprotic solvent. This result revealed that protic solvents are necessary for the reduction of Au ions by dangling bond defects.

Chapter 3: I quantitatively evaluated the total volume of gold nanostructures grown on
the FIB-irradiated silicon surface with a fixed area by measuring the thickness of the aggregate of gold nanostructures. The result indicated that the reduction mechanism of Au ions in our method consists of a nucleation step and a growth step. In the nucleation step, electrons from dangling bond defects reduce Au ions in the solution as described in the chapter 2. In the growth step, on the other hand, Au ions are reduced at the surface of gold by electrons from crystalline silicon surrounding the FIB-irradiated silicon across the silicon/gold interface. Finally, based on this find, I proposed a new two-step-growth method that enabled more flexibility in the shape of gold nanostructures than than our conventional method.

**Chapter 4:** I applied our electroless method to silicon carbide, a wide-gap semiconductor consisting of silicon and carbon. This demonstrated the applicability of our method to semiconductor other than silicon. Quantitative evaluation of the number and the total volume of gold nanostructures grown on the FIB-irradiated area of silicon carbide and comparison with the result for silicon revealed that total volume of gold predominantly determined by the energetical difference between the Fermi level of semiconductor and the redox potential of Au ions in the solution.

**Chapter 5:** I applied our method to a silicon AFM probe in order to fabricate nanotips for tip-enhanced Raman spectroscopy (TERS). Gold nanostructures selectively grew at
the tip apex regardless of geometry of probes. Addition of NaCl to the HAuCl₄ aqueous solution enables gold to grow with sharp needle-shaped structures. The result of finite-difference time-domain (FDTD) simulation demonstrated strong enhancement of electric fields at needle apexes of such gold nanostructures. Finally, the TERS spectra of carbon nanotubes were obtained by using our fabricated nanotips.
References


Chapter 1

Correlation between the number of nucleation of gold and surface oxidation of silicon

1.1 Introduction

Gold nanostructures have attracted increasing attention because of their size-dependent properties such as localized surface plasmon resonance (LSPR),\(^1\) coulomb blockade,\(^2\) and catalytic activity.\(^3\) In order to utilize these properties efficiently, it is necessary to control the size and the integrated structure of gold nanostructures. Electron beam and UV lithographies are popular options for fabricating precise nanostructures.\(^4,5\) These techniques, however, require many steps due to their use of resist films for temporary-mask fabrication. A relatively simpler option for fabricating patterned gold nanostructures is maskless electrolytic deposition.\(^6\)

In the previous work of our laboratory,\(^7,8\) patterned gold nanostructures were successfully prepared on a crystalline silicon wafer with a maskless and electroless process as follows: an aqueous solution of hydrogen tetrachloroaurate (HAuCl\(_4\)·4H\(_2\)O) was reacted with 3-mercaptopropyltrimethoxysilane (MPTMS) at 100 °C. The product solution was dropped onto a silicon substrate surface that was previously exposed to a focused ion beam (FIB) or a femtosecond pulsed laser in preselected regions, followed
by drying at 80 °C in an electric furnace. MPTMS functioned as a reducing agent for Au (III) ions to Au (I) ions in the solution and did not work as a coupling agent. Hydrofluoric acid, which is commonly used for electroless methods, was unnecessary for this method. Micro-Raman spectroscopy revealed that amorphization of silicon was induced by FIB or femtosecond laser irradiations when gold nanostructures successfully grew on the irradiated area; therefore, the amorphization of silicon was the first crucial step for the growth of gold nanostructures. However, the details of the growth mechanism have remained unclear so far.

In this chapter, I pursue two basic questions concerning the role of the amorphized silicon in the gold-nanostructure growth: (1) Do gold nanostructures grow on the preprocessed surface before drying or during drying? (2) What is it in the amorphized silicon, but not in crystalline silicon, that leads to the growth of gold nanostructures? To answer the first question, the silicon substrate, on which a drop of Au ion-containing solution has been placed, is rinsed with ethanol before drying. If gold nanostructures are observed on the preprocessed area, they should have grown before drying. To answer the second question, I focus on dangling-bond defects, which exist in much higher concentration in the amorphized silicon than in crystalline silicon. Since the dangling-bond defects are reactive and easily oxidize, the extent of growth of gold nanostructures should depend on the surface oxidation of the amorphized silicon. To investigate such correlation, a sputter-deposited amorphous silicon thin film, instead of
locally amorphized silicon, is used as the test surface. An amorphous silicon thin film can be easily produced by sputtering in vacuum, and the film is wide enough for the spatial resolution of a conventional X-ray photoelectron spectroscopy (XPS) equipment, which is an effective tool for evaluating surface oxidation. Therefore, a thin film of the sputtered amorphous silicon fits our present purpose. For comparison, fracture surfaces of a crystalline silicon substrate, which also have dangling bonds, are subjected both to the gold growth procedure and XPS analysis.

1.2 Experiment

To investigate whether gold nanostructures grew on the preprocessed area before or during drying, the silicon substrate, on which a drop of Au ion-containing solution was placed, was rinsed with ethanol before drying as follows. Undoped Si (100) wafer was cut into 5 mm squares and pre-cleaned by sonication for 5 min in ethanol. A preselected region of the substrate was irradiated with a 1 kHz amplified fiber laser (Ifrit, Cyber Laser), which delivers pulses with a duration of 238 fs and a center wavelength of 780 nm. The laser beam was focused with an objective lens, and its energy fluence \((2E/\pi\omega_0^2)\) was 2.8 J/cm². A suspension, which was prepared by stirring a mixture of 17.5 µl of 2-mercaptoethanol and 3 ml of 0.05 M HAuCl₄ \(aq\) on a hot plate set to 100 °C for 10 min, was then dropped onto the substrate. Here, 2-mercaptoethanol was used instead of MPTMS that was used in our previous study. After 5 minutes, the
substrate was rinsed with ethanol and dried in air at room temperature. The surface of the substrate was observed using an FE-SEM (JSM6700F, JEOL, Japan).

I followed the following procedure to investigate whether or not the gold-nanostructure growth depends on the degree of oxidation of the silicon surface. Amorphous silicon thin films with the thickness of about 100 nm were prepared on a crystalline silicon substrate by radio frequency sputtering (SPF-332H, ANELVA) at room temperature. The sputtering deposition was carried out with an rf power of 50 W at a sputter gas pressure of 0.3 Pa under pure Ar gas. The thickness of the sputtered thin film was measured by Alpha-Step IQ (KLA-Tencor). The amorphous nature of silicon film was identified by X-ray diffraction (XRD) analysis. The thin films obtained were stored in a desiccator for 2–432 hours. Then, the Au ion-containing suspension described above was dropped onto the thin films. After 1 minute, the thin films were rinsed with ethanol and then dried in air. Fracture surfaces of crystalline silicon were also exposed to the same procedure. To evaluate the degree of oxidation of the silicon surfaces, XPS Si 2p spectrum was measured by using Mg Kα excitation (MT-5500, ULVAC-PHI, Inc.).

1.3 Results and Discussion

Figure 1 shows SEM images of the femtosecond-laser-irradiated area after the gold-growth procedure that (a) includes the rinse with ethanol before drying at room
Figure 1. SEM images of the femtosecond-laser-irradiated area after the gold-growth procedure that (a) includes the rinse with ethanol before drying at room temperature, or (b) excludes the rinse but includes drying at 80 °C.
temperature, or (b) excludes the rinse but includes drying at 80 °C. As can be seen, gold nanostructures selectively grew on the laser-irradiated area whether the gold-growth procedure included the ethanol rinse or not. This result proves that gold nanostructures grow before drying.

The rinse procedure gave us a new finding: even if a simple HAuCl₄ aqueous solution is used, the gold nanostructures successfully grow on the preprocessed area. Figure 2 shows an SEM image of a prepared pattern composed of gold nanostructures that grew from a simple HAuCl₄ aqueous solution on the FIB-amorphized silicon surface. All procedures that included rinsing and drying were performed at room temperature. These results revealed that FIB- or femtosecond-laser-induced amorphous silicon reduced Au ions to gold nanostructures.

MPTMS, which appeared necessary in the previous non-rinse procedure, is not required in fact. The reason can be as follows: If a HAuCl₄ aqueous solution is used in the previous non-rinse procedure, a gold chloride thin layer forms on the substrate under drying due to concentration, and prevents us from identifying the gold nanostructures by SEM observation. Conversely, the thin layer formation is avoided when MPTMS is added. MPTMS-derived small impurity particles, which form via hydrolytic condensation when MPTMS is mixed into HAuCl₄ aqueous solution, can remove their surrounding solution on the substrate under drying, and enable us to identify the gold nanostructures by SEM observation. Rinse procedure before drying can also remove the
Figure 2. An SEM image of a prepared pattern composed of gold nanostructures that grew from a simple HAuCl₄ aqueous solution on the FIB-amorphized silicon surface. The substrate, on which the HAuCl₄ aqueous solution was dropped, was rinsed with ethanol before drying. All procedures were performed at room temperature.
solution on the substrate.

The amorphized silicon, which can reduce Au ions to gold nanostructures as shown and discussed above, commonly has much more dangling-bond defects than crystalline silicon. These defects, which are energetically located at around the Fermi level of the intrinsic silicon, seem to reduce Au ions. They are reactive and easily oxidize. Therefore, gold-nanostructure growth should depend on the oxidation of the amorphized silicon surface. Figures 3 (a)–(d) show SEM images of gold nanostructures that grew on the sputter-deposited amorphous-silicon thin films stored in a desiccator for 2–432 hours after the thin-film preparation. The sputter-deposited amorphous silicon was used here instead of FIB- or femtosecond-laser-induced amorphous silicon due to the limitation in spatial resolution of available XPS equipment. As can be seen, gold nanostructures grew on each surface of the sputter-deposited amorphous silicon, and their number decreased with the increasing storage time of the as-sputter-deposited thin film in the desiccator. Figure 4 shows Si 2p XPS spectra of the surfaces of the as-sputter-deposited thin films stored in a desiccator. The intensity ratio of the peak at \(~102–103\) eV to that at \(~99\) eV increased with the increasing storage time. The former and latter peaks indicate silicon oxide (SiOx) and silicon, respectively.\(^10,11\) These results correlate very well to the reduction of the number of gold nanostructures with oxidation of the amorphous silicon surface. Deactivation of dangling-bond defects by surface oxidation\(^12,13\) can be one reason for the decrease in the number of gold nanostructures.
Figure 3. SEM images of gold nanostructures that grew on the sputter-deposited amorphous-silicon thin film stored in a desiccator for (a) 8 min, (b) 24 hours, (c) 48 hours, and (d) 96 hours after the thin-film preparation.
Figure 4. Si 2p XPS spectra of the surfaces of the amorphous-silicon thin films stored in a desiccator. The spectra are normalized at 99 eV.
The surface of freshly fractured crystalline silicon has dangling-bond defects like the amorphized silicon. Figure 5 shows SEM images of gold nanostructures that grew on the fracture surface of a crystalline silicon substrate stored in the desiccator for (a) 5 min and (b) 24 hours after the silicon substrate was fractured. As in the case of the sputter-deposited amorphous-silicon surface, gold nanostructures grew on each surface of the fracture surface, and their number decreased with the increasing storage time in the desiccator. The fracture surface of the crystalline silicon substrate, however, had a much smaller number of gold nanostructures than the sputter-deposited amorphous-silicon surface at the same storage time in the desiccator.

The numbers of gold nanostructures that grew on the sputter-deposited amorphous-silicon surface and the fracture surface of crystalline silicon were quantitatively measured by image processing of SEM images using Igor Pro 5 software program (Wavemetrics, Inc.). Figure 6 shows (a) the number of gold nanostructures per unit area and (b) the area ratio of gold to silicon as a function of the storage time of the sputter-deposited and the fractured silicon in the desiccator. On the fracture surface of crystalline silicon, both the number per unit area and the area ratio of the gold nanostructures decreased more rapidly with the increasing storage time than those on the sputter-deposited amorphous-silicon surface. Figure 6 shows the degrees of surface-silicon oxidation of the sputter-deposited amorphous silicon surface and the fracture surface of crystalline silicon as a function of the storage time in the desiccator.
Figure 5. SEM images of gold nanostructures that grew on a fracture surface of crystalline silicon substrate stored in a desiccator for (a) 5 min and (b) 24 hours after the substrate was fractured.
Figure 6. Results of SEM-image processing of the gold nanostructures that grew on the sputter-deposited amorphous-silicon surface and the fracture surface of crystalline silicon: (a) the number of gold nanostructures per unit area and (b) the area ratio of gold to silicon as a function of the storage time of the sputter-deposited and the fractured silicon in the desiccator.
after preparation of the target silicon surfaces. The degree of oxidation is here defined as 

\[ \frac{A_{SiOx}}{A_{Si} + A_{SiOx}} \]

where \( A_{Si} \) and \( A_{SiOx} \) are the areas of Si 2p XPS peaks assigned to silicon and oxidized silicon, respectively. No noticeable difference in the degree and the rate of oxidation was observed between the sputter-deposited amorphous-silicon surface and the fracture surface of crystalline silicon during initial 100 hours in Fig. 7 despite the remarkable difference in the gold growth behavior in the same time region as shown in Fig. 6. After 100 hours, the degree of oxidation of the sputter-deposited amorphous silicon surface slightly increased, while that of the fracture surface of crystalline silicon seemed to be saturated. It is worth mentioning that XPS provides the information from the top 3 nm of silicon surface under the present experimental conditions.\(^{14,15} \)

The difference in gold growth behavior between the sputter-deposited amorphous-silicon surface and the fracture surface of crystalline silicon seems to originate from the difference in the number of the reactive silicon-dangling-bond defects. The dangling-bond defects exist only at the fracture surface of crystalline silicon. In contrast, the dangling-bond defects exist everywhere in the sputter-deposited amorphous-silicon with a thickness of 100 nm. The amorphous silicon has the reactive surface layer thicker than the fracture surface of crystalline silicon, and the amorphous silicon still has reactive dangling-bond defects even after the fracture surface of crystalline silicon has lost the reactive dangling-bond defects due to oxidation. The difference in the oxidation behavior after 100 hours also suggests amorphous silicon has
Figure 7. The degrees of surface-silicon oxidation of the sputter-deposited amorphous-silicon surface and the fracture surface of crystalline silicon as a function of the storage time in the desiccator. The degree of oxidation is defined as $A_{SiOx} / (A_{Si} + A_{SiOx})$, where $A_{Si}$ and $A_{SiOx}$ are the areas of Si 2p XPS peaks assigned to silicon and oxidized silicon, respectively.
more reactive dangling-bond defects than crystalline silicon. The difference in the gold growth behavior appeared in a shorter time than the difference in the oxidation behavior, because the active chemical species, which react with dangling-bond defects, exist at much higher density in the aqueous solution than in the air.

Therefore, locally producing non-oxidized amorphous silicon surface on a naturally oxidized crystalline silicon surface is the key to the local selective growth of gold nanostructures on a silicon wafer.

1.4 Conclusions

Gold nanostructures selectively grew on the FIB-amorphized silicon surface on a crystalline silicon wafer when exposed to a simple HAuCl$_4$ aqueous solution. MPTMS, which was considered necessary in the previous report of our laboratory, is not required; but the present method includes a new rinse step to the previous method. The Au ions in the solution that were dropped onto the FIB-processed silicon are reduced by the FIB-amorphized silicon, resulting in the growth of gold nanostructures locally and selectively. The dangling-bond defects, which are energetically located at around the Fermi level and exist in large concentration in the amorphized silicon, seem to reduce the Au ions. Locally producing non-oxidized amorphous silicon on a naturally oxidized crystalline silicon surface is the key to the local selective growth of gold nanostructures on a silicon wafer.
References


Chapter 2

Role of solvent molecules in reduction of Au ions by dangling bond defects

2.1 Introduction

Nano-sized gold is a promising material for electronic, photonic, and plasmonic applications due to its unique properties, for example localized surface plasmon resonance (LSPR). In order to achieve these applications, it is necessary to control the size and the integrated structure of gold nanostructures. Electron beam and UV lithographies are popular options for fabricating precise nanostructures. These techniques, however, require many steps due to their use of resist films for temporary-mask fabrication. A relatively simpler option for fabricating patterned gold nanostructures is maskless electrolytic deposition.

The previous work in our laboratory reported a new method to fabricate patterned gold nanostructures on crystalline silicon with a maskless and electroless process. In this method, hydrofluoric acid, commonly used for electroless deposition of metal on silicon, is unnecessary. Au ion-containing solution is dropped onto a silicon substrate preprocessed with a focused ion beam (FIB) or a femtosecond laser. Gold nanostructures selectively grow on the amorphous silicon that has been induced by
The progress in this method as described in chapter 1 enabled us to make gold nanostructures grow with a simple HAuCl₄ aqueous solution, and suggested that silicon dangling bonds, which commonly exist in much higher concentration in the amorphized silicon than in crystalline silicon, reduce Au ions in the solution. In chapter 1, sputter-deposited amorphous silicon thin films and fracture surfaces of a crystalline silicon wafer were subjected both to the gold-growth procedure and X-ray photoelectron spectroscopy for determination of the degree of oxidation as a function of storage time in a conventional desiccator after preparation of the surfaces. The results showed that gold grew on both surfaces; however, the number of gold nanostructures per unit area on the amorphous surface is much greater than on the fracture surface of crystalline silicon, and decreased much more slowly as a function of storage time. Therefore, fabricating non-oxidized amorphous silicon on the naturally oxidized crystalline silicon surface is important for our method. Dangling bonds can give their electrons to Au ions, since dangling bonds are energetically located at the Fermi level of undoped silicon. The Fermi level of undoped silicon is higher than that of the HAuCl₄ aqueous solution. In other words, redox potential for Si⁺/Si• is more negative than that for Au³⁺/Au in an aqueous solution, where Si• represents the silicon atom which has a single dangling bond and three covalent bonds with other silicon atoms.

Here, I suggest a chemical equation of the reaction between Au ion and dangling bonds as follows:
3Si• + Au$^{3+}$ + 3H$_2$O → 3Si-OH + Au + 3H$^+$  \hspace{1cm} (1)

Water molecules are necessary for the formation of Si-OH so as to stabilize Si$^+$ and promote this reaction. In this sense, other protic solvents, which have a hydroxyl group, can also be used instead of water for selective growth of gold nanostructures; however, aprotic solvents, which do not have any hydroxyl group, cannot be used. In this chapter, I investigate the role of solvents in the selective growth of gold nanostructures by using protic and aprotic solvents. I also investigate the deactivation of dangling bonds on the FIB-amorphized silicon with protic solvents and its effect on the growth of gold, since the deactivation of dangling bonds with protic solvents has been investigated on a crystalline silicon surface theoretically and experimentally.$^{20-27}$

2.2 Experiment

An undoped Si (100) wafer was cut into 5 mm squares and pre-cleaned by sonication for 5 minutes in ethanol. Five micrometers square areas on the substrate were irradiated with a Ga$^+$ FIB (JIB-4600F, JEOL, Japan) at an accelerating voltage of 30 kV and an ion dose of 0.5 nC/µm$^2$.

The FIB-irradiated substrates were exposed to a 5 mM Au ion-containing solution for 1 minute followed by ethanol rinse and air drying at room temperature. The Au-ion containing solutions were prepared by dissolving HAuCl$_4$ with each of following solvents: water, methanol, ethanol, 1-propanol, 1-butanol, 2-methyl-2-propanol and
2,2,2-trifluoroethanol, and dimethyl sulfoxide (DMSO), where all solvents, except DMSO, are protic solvents; DMSO is an aprotic solvent. The FIB-irradiated regions on the substrates were observed using an FE-SEM (JSM6700F, JEOL, Japan).

To investigate the effect of the deactivation of dangling bonds with protic solvents on the growth of gold, the FIB-irradiated silicon substrate was exposed to a solvent (deactivator) for 5 minutes before the exposure to a 50 mM HAuCl₄ aqueous solution for 1 minute. The deactivators used in this study were water, methanol and ethanol. After the exposure to the HAuCl₄ aqueous solution, the substrate was rinsed with ethanol and dried in air at room temperature. Then, the FIB-irradiated regions were observed using the FE-SEM.

The surfaces of the FIB-irradiated silicon substrates, which were exposed to a 50 mM HAuCl₄ deuterium oxide solution for the gold growth or deuterium oxide for the deactivation, were analyzed by TOF-SIMS (TRIFT V nanoTOF, ULVAC-PHI, Inc., Japan). In both cases, the exposure time was 24 hours, which can be enough for our purpose. For the silicon surface on which gold nanostructures have grown, the silicon surface was analyzed after the gold nanostructures were removed. The gold structures, which grew under the exposure for 24 hours, are so large that the gold structures are removed with running ethanol rinse due to the weak interaction between gold and silicon. Mass spectra were measured using a 30 kV Ga⁺ primary ion source at a current of 2.5 nA with a raster size of 100 µm × 100 µm.
2.3 Results and Discussion

Figures 1(a)-(g) show gold nanostructures that grew on the FIB-amorphized silicon using protic solvents. The nanostructures were identified as gold with an energy dispersive X-ray spectrometer equipped with an SEM. An upper inset in each figure shows the high magnification image. Gold nanostructures were observed regardless of the kinds of protic solvents. On the other hand, no gold nanostructures were observed in the case of DMSO, an aprotic solvent, as shown in Fig. 1(h). Therefore, protic solvents are necessary for the growth of gold as suggested in eq. (1).

The dependence of the morphology and size of the gold nanostructures on the solvents is beyond the reach of the present work as described below. Instead, the dependence of the area ratio of gold in the FIB-irradiated area on the solvents may be worth discussing. Although the details are not described here, the study in chapter 3 reveals that the total volume of gold nanostructures is greater than that estimated using an excessively-expected number of dangling bonds. This implication means that once the Au-Si interface forms by reduction of Au ions by the dangling bonds with participation of protic solvent molecules, the electrons in the non-FIB-irradiated crystalline silicon around or under the FIB-amorphized silicon also reduce Au ions on the gold surface across the Au-Si interface. This phenomenon is not surprising since the junction of Au-Si is the Schottky contact, and since the Fermi level of gold is higher than that of the Au ion-containing solution.\textsuperscript{18,19,28} The electrons in silicon should flow
Figure 1. SEM images of gold nanostructures that grew on the FIB-irradiated regions of the silicon substrates, where the substrates were exposed to 5 mM HAuCl₄ (a) aqueous, (b) 2,2,2-trifluoroethanol, (c) methanol, (d) ethanol, (e) 1-propanol, (f) 1-butanol, (g) 2-methyl-2-propanol, and (h) dimethyl sulfoxide solutions. Upper insets of (a)-(g) show high magnification SEM images of gold nanostructures that grew using each solution.
into the Au ion-containing solution across the gold nanostructures until the equilibrium is reached. Therefore, eq. (1) mainly explains the number of gold nanostructures directly on the FIB-amorphized silicon, not fully explaining the morphology, size, and the volume of gold nanostructures on the gold nanostructures. In this sense, the dependence of the area ratio of gold in the FIB-irradiated area on the solvent may be worth discussing, although the area ratio is not exactly proportional to the number of gold nanostructures directly on the FIB-irradiated silicon due to, for example, the difference in size of gold.

Figure 2 shows the mean area ratio covered by gold in the FIB-irradiated area, which is obtained from SEM images by image processing using Igor 5, as a function of the autoprotolysis constants of protic solvents. The unity of the area ratio means that gold completely covers the FIB-irradiated area. The autoprotolysis equilibria in a solvent SH is defined by the IUPAC as follows:

\[
SH + SH \rightleftharpoons SH_2^+ + S^-
\]  

(2)

The autoprotolysis constant \(K_{ap}\) is defined as

\[
K_{ap} = a_{SH^2} \cdot a_{S^-} / a_{SH}^2
\]

(3)

where \(a_{SH^2}\), \(a_{S^-}\), and \(a_{SH}\) are the activities of chemical species \(SH_2^+\), \(S^-\), and \(SH\), respectively. Equation (1) suggests that proton elimination is involved in the intermediate state, and difficulty of proton elimination should cause difficulty of the growth of gold. Table I shows the values of autoprotolysis constants \(K_{ap}\) on a
**Figure 2.** The mean area ratio covered by gold in the FIB-irradiated area, which is obtained from SEM images by image processing using Igor 5, as a function of the autoprotolysis constants of protic solvents, where the $pK_{ap}$ is the negative logarithm of the autoprotolysis constant.
Table I. Values of autoprotolysis constants $K_{ap}$ on a logarithmic scale ($pK_{ap} = -\log K_{ap}$) at 298.15 K for protic solvents used in this study.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$pK_{ap}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>14.00</td>
<td>29</td>
</tr>
<tr>
<td>2,2,2-trifluoroethanol</td>
<td>15.00</td>
<td>31</td>
</tr>
<tr>
<td>methanol</td>
<td>16.56</td>
<td>29</td>
</tr>
<tr>
<td>ethanol</td>
<td>18.94</td>
<td>29</td>
</tr>
<tr>
<td>1-propanol</td>
<td>19.28</td>
<td>29</td>
</tr>
<tr>
<td>1-butanol</td>
<td>21.56</td>
<td>29</td>
</tr>
<tr>
<td>2-methyl-2-propanol</td>
<td>28.50</td>
<td>30</td>
</tr>
</tbody>
</table>
logarithmic scale ($pK_{ap} = -\log K_{ap}$) for protic solvents used in this study. A smaller value of a $pK_{ap}$ means that protons are more easily eliminated from the solvent molecules. The area ratio of gold shown in Fig. 2 decreased with increase in the $pK_{ap}$, which is consistent with eq. (1). Equation (1) suggests that proton elimination is involved in the intermediate state, and difficulty of proton elimination should cause difficulty of the growth of gold. The results allow us to generalize eq. (1) as follows:

$$3\text{Si}• + \text{Au}^{3+} + 3\text{ROH} \rightarrow 3\text{Si-OR} + \text{Au} + 3\text{H}^+ \quad (R = \text{H or C}_n\text{H}_{2n+1})$$

(4)

A protic solvent with high $pK_{ap}$ provides high activation energy for the growth of gold.

Some researchers previously reported that water and alcohol molecules are dissociatively adsorbed on a crystalline silicon surface that has dangling bonds, and the chemical equation is written as follows:

$$2\text{Si}• + \text{ROH} \rightarrow \text{Si-H} + \text{Si-OR} \quad (R = \text{H or C}_n\text{H}_{2n+1})$$

(5)

Dangling bonds are deactivated by H or OR termination. The same deactivation can also occur on the amorphized silicon surface, inhibiting the growth of gold. Figure 3 shows SEM images of gold nanostructures that grew on the FIB-amorphized silicon substrates, where the substrates were exposed to (a) water, (b) methanol, and (c) ethanol for 5 minutes before the exposure to a HAuCl$_4$ (aq) for 1 minute. For comparison, an SEM image of gold nanostructures obtained without exposure to any solvents before the exposure to a HAuCl$_4$ (aq) is shown in Fig. 3(d). The area ratios of gold in Figs. 3(a)–(c) are clearly less than that in Fig. 3(d). The growth of gold was inhibited when the
Figure 3. SEM images of gold nanostructures that grew on the FIB-irradiated silicon substrates, where the substrate was exposed to (a) water, (b) methanol, and (c) ethanol for 5 minutes before the exposure to a HAuCl$_4$(aq) for 1 minute. An SEM image of gold nanostructures that grew without the exposure to the deactivator was shown in (d) for comparison. All procedures were carried out at room temperature.
FIB-amorphized silicon was exposed to the solvents before exposure to a \( \text{HAuCl}_4 \) (aq).

Therefore, each protic solvent deactivates the FIB-amorphized silicon surface in the absence of Au ions. The smaller the \( pK_{ap} \) of the deactivator solvent is, the smaller the area ratio of gold is. This fact implies that the proton elimination is involved in the deactivation reaction shown in eq. (5) as well as in the growth of gold.

For further understanding of the effect of the deactivation on the growth of gold, we investigated temperature dependence of the deactivation by water. Figure 4 shows the gold nanostructures, where the substrates were exposed to water at various temperatures before exposure to a 50 mM \( \text{HAuCl}_4 \) (aq) at room temperature. The area ratio of gold clearly decreased with rise in the deactivation temperature. Thus, the deactivation becomes fast with rise in temperature. This result suggests that lower temperatures should be favorable for the growth of gold.

To confirm this suggestion, we also investigated temperature dependence of the growth of gold without the deactivation. Figure 5 shows gold nanostructures that grew using a 50 mM \( \text{HAuCl}_4 \) (aq) at various temperatures without the deactivation treatment. In fact, the area ratio of gold that grew at around room temperature (Fig. 5(b)) was greater than those at other lower and higher temperatures. This fact implies that the FIB-irradiated surface exposed to \( \text{HAuCl}_4 \) (aq) undergoes both deactivation and growth of gold simultaneously. At the solution temperatures of 40 °C and 80 °C (Figs. 5(c) and (d)), the deactivation of dangling bonds is faster than the growth of gold. At 4 °C (Fig.
Figure 4. SEM images of the gold nanostructures that grew on the FIB-irradiated regions of the silicon substrates, where the substrates were exposed to water at (a) 4 °C, (b) 20 °C, (c) 40 °C, and (d) 80 °C for 5 minutes, before exposure to 50 mM HAuCl₄(aq) at room temperature.
Figure 5. SEM images of gold nanostructures that grew on the FIB-irradiated regions of the silicon substrate using a 50 mM HAuCl$_4$(aq) at (a) 4 °C, (b) 20 °C, (c) 40 °C, and (d) 80 °C without the deactivation treatment.
5(a)), the growth of gold can be faster than the deactivation; however, the frequency to overcome the activation energy of the growth of gold can be smaller than that at room temperature. Therefore, around room temperature is the optimum temperature for fast growth of gold in our fabrication method using HAuCl₄ (aq).

Finally, surface analysis of the silicon substrate was carried out by TOF-SIMS to confirm eqs. (4) and (5). Figure 6 shows the peak intensity ratio of OD⁻ fragments to D⁻ fragments calculated from the mass spectra of the two sample surfaces: one sample surface (Fig. 6(a)) is the surface of the FIB-amorphized silicon substrates that was exposed to a 50 mM HAuCl₄ deuterium oxide solution for the gold growth, followed by removing the gold nanostructures. The other sample surface (Fig. 6(b)) is the surface of the FIB-amorphized silicon substrates that was exposed to deuterium oxide for the deactivation. Deuterium oxide was used to reduce contamination. Equations (4) and (5) suggest that the former sample surface should have much more Si-OD bonds than the latter one when the FIB-induced dangling bonds completely consumed in the growth of gold or in the deactivation: the former surface shall undergo both eqs. (4) and (5), while the latter one shall undergo only eq. (5). In other words, the former sample surface should have a higher OD/D peak intensity ratio than the latter one. It may say worth saying that only relative intensity ratio is able to be compared between samples by TOF-SIMS. Additionally, the OD/D peak intensity ratio is proportional to, but not equal to the abundance ratio of Si-OD to Si-D due to different ionization probabilities of OD⁻
Figure 6. TOF-SIMS peak intensity ratio of OD- fragments to D- fragment on (a) the surface of the FIB-amorphized silicon substrate that was exposed to a 50 mM HAuCl₄ deuterium oxide solution for the gold growth, followed by removing the gold nanostructures, and (b) the surface of the FIB-amorphized silicon substrate that was exposed to deuterium oxide for the deactivation.
and D fragments. As is shown in Fig. 6, the FIB-irradiated region of the former sample surface has a higher OD/D peak intensity ratio than that of the latter sample surface, while no noticeable difference was observed between the non-irradiated regions of the both sample surfaces. This result clearly supports the reaction mechanisms suggested above.

2.4 Conclusions

I demonstrated direct growth of gold nanostructures at the interface between an FIB-irradiated silicon surface and a HAuCl₄-dissolved solution, and discussed the mechanism in terms of solvents for HAuCl₄. Protic solvents, which promote the reduction of Au ions by silicon dangling bonds, are necessary for the growth of gold nanostructures in our area-selective electroless method. A protic solvent with small pK_{ap} is favorable to cover the FIB-irradiated area with gold. Additionally, the morphology of gold was affected by the solvent. Since protic solvents can also deactivate the dangling bonds, the FIB-irradiated surface exposed to HAuCl₄ (aq) undergoes both deactivation and growth of gold simultaneously. Consequently, in the case of HAuCl₄ (aq), around room temperature is the optimum temperature for the fast growth of gold.
References


Chapter 3

Electron transfer to Au ions from crystalline silicon across the silicon/gold interface

3.1 Introduction

Electrochemical metal deposition onto silicon substrates is widely used to fabricate micro- and nano-structures for photonic, electronic and plasmonic applications. Among the electrochemical approaches, selective electroless deposition has the advantage in terms of the fabrication of patterned metal nanostructures without resists and current supply. Several researchers previously reported selective electroless deposition of metal nanostructures on silicon substrates by using focused ion beam (FIB) irradiation\(^1\) and atomic force microscopy (AFM) scratching\(^2\)\(^-\)\(^4\). For practical use of electroless deposition for nano-fabrication, understanding its growth mechanism is significantly important. The most electroless approaches use hydrofluoric acid (HF) and they can be divided into two main types on the basis of the role of HF in electroless deposition. In the first type, HF is used for galvanic displacement described as follows: \(^5\)

\[
M^{z+} + ze^- \rightarrow M^0
\]  
\[
Si + 6HF \rightarrow SiF_6^- + 6H^+ + 6e^-
\]

The second type uses HF only for H-termination of silicon surface and not added to the
metal precursor solution. In this case, H-terminated silicon reduces metal ions in the precursor solution instead of the oxidation of silicon.  

In previous chapters, I demonstrated the selective electroless deposition of gold nanostructures on silicon substrates without HF. In this method, gold nanostructures grow from a pure HAuCl₄ aqueous solution selectively on the FIB-irradiated silicon surface. The mechanism of nucleation of gold described in chapter 2 is completely different from that previously reported in other electroless methods using HF. Dangling bonds defects induced by FIB irradiation reduce Au ion in the solution assisted by protic solvent molecules:

\[
3\text{Si}^* + \text{Au}^{3+} + 3\text{ROH} \rightarrow 3\text{Si-OR} + \text{Au} + 3\text{H}^+ \quad (R = \text{H or C}_n\text{H}_{2n+1}),
\]

where Si* represents the silicon atom which has a single dangling bond and three covalent bonds with other silicon atoms. Further investigation of the selective gold growth in this method could provide fundamental insights into electroless deposition of metal on semiconductor.

In this chapter, I quantitatively evaluated the amount of gold nanostructures by measuring the thickness of gold nanostructures using a dual-beam FIB-scanning electron microscope system (FIB-SEM). The result of the quantitative evaluation reveals that the total number of gold atoms deposited on the FIB-irradiated silicon is much larger than that expected from the number of electrons from dangling bond defects, suggesting that electrons from crystalline silicon surrounding FIB-irradiated
silicon also reduce Au ions in the solution. This mechanism is confirmed by introducing a new two-step growth process in our method. Furthermore, the two-step growth process allows more flexibility of morphology of gold nanostructures than that in our conventional one-step growth process.

3.2 Experiment

3.2.1 Preparation of silicon substrates and FIB preprocessing

An undoped Si(100) wafer was cut into 5 mm squares and precleaned by sonication for 5 min in ethanol. Square areas (5 μm side) on the substrate were irradiated with a Ga⁺ FIB at an acceleration voltage of 30 kV, a current of 1000 pA, and an ion dose of 0.5 nC/μm² by using a dual beam FIB-SEM (JEOL, JIB-4600F).

3.2.2 Evaluation of the thickness and total volume of gold nanostructures

The FIB-irradiated substrates were exposed to a 50 mM HAuCl₄ aqueous solution for varied times, followed by an ethanol rinse and air drying. The morphology of gold nanostructures grown on the FIB-irradiated areas was observed with the SEM. The aggregates of gold nanostructures were partly milled by FIB to expose their cross-sections. Then, the thickness of gold nanostructures was measured by SEM observation of the cross-section. For estimation of the total volume of the gold nanostructures, we approximated the aggregates of gold nanostructures by continuous
and flat gold films having an area of 5 μm x 5 μm, since the gold nanostructures coalesced together and completely covered the FIB-irradiated area. The total volumes of gold nanostructures were calculated from their thicknesses and an area of 5 μm x 5 μm.

3.2.3 Two-step growth process

The FIB-irradiated substrates were exposed to a 50 mM HAuCl₄ aqueous solution for 30 seconds, followed by an ethanol rinse and air drying (a first growth step). Gold nanostructures grown on the FIB-irradiated areas were observed with the SEM. After the SEM observation, the substrates were exposed to Au ion-containing solutions for 1 hour, followed by an ethanol rinse and air drying (a second growth step). Two types of 50 mM HAuCl₄ solutions were prepared for the second step: an aqueous solution and a DMSO solution. The morphology of the obtained gold nanostructures was observed with the SEM.

3.3 Results and Discussion

To investigate the time dependence of the gold growth, we prepared gold nanostructures with varied growth times. Figure 1 shows top-down SEM images of the gold nanostructures grown on the FIB-irradiated area on silicon substrates with the growth time of 30 second to 72 hours. The time series of SEM images demonstrates that the size of gold nanostructures inhomogeneously increased as the growth time becomes
Figure 1. Top-down SEM images of gold nanostructures grown in 30 s, 60 s, 1 h, 6 h, 24 h, and 72 h.
longer. The value of their size, however, cannot be evaluated precisely because of their complex shapes and coalescence. It is noteworthy that coalescent gold nanostructures grew even for 30 second, forming completely continuous film and covering the FIB-irradiated area (figure 1 (a)). This result suggests that the nucleation of gold on the amorphized silicon surface occurs and almost completes within 30 second, similar to the nucleation by H-terminated silicon.7)

For quantitative evaluation of the amount of gold nanostructures, we measured their thickness by using a FIB-SEM. Figure 2 (a) shows a 55-tilted SEM image of the aggregate of gold nanostructures cross-sectioned by FIB milling. We measured the thickness of gold nanostructures from a highly magnified image of the cross-section as shown in figure 2 (b). Since the aggregate of gold nanostructures has a rough surface, the mean value of thickness was obtained by averaging values of thickness measured at equally-spaced 10 points in the SEM image of the cross-section. Figure 3 shows the mean values of thicknesses of gold nanostructures grown in 30 second to 72 hours. As can be seen, gold continued to grow for at least more than 24 hours in the aqueous solution and the thickness of their aggregate increased up to about 200 nm. In chapter 2, I found that dangling bond defects are unstable in water and most of them are deactivated in just 5 minutes. The duration of the gold growth, therefore, implies that another electron source contributes to the gold growth, although dangling bond defects initiate the nucleation of gold.
**Figure 2.** 55°-tilted SEM images of gold nanostructures partly milled by FIB (left) and their cross-section (right).
Figure 3. The mean thickness of gold nanostructures plotted against the growth times.
To confirm this, I calculated the total number of gold atoms deposited on the FIB-irradiated area, $N_{\text{gold}}$, and comparing $N_{\text{gold}}$ with the total number of gold atoms expected from equation (3). $N_{\text{gold}}$ was calculated from the total volume of gold estimated above and the density of gold, 19.3 g/cm$^3$. The calculated $N_{\text{gold}}$ for the gold grown in 30 seconds and 72 hours was summarized in figure 4. In order to calculate the total number of gold atoms expected from equation (3), I employed an extremely overestimated number of silicon dangling bonds that is defined as equal to the number of silicon atoms existing in the FIB-irradiated volume of silicon. This volume is the product of the FIB-irradiated area, 5 µm x 5 µm and the penetration depth of a 30 keV Ga$^+$ ion into silicon. The penetration depth of Ga$^+$ was predicted by using the stopping and range of ions in matter (SRIM 2008 version software) Monte Carlo calculation. The calculated value of penetration depth was consistent with previous report$^8$ that investigated the depth profile of Ga$^+$ implanted into silicon with the same acceleration voltage by using secondary ion mass spectrometry. The resultant total number of gold atoms expected from the extremely overestimated silicon dangling bonds was also summarized in Figure 4. Comparing these numbers reveals that the experimentally obtained $N_{\text{gold}}$ is much greater than the number expected by dangling bonds even in 30 seconds. This difference between the numbers experimentally obtained and expected by equation (3) can be explained electron transfer from crystalline silicon. Once the nucleation of gold occurs by dangling bond defects, the silicon/gold interface is formed.
Figure 4. The total number of gold atoms deposited on the FIB-irradiated area, $N_{\text{gold}}$, and the total number of gold atoms expected from equation (3) and the overestimated number of dangling bonds. $N_{\text{gold}}$ was calculated from the total volume of gold nanostructures grown in 30s and 72 h.
Since the Fermi level of silicon is higher than gold,\textsuperscript{9,10} electrons in crystalline silicon surrounding the FIB-irradiated volume transfer to gold across the interface and, on the gold surface, reduce Au ions in a HAuCl\textsubscript{4} solution, which has the lower Fermi level than gold.\textsuperscript{11,12} The difference in the Fermi level between silicon and a HAuCl\textsubscript{4} solution is eventually the driving force for the gold growth. The result shown in Figure 4 indicates that the total volume of gold is predominantly determined by electron transfer from crystalline silicon rather than dangling bonds. As a consequence, the mechanism of the selective growth of gold can be divided into the nucleation stage and the growth stage as schematically illustrated in Figure 5.

Our presented growth mechanism indicates that once the silicon/gold interface was formed, gold nanostructures can grow without electrons from dangling bond defects. To further investigate this, I introduced a new two-step growth process in our method. In our conventional method, gold nanostructures grew during the single exposure of the substrate to a HAuCl\textsubscript{4} solution (an one-step growth process). In the two-step growth process, on the other hand, the substrate is separately exposed two times to the solutions. The first exposure (the first growth step) is simply intended to form the silicon/gold interface. According to the mechanism described above, once the silicon/gold interface formed in the first growth step, gold should grow without electrons from dangling bond defects in the second exposure (the second growth step). In other words, gold should grow without protic solvents or dangling bond defects in the second growth step.
Figure 5. Summary of the growth mechanism of gold nanostructures in our electroless method. In the nucleation stage, dangling bond defects reduce Au ions in the solution assisted by protic solvents. In the growth stage, electrons from crystalline silicon surrounding the FIB-irradiated volume reduce Au ions on the gold surface across the silicon/gold interface formed in the nucleation stage.
To investigate the effect of solvents in the second growth step, I used 50 mM HAuCl$_4$ solutions using water, a protic solvent, and DMSO, an aprotic solvent. In the first growth step, the FIB-irradiated silicon substrate was exposed to a 50 mM HAuCl$_4$ aqueous solution for 30 seconds for formation of the silicon/gold interface with the minimal thickness of gold. Figure 6 shows 55°-tilted SEM images of the FIB-irradiated area after (a) the first growth step, (b) exposure to the aqueous solution (the second growth step), and (c) exposure to the DMSO solution (the second growth step). After the second growth step, the volume of gold clearly increased in both cases using the aqueous and DMSO solutions comparing with the gold grown in the first growth step. This result supports our proposed mechanism of the growth stage, in which gold grow by electrons from crystalline silicon through the silicon/gold interface.

I also investigated the effect of deactivation of dangling bonds in the growth stage. The substrate subjected to the first growth step was stored in the air for 168 hours to completely deactivate dangling bonds. After the storage in the air, the substrate was exposed to an 50 mM HAuCl$_4$ aqueous solution for 1 hour. Figure 6 (d) shows 55°-tilted SEM images of the gold nanostructures after the second growth step. The volume of gold was dramatically increased. This result also indicates that dangling bonds are not necessary for the gold growth after formation of the silicon/gold interface.

Interestingly, gold nanostructures shown in Figure (b)-(d) have morphologies different from that of gold nanostructures grown by the one-step growth process and
**Figure 6.** 55°-tilted SEM images of gold nanostructures grown in different conditions: (a) in a 50 mM HAuCl$_4$ aqueous solution for 30 s (the first growth step), (b) in a 50 mM HAuCl$_4$ aqueous solution for 1 h (the second growth step), (c) in a 50 mM HAuCl$_4$ DMSO solution for 1 h (the second growth step), and (d) in a 50 mM HAuCl$_4$ aqueous solution for 1 h (the second growth step) after the storage in the air for 168 h.
each other. In the case of the DMSO solution, the morphological difference may be attributed to the difference in the interface energy between gold and the solution, and electron and ion mobility in the solution. On the other hand, in the case of the aqueous solution, the morphological difference seems to be attributed to adsorbed molecules on the gold surface such as ethanol used for rinse and organic compounds adsorbing during the storage. This morphological variety of gold shows potential of this method to control the shape of gold by adequately selecting conditions in the second growth step.

3.4 Conclusions

The amount of gold nanostructures was quantitatively evaluated by measuring the thickness of gold nanostructures. The results shows that the gold growth continued for more than 24 hours and the thickness of gold increased to about 200 nm. The evaluation of the number of gold atoms deposited on the FIB-irradiated area revealed that the mechanism of the electroless deposition in our method consists of the nucleation stage and the growth stage. In the nucleation stage, dangling bond defects reduce Au ions in the solution assisted by protic solvents. In the growth stage, electrons from crystalline silicon surrounding the FIB-irradiated volume reduce Au ions on the gold surface across the silicon/gold interface formed in the nucleation stage.

This proposed mechanism allowed us to introduce the two-step growth process in our method. The new process achieved more flexibility in the morphology of gold
nanostructures than our conventional process and demonstrated the potential to fabricate the functional surface of metal nanostructures.
References


Chapter 4

Area-selective electroless deposition of gold nanostructures on focused-ion-beam-irradiated SiC

4.1 Introduction

Nano-sized gold is a promising material for electronic, photonic, and plasmonic applications due to its unique properties, for example localized surface plasmon resonance (LSPR). For these applications, area-selective fabrication of gold with a desired size and shape on a substrate is a key technology. In previous chapters, I demonstrated a new option to area-selectively fabricate gold nanostructures on crystalline silicon: A pure HAuCl$_4$ aqueous solution with no additives is dropped onto a silicon substrate preprocessed with, for instance, a focused ion beam (FIB). Gold nanostructures selectively grow on the preprocessed area. All procedures are performed at room temperature. This maskless and electroless direct method does not use any silane-coupling agents or hydrofluoric acid that commonly used for the electroless deposition of metal onto silicon.$^1$ The previous chapters also revealed that silicon-dangling bonds, which are induced by the preprocessing and energetically located at around the Fermi level of silicon, reduce Au ions with the formation of silanol groups, initiating the nucleation of gold.
In this chapter, I apply the above-mentioned method to 6H-SiC, a compound semiconductor, to further understand the mechanism in the growth stage of the electroless deposition and to explore the potential of the method. 6H-SiC has Si-rich (0001) face (Si face) and C-rich (0001) face (C face). The growth behavior of gold on each crystalline face is investigated. I also quantitatively evaluate the amount of gold that grew on 6H-SiC, comparing the result with that on silicon. This allows us to discuss the growth stage of gold as well as its nucleation.

4.2 Experiment

A 6H-SiC substrate (Shinko MechatroTech Co. Ltd., Japan) was cut into 5 mm squares and precleaned by sonication for 5 min in ethanol. Square areas (5 μm side) on Si- and C-face surfaces of SiC substrates were irradiated with a Ga⁺ FIB at an acceleration voltage of 30 kV, a current of 1000 pA, and an ion dose of 0.5 nC/μm² by using a FIB (JEOL, JIB-4600F MultiBeam SEM-FIB). The FIB-irradiated substrates were exposed to a HAuCl₄ aqueous solution for 1 to 60 seconds, followed by an ethanol rinse and air drying. The concentration of the aqueous solution was varied from 0.5 to 50 mM. The resultant gold nanostructures on the FIB-irradiated area were observed using the scanning electron microscope (SEM). The Si- and C-face surfaces of a SiC substrate was analyzed by using a Raman microscope with laser excitation at 633 nm (HORIBA, LabRAM HR Evolution). All procedures were performed at room
4.3 Results

Figure 1 shows SEM images of nanostructures that formed on the FIB-irradiated area on the Si and C faces of a SiC substrate from a 50 mM HAuCl₄ aqueous solution in 60 seconds. The nanostructures were identified as metal gold using an energy dispersive X-ray spectrometer equipped with an SEM (JEOL, JSM6700F). Figure 2 shows high-magnification SEM images of gold nanostructures that grew from the HAuCl₄ solutions with various concentrations during 60 seconds on Si and C faces. On both the faces, the size of gold nanostructures increased with a rise in the concentration of Au ions in the solution. The number density of gold nanostructures, which is defined here as the number of gold nanostructures on the FIB-irradiated 5-μm square, also seemed to depend on the Au-ion concentration. Figure 3 shows high-magnification SEM images of gold nanostructures that grew in 1 second from a 50 mM HAuCl₄ aqueous solution. Gold nanostructures were clearly observed even in a short, 1-second, reaction time. As can been seen in Figs. 2 and 3, the Si face seems to be more favorable for nucleation of gold than the C face. Table I summarizes the size and the number density of gold nanostructures grown from a 50 mM HAuCl₄ aqueous solution in 1 and 60 seconds on each face. At both the reaction time, the number density of the gold nanostructures on the Si face is greater than that on the C face, while their size on the Si face is smaller.
Figure 1. SEM images of gold nanostructures that formed on the FIB-irradiated area on Si- and C-face surfaces of a SiC substrate from a 50 mM HAuCl₄ (aq) in 60 seconds. Each scale bar represents 1 µm.
**Figure 2.** High-magnification SEM images of gold nanostructures grown on the FIB-irradiated area on Si- and C-face surfaces of a SiC substrate in 60 seconds by using HAuCl₄ (aq) with its concentration of 50, 5, 0.5 mM. Each scale bar represents 100 nm.
Figure 3. High-magnified SEM images of gold nanostructures grown on the FIB-irradiated area on Si- and C-face surfaces of a SiC substrate in 1 second by using a 50 mM HAuCl₄ (aq). The scale bars represent 100 nm.
Table I. Quantitative parameters for evaluating the growth behavior of gold nanostructures on SiC and silicon. $A_{\text{gold}}$ and $N_{\text{gold}}$ are the area ratio covered by gold in the FIB-irradiated area and the total number of gold atoms deposited on the FIB-irradiated area, respectively.

<table>
<thead>
<tr>
<th>Growth time</th>
<th>Size</th>
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<tr>
<td>(second)</td>
<td>(nm)</td>
<td>($\mu$m$^2$)</td>
<td></td>
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</tr>
<tr>
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<td></td>
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<td></td>
<td>60</td>
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<td>1355</td>
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</tr>
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</tr>
<tr>
<td>Silicon</td>
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<td>0.92</td>
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75
than that on the C face. Table I also shows the area ratio covered by gold in the FIB-irradiated area, $A_{\text{gold}}$, and the total number of gold atoms deposited on the FIB-irradiated area, $N_{\text{gold}}$, on each face of a SiC substrate. For comparison, the values of $A_{\text{gold}}$ and $N_{\text{gold}}$ on an intrinsic silicon substrate are also shown in Table I, where the size and the number density for silicon are not available because individual nanostructures cannot be distinguished owing to their coalescence. $A_{\text{gold}}$ was calculated from SEM images by image processing using Igor 5. $N_{\text{gold}}$ was calculated via estimating total volume of gold nanostructures: in the case of SiC, the product of the spherical volume having the diameter of the size in Table I and the number density; in the case of silicon, the product of the thickness of gold aggregate and the gold-covered area, 5 $\mu$m x 5 $\mu$m x $A_{\text{gold}}$. Although $A_{\text{gold}}$ (SiC) is only 0.65 on the C face and 0.81 on the Si face at 60 seconds, $A_{\text{gold}}$ (Si) is 0.92 even at 1 second. $N_{\text{gold}}$ (Si) is also greater than $N_{\text{gold}}$ (SiC) at both the reaction time: $N_{\text{gold}}$ (Si) is about 4 times at 1 second and 10 times at 60 seconds greater than $N_{\text{gold}}$ (SiC). Thus, silicon is much more favorable for growth of gold than SiC.

Since, in the case of silicon, the irradiation-induced amorphous phase has a positive effect on the growth of gold as shown in chapter 1, Raman spectra were measured on the non-irradiated and the FIB-irradiated surfaces on a SiC substrate. Figure 4 shows Raman spectra on (a) the non-irradiated and (b) the FIB-irradiated areas on the Si face of a SiC substrate. The major peaks in 6H-SiC can be seen in Figure 4 (a).
Figure 4. Raman spectra on (a) the non-irradiated area and (b) the FIB-irradiated area on the Si face surface of a SiC substrate. The spectra were obtained by using laser excitation at 633 nm.
The peak at 150 cm\(^{-1}\) is an E2 planar acoustic mode, at 768 and 788 cm\(^{-1}\) are two planar or transverse optical modes of E2 symmetry, and at 966 cm\(^{-1}\) is an A1 longitudinal optical phonon mode.\(^2\) Some studies reported that broad peaks of amorphous silicon (100-600 cm\(^{-1}\)), amorphous SiC (700-1000) cm\(^{-1}\), and amorphous carbon (1100-1800 cm\(^{-1}\)) appear in Raman spectra of 6H-SiC irradiated by ion beam.\(^3,4\) In the present case, however, no significant change in the spectrum was observed on the FIB-irradiated area (see Figure 4 (b)) owing to our irradiation condition much weaker than those in Refs. 3 and 4. It is noted that, on the C face, Raman spectra of the non-irradiated and the FIB-irradiated areas are identical with the Si face (data not shown). These results indicate that FIB irradiation with the present condition or so, which amorphizes silicon surface,\(^5\) does not amorphize either face of a SiC substrate.

4.4 Discussion

As shown above, gold nanostructures were successfully and selectively grown on the FIB-irradiated area both on the Si and the C faces of a SiC substrate by using our method. As in the case of silicon, the nucleation of gold on SiC is probably initiated by silicon dangling bonds as follows: I presented the following chemical equation for the nucleation of gold on silicon in chapter 2,

\[
3\text{Si}^+ + \text{Au}^{3+} + 3\text{ROH} \rightarrow 3\text{Si-OR} + \text{Au} + 3\text{H}^+ \quad (R = \text{H or C}_{n}\text{H}_{2n+1}),
\]  (1)
where $\text{Si}^\bullet$ represents a silicon atom that has one dangling bond and three Si-Si covalent bonds. As in the case of silicon, no gold nanostructures grew on SiC if the FIB-irradiated SiC substrate was, for example, exposed to water for a period long enough to deactivate dangling bonds before its exposure to a HAuCl$_4$ solution, and if an aprotic solvent having no hydroxyl group, such as DMSO, was used for a HAuCl$_4$ solution. This equation can also explain the difference in the number density of gold nanostructures between the Si and the C faces of SiC, because the number density can be determined by the number of nucleation of gold. The ideal, clean Si- and C-face surfaces of crystalline SiC terminates at silicon atoms and carbon atoms, respectively. FIB irradiation removes the native oxide surface layer and may slightly damage the surface, but does not amorphize SiC as shown in Fig. 4. Considering these facts, the Si-face surface irradiated with an FIB probably has lager number of silicon dangling bonds than the irradiated C-face surface. Since the energy level of silicon dangling bonds is higher than that of carbon dangling bonds,$^6,7)$ silicon dangling bonds are more reactive than carbon ones. Therefore, the number density on the Si face is greater than that on the C face, and stopped increasing only at 1 second or less, while it increased even after 1 second on the C face.

The fact that FIB irradiation amorphizes silicon partially explains that $A_{\text{gold}}$ on silicon is greater than those on SiC. In chapter 1, I revealed that greater number of gold nanostructures grow on the spatter-deposited amorphous silicon surface than on the
fractured surface of crystalline silicon because the amorphous silicon has much more dangling bonds as described. Less-damaged crystalline structures of the FIB-irradiated SiC has smaller number of silicon dangling bonds than the FIB-amorphized silicon. Therefore, the number of nucleation of gold on silicon should be much greater than those on SiC. Since the nucleation of gold on silicon as well as on the Si face of SiC is expected to stop increasing at less than 1 second, the growth stage of gold nanostructures determines the increase in $A_{\text{gold}}$ and $N_{\text{gold}}$ in Table I, especially those on silicon and the Si face of SiC.

Before discussing the growth stage of gold, the total number of gold atoms expected by equation (1) was calculated both on SiC and silicon using an extremely overestimated number of silicon dangling bonds that is defined here as equal to the number of silicon atoms existing in the FIB-damaged volume. This volume is the product of the FIB-irradiated area, 5 μm x 5 μm and the penetration depth of a 30 keV Ga⁺ ion into SiC or silicon. The penetration depth of Ga⁺ was predicted by using the stopping and range of ions in matter (SRIM 2008 version software) Monte Carlo calculation. The resultant total numbers of gold atoms expected by the extremely overestimated silicon dangling bonds were $7.4 \times 10^9$ on SiC and $1.1 \times 10^{10}$ on silicon. Comparing this result with the experimentally obtained $N_{\text{gold}}$ reveals that, at only 1 second, the total volume of gold becomes greater than expected by silicon dangling bonds, especially on silicon. Note that the calculated one, which is extremely
overestimated, allows us to exclude small difference and the contribution of carbon dangling bonds on SiC.

This difference between the experimentally obtained $N_{\text{gold}}$ and the total numbers of gold calculated by equation (1) using the extremely overestimated dangling bonds can be explained by the following growth mechanism: once the silicon-gold or the SiC-gold boundary, both of which are Schottky contacts,\(^8\) has formed via the nucleation of gold, electrons in the non-FIB-irradiated region under/around the FIB-irradiated one go through the boundary and reduce Au ions on the gold surface. The difference in the Fermi level between silicon, or SiC, and a HAuCl\(_4\) solution is the driving force for the gold growth. This mechanism can also explain the fact that $N_{\text{gold}}$ on Si and C faces are close to each other (see Table I) in spite of the difference in the size and the number density of gold nanostructures. Therefore, silicon, which has the Fermi level higher than SiC,\(^9,10\) can provide more electrons for a HAuCl\(_4\) solution at the Au-solution interface.

The results obtained in this study imply that our method is applicable to a metal ion solution-semiconductor system that meets the following conditions: (i) the semiconductor has a native insulating layer at its surface and its fresh surface has dangling bonds reactive enough to reduce metal ions, and (ii) the Fermi level of the semiconductor is larger than that of the metal ion solution, where the semiconductor-metal interface meeting the Shottoky contact condition is effective for the growth of metal nanostructures.
4.5 Conclusions

Our method of local electroless metal deposition, which was previously reported on silicon, was successfully applied to 6H-SiC. The result supports our proposed mechanism as follows: dangling bonds, which forms via FIB irradiation, initiate the nucleation of gold, and then electrons in the non-FIB-irradiated SiC or silicon under/around the FIB-irradiated one reduce Au ions on the gold surface through the nucleation induced the SiC-gold or the silicon-gold boundary. This finding gives us insights into other metal-semiconductor systems.
References

Chapter 5

Fabrication of gold nanostructures at AFM tip apexes for tip-enhanced Raman spectroscopy

5.1 Introduction

Tip-enhanced Raman spectroscopy (TERS), which combines surface-enhanced Raman spectroscopy with scanning probe microscopy (SPM), provides chemical information at nanoscale spatial resolutions.\(^1\)-\(^4\) In TERS, extremely enhanced electric fields of incident and scattered light at the surface of the metallic apex of a probe tip enable us to detect otherwise undetectable ultraweak Raman signals from nanoscale volumes including a single molecule.\(^5\),\(^6\) This enhancement, resulting from localized surface plasmon resonance (LSPR), effectively occurs when the size and shape of the metallic nanostructure at the tip apex is well suited to the wavelength of incident light. Probes used in TERS measurement are typically metal probes for scanning tunnelling microscopy (STM) and metal-coated silicon probes for atomic force microscopy (AFM).\(^7\) Such probes are, however, supposed to enhance the electric fields less effectively than a probe with a metal nanoparticle on its tip apex;\(^8\)-\(^10\) their metal structure along the tip axis is too large to work for the enhancement of visible light, which is commonly used as an excitation light for Raman measurement.
In this chapter, I report the method to prepare a nanotip with the gold nanostructure on its apex by using our area selective electroless deposition described in previous chapters. The apex of a silicon AFM tip is irradiated using a focused ion beam (FIB), and then the FIB-irradiated AFM tip is exposed to a pure HAuCl\textsubscript{4} aqueous solution. With this method, a gold nanostructure selectively grows on the tip apex where the native oxide layer has been removed by FIB irradiation. The previous chapters revealed the gold growth mechanism as follows: Electrons flow from silicon into the solution through the silicon-solution and silicon-metal-solution boundaries owing to the difference in Fermi energy between silicon and the solution, and thus reduce the metal ions on the boundaries. I demonstrate direct growth of a gold nanostructure on two types of AFM tip apexes, and the size and shape dependence of the gold nanostructure on experimental conditions, including the concentration of HAuCl\textsubscript{4} solution and sodium chloride (NaCl) added to the solution. Finally, I also demonstrate the TERS spectrum of carbon nanotube (CNT) obtained by using our fabricated nanotip.

5.2 Experiment

5.2.1 Fabrication of TERS tips

To investigate how the geometry of tip apex affects the gold growth, two types of commercially available silicon AFM probes were employed in this study: model HQ:NSC14/NO AL (Mikromasch) and model OMCL-AC160TN-R3 (Olympus). The
geometry of these probes was shown in Figure 1. For the Mikromasch tip, the tip apex was irradiated with a Ga\textsuperscript{+} FIB (JIB-4600F, JEOL, Japan) at an acceleration voltage of 30 kV, a current of 3.0 pA, and an ion dose of 50 nC/\(\mu m^2\) to mill a hole at the apex. The diameter of the hole is 100 to 200 nm. Milling a hole is aimed at strengthening adhesion of the gold nanostructure to the AFM tip apex by increasing the adsorption area of them, since the gold nanostructure attaches the tip apex only by the van der Waals' force. For the Olympus tip, its apex was truncated by FIB irradiation before milling a hole to ensure its strength; otherwise its apex became so fragile that it was easily broken during the subsequent exposure to the HAuCl\textsubscript{4} aqueous solution. The FIB irradiation condition for the Olympus tip was identical to the condition for the Mikromasch tip excepting the ion dose (30 nC/\(\mu m^2\)). After milling a hole at the apex, the AFM tip was exposure to pure HAuCl\textsubscript{4} aqueous solutions with various concentrations for 60 seconds and then dry in air. To control the size and shape of the gold nanostructure, a NaCl added HAuCl\textsubscript{4} aqueous solution was also used for the gold growth. The fabrication processes are schematically illustrated in Figure 2. All procedures were carried out at room temperature. Geometry of gold nanostructures grown on the tip apexes were observed with a scanning electron microscopy (SEM).

5.2.2 TERS measurement

For TERS measurement, I used a commercial AFM-Raman system combining an
Figure 1. SEM images of the Mikromasch tip (model HQ:NSC14/NO AL) and the Olympus tip (model OMCL-AC160TN-R3).
Figure 2. Schematically illustrated fabrication processes for Mikromasch and Olympus AFM tips.
AFM unit (AIST-NT, SmartSPM™ 1000) with a Raman microscope (HORIBA, LabRAM HR Evolution). This TERS setup employs the side-illumination geometry, in which the tip apex is illuminated at incident angle of 65° to the tip axis. A continuous-wave laser beam with a wavelength at 633 nm was linearly polarized along the tip axis and focused by an objective (100×, NA = 0.70). The TERS measurement was performed for CNTs and graphene flakes dispersed on a gold-coated glass substrate, which was purchased from AIST-NT Co. Ltd. Our fabricated nanotip was controlled by tapping (AC) mode and contact mode for obtaining the topographic image of the sample surface and the near field Raman spectra, respectively. The Raman spectra were recorded with an integration time of 0.5 second.

5.3 Results and Discussion

Figure 3 shows SEM images of the tip apexes of Mikromasch and Olympus tips exposed to a 50 mM HAuCl₄ aqueous solution. As can be seen, gold nanostructures selectively grew on the tip apexes, while no gold growth was observed on other area covered by silicon oxide layers. This result demonstrates that our fabrication method is applicable to different types of AFM tips. Interestingly, gold nanostructures on these types of tips have similar morphology regardless of the different tip geometry. This implies that the shape of gold nanostructures depends on the concentration of the HAuCl₄ aqueous solution rather than tip geometry.
Figure 3. SEM images of the apexes of Mikromasch tip and Olympus tip exposed to a 50 mM HAuCl$_4$ aqueous solution.
For investigation of the morphological dependence of gold nanostructures on the concentration of the solution, pure HAuCl₄ aqueous solutions with varied concentrations were used for the gold growth. Since the geometry of the Olympus tip is more appreciate for TERS measurement than the Mikromacsh tip, I employed the Olympus tip for the following experiments. Figure 4 shows SEM images of the tip apexes exposed to 0.5, 5.0, and 50 mM HAuCl₄ aqueous solutions. The morphologies of gold nanostructures changed depending on the concentration of the solution. Although this result indicates that the size and shape of the gold nanostructure can be changed by controlling the concentration of the solution, the size of the gold nanostructures grown from these solutions is too large for the TERS measurement.

To control the size and shape of the gold nanostructure at the tip apex, NaCl was added to the HAuCl₄ aqueous solution. Previous study reported that anisotropic growth of gold nanoparticles was facilitated by increasing the concentration of NaCl in the growth solution of gold nanoparticles.¹¹ Such anisotropic growth can be explained by face-selective adsorption of Cl ions on gold. Figure 5 (a) shows SEM images of the tip apex exposed to the aqueous solution (5.0 mM HAuCl₄, 2.0 × 10⁻³ mM). A sharp needle-shaped gold nanostructure grew at the tip apex. The diameter of the apex of the needle-shaped gold is about 20 nm. Furthermore, the size of the gold nanostructure grown from the NaCl-added aqueous solution is smaller, comparing with the one grown from the pure HAuCl₄ aqueous solution. This result demonstrates that the addition of
Figure 4. SEM images of the tip apexes exposed to 0.5, 5.0, and 50 mM HAuCl₄ aqueous solutions.
Figure 5. (a) The SEM images of the needle-shaped gold nanostructure grown on the tip apex from the aqueous solution (5.0 mM HAuCl₄, 2.0 × 10³ mM NaCl). (b) The simplified model of the needle-shaped gold nanostructure and the distribution of electric field calculated by using FDTD simulation.
NaCl to the aqueous solution successfully promotes anisotropic growth of gold and inhibits the growth rate of gold in our fabrication method.

In order to verify the utility of our fabricated tip for TERS, I investigate the distribution of enhanced electric field by using a finite-difference time-domain (FDTD) simulation software (KeyFDTD, Kagiken, Japan). The simplified model of the needle-shaped gold nanostructure was designed by combining an oval sphere and a rounded cone with the tip diameter of 20 nm. The simulation was performed at a wavelength of 653 nm. Figure 5 (b) shows the model structure and the field distribution calculated by FDTD simulation. The enhanced electric field can be observed at the apex of the needle-shaped gold nanostructure model. This result indicates that the gold nanostructure with such morphology is suitable to TERS measurement with a high spatial resolution.

Finally, our fabricated tip was used for TERS measurement of CNTs. Figure 6 (a) shows the side view of the apex of the tip used in this measurement, which was prepared using the aqueous solution (0.5 mM H\textsubscript{Au}Cl\textsubscript{4}, 1.0 M NaCl). The diameter of the tip apex is about 20 nm. Figure 6 (b) shows the topographic image of CNTs and graphene flakes dispersed on a gold coated glass substrate obtained by using the fabricated tip. The tip was sustainable during AFM scanning in the AC mode. The near-field Raman spectrum acquired at the point marked by the white arrow in the topographic image is shown in Figure 6 (c) along with the far-field Raman spectrum at
Figure 6. (a) An SEM image of our fabricated nanotip used for TERS measurement. (b) A topographic image of CNTs and a graphene flake on the substrate acquired by using the nanotip shown in (a). (c) Near-field and far-field Raman spectra of the CNTs acquired at the point marked by the white arrow in (b).
the same point. When acquiring the far-field Raman spectra, the tip apex was placed 10-"nm away from the sample surface by using AC mode. With increasing the distance, the enhanced electric field at the tip apex no longer reaches the sample surface. The strong enhancement of D-band (1321 cm\(^{-1}\)) and G-band (1585 cm\(^{-1}\)) Raman signals from the CNT\(^{12,13}\) can be observed when our fabricated tip contacted on the CNT (upper spectrum), comparing with the case when the tip was away from the CNT (lower spectrum). It should be noted that our fabricated tip was sustainable during the repetition of contact and uncontact on the sample. These results could clearly demonstrate the applicability of our fabricated tip to TERS measurement.

**Conclusions**

Our area-selective electroless deposition was successfully applied to the fabrication of the nanotip with a gold nanostructure at its apex. Gold nanostructures selectively grew on the FIB-irradiated tip apexes of commercially available silicon AFM probes. The morphology of the gold nanostructure grown at the tip apex depends on the concentration of the HAuCl\(_4\) aqueous solution. The addition of NaCl to the aqueous solution enables fabrication of a needle-shaped gold nanostructure, which seems to be suitable for TERS measurement. The strong enhancement of Raman signals from the CNTs was observed by using our fabricated tip. This work provides a potential option to fabricate nanotips for high-resolution TERS imaging.
References

List of Publications

Chapter 1

“Selective growth of gold nanostructures on locally amorphized silicon”,
Hiroki Itasaka, Masayuki Nishi, Yasuhiko Shimotsuma, Kiyotaka Miura, Masashi Watanabe, Himanshu Jain, Kazuyuki Hirao,

Chapter 2

“Patterned growth of gold nanostructures on silicon via reaction between induced silicon dangling bonds and protic solvents”,
Hiroki Itasaka, Masayuki Nishi, Kazuyuki Hirao,
Proc.27th International Microprocesses and Nanotechnology Conference, pp. 7D-5-3 (2013).

“Role of solvent in direct growth of gold nanostructures at the interface between focused ion beam-amorphized silicon and Au-ion-containing solution”,
Hiroki Itasaka, Masayuki Nishi, Kazuyuki Hirao,

Chapter 3

“Fabrication of gold nanostructures with various morphologies by area-selective electroless deposition”
Hiroki Itasaka, Masayuki Nishi, Masahiro Shimizu, Kazuyuki Hirao
Chapter 4

“Area-Selective Electroless Deposition of Gold Nanostructures on SiC Using Focused-Ion-Beam Preprocessing”,
Hiroki Itasaka, Masayuki Nishi, Masahiro Shimizu, Kazuyuki Hirao,

Chapter 5

“Area-selective electroless deposition of gold on AFM tip apexes for tip-enhanced Raman spectroscopy”,
Hiroki Itasaka, Masayuki Nishi, Masahiro Shimizu, Kazuyuki Hirao,

“Silver Growth on AFM Tip Apexes from Silver Nitrate Solutions Triggered by Focused-Ion-Beam Irradiation”,
Masayuki Nishi, Daisuke Teranishi, Hiroki Itasaka, Masahiro Shimizu, Kazuyuki Hirao
To be published for Mater. Res. Soc.

“Fabrication of nanotips for tip-enhanced Raman spectroscopy by electroless deposition of gold at AFM tip apexes”
Hiroki Itasaka, Masayuki Nishi, Masahiro Shimizu, Kazuyuki Hirao
Submitted for Adv. Mater.
Awards


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