Focused-ion-beam-enabled electroless growth of gold nanoparticles on silicon

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Gold nanoparticles grow area-selectively on focused-ion-beam-irradiated areas of a silicon substrate in response to exposure to a pure chloroauric acid solution. Thus, this area-selective metal deposition does not use resist films, silane-coupling agents, and electrolysis. Hydrofluoric acid, almost always used in electroless deposition of gold on silicon, is also unnecessary as long as micro/nanoscopic areas are targeted. This review highlights how we developed the method for the growth of gold on a desired local region of silicon products, including commercially available atomic force microscopy probes as well as silicon wafers, and discusses the mechanism.

Key-words : Gold nanoparticles, Silicon, Focused ion beam (FIB), Electroless deposition, Enhanced Raman scattering

1. Introduction

Gold nanoparticles have attracted much attention because of their distinctive properties and applications in analytical chemistry, catalysis, and medical therapy1–5) Their beautiful red color in glass, which is currently understood to be due to localized surface plasmon resonance, is well-known, and was already used in ancient times. As to scientific research, Michael Faraday, in 1857, reported a solution route to produce “a beautiful ruby fluid,” and deduced from his numerous experimental results that “finely-divided metallic gold is the source of the ruby colour”.6) Of course, there was no electron microscope at that time. In 1908, Mie theoretically explained the origin of the varied color of gold colloids, including the red color.7,8) Perhaps, the most popular solution routes to control the size of gold nanoparticles are the following two methods: One is citrate reduction. It was selected from ten different methods through electron microscopic examination of the resultant sols by Turkevich et al. in 1951.9) In 1973, Frens reported synthesis of six monodisperse gold suspensions with the diameter 16–150 nm using Turkevich-modified citrate reduction.10) The other method is the Brust–Schiffrin method, reported in 1994.11) They used Faraday-inspired two-phase (water-toluene) reduction in presence of a stabilizer/capping agent for gold nanoparticles (dodecanethiol) and a phase-transfer reagent, and synthesized 1–3 nm gold nanoparticles. In the 2000s decade, a lot of achievements were reported in shape-controlled synthesis12–18) as well as size-controlled synthesis.19)

We reported a shape-controlled synthesis of gold using (3-mercaptopropyl)trimethoxysilane (MPTMS) as a reducing agent.20) Here, we firstly mention this MPTMS reduction. In fact, this research accidentally led to the start of our research on area-selective growth of gold nanoparticles on silicon. Area-selective deposition of gold on a substrate is a useful technique for fabricating micro/nano electronic/optical devices and substrates for chemical analysis such as surface-enhanced Raman spectroscopy. The most popular method is probably photo/electron-beam lithography.21,22) Perhaps, the following three methods are close to our method in terms of a direct method, no use of resist unlike such lithography: In a method, reported by Schmuki and Erickson in 2000,23) p-type silicon is irradiated using a Si++ focused ion beam (FIB), and is then electrochemically treated in an aqueous solution of potassium cyanide and gold(I) potassium cyanide at potentials in the processing window. Gold is electrodeposited selectively on the Si++ FIB irradiated area. In another method, reported by Weller et al. in 2003,24) an n-type silicon wafer is first heat-treated for growth of the surface oxide. Then it is irradiated using a Ga++ FIB. After that, it is exposed to a hydrofluoric acid solution. Finally, it is placed into a commercial electroless gold-plating solution at 60°C. Gold nanoparticles grow selectively on the FIB-irradiated area. In the other method, reported by Homma’s group in 2005,25) p-type silicon is exposed to a hydrofluoric acid solution to have hydrogen-terminated surface. Then, it undergoes nanoindentation with a diamond probe of a
scanning probe microscope. After that it is exposed to a hydrofluoric acid solution, again. Finally, it is exposed to hydrofluoric acid solution containing trace amount of gold ions. Gold is deposited selectively on the indentation spot. In our method, a silicon substrate, any type: intrinsic, n, p, is irradiated using a Ga⁺ FIB, and is exposed to a pure chloroauric acid solution. Gold nanoparticles grow selectively on the FIB-irradiated area. Thus, our area-selective method is characterized by no use of resist, electrolysis, reducing additives, and hydrofluoric acid. This simplicity in the reaction system can be useful for further understanding of phenomena at the interface between semiconductors and metal-ion-containing solutions. As mentioned above, research on MPTMS reduction led to the area-selective growth of gold on silicon. We accidentally found a hint to area-selective growth of gold (for the details, see the next section), and have improved the method in parallel with examination of the mechanism. Thus, this review focuses on how we developed our method. Finally, recent challenge of applying the method to produce probes for tip-enhanced Raman spectroscopy is mentioned.

2. Growth of gold using MPTMS as a reducing agent

MPTMS is a silane coupling agent, having one thiol group and three methoxy groups. Thiol groups prefer to bind to gold surfaces as is used in the Brust-Schiffrin method. Methoxy groups can react with hydroxyl groups of other compounds to form chemical bonds through dealcoholization condensation or hydrolysis and dehydration condensation. Thus, MPTMS is, for example, a useful compound to attach gold to glass substrates.

Since thiol groups not only bind to specific metals such as gold and silver, but also bind to their ions, we attempted to cap gold ions using MPTMS-derived polymers and then to reduce the gold ions using a reducing agent. However, in fact, gold grew before the addition of the reducing agent. Figures show scanning electron microscope (SEM) images (JEOL JSM-6700F) of gold particles synthesized just by mixing an MPTMS ethanol solution and a chloroauric acid solution. The gold particles were triangular and hexagonal microplates with the thickness of 50–70 nm. It was found that thiol groups of MPTMS-derived polymers reduce gold ions through the formation of disulfide. Sulfonation of the thiol groups also contributes to reduction of gold ions, especially at the elevated temperatures. Oxidation of thiol groups to the oxidizability of dithiols increases as the distance between the thiol groups decreases. Negishi and Tsukuda synthesized gold clusters using the oxidation of a dithiol: meso-2,3-dimercaptosuccinic acid. They also mentioned that this dithiol shows a much higher yield of gold clusters than the relating monothiol: mercaptosuccinic acid. In our case, MPTMS undergoes hydrolysis and dehydration condensation as well as formation of MPTMS–gold ion complexes, in response to mixing with a chloroauric acid solution, resulting in formation of MPTMS-derived polymers with intramolecular thiols. The number of the intramolecular thiols is equal to the degree of polymerization. Polymerization of MPTMS decreases the distance of the thiol groups, and accelerates formation of the disulfides and gold. Since the usage of 2-mercaptoethanol instead of MPTMS resulted in spherical gold microparticles, MPTMS-derived polymers played an important role in the anisotropic growth of gold.

MPTMS, which is a liquid at room temperature and has a boiling point of 213–215°C, can also be used both as a solvent and a reducing agent up to the boiling point like ethylene glycol (the boiling point is about 196°C) in the polyol method. Fig. 1(d) shows an SEM image of gold nanoparticles synthesized by heat-treating chloroauric acid in MPTMS at 200°C for 2 h. In this experiment, poly(vinylpyrrolidone), which is commonly added to stabilize the resulting colloidal particles in the polyol method, was not used.

3. Area-selective growth of gold on silicon

When we observed a product of a reaction similar to those mentioned in Section 2 on a silicon substrate using an SEM, we found a part of gold nanoparticles assembling on lines by chance. Such gold nanoparticles were smaller than those that we synthesized by the reaction. We speculated that the silicon substrate had some effects on the growth of gold, and that the lines, on which gold nanoparticles assembled, was cracks propagated on the surface. To confirm this speculation, we started by scratching silicon surfaces by tweezers. In fact, gold nanoparticles grew on the scratched lines: however, energy dispersive X-ray spectroscopy showed that scratching a silicon surface by tweezers formed Fe and Cr on the scratched lines. They are components of the tweezers. Although such external impu-
show SEM images (Hitachi S-4300) of phosphorus silicon on gold growth is discussed later. Electron microscope (TEM) observations of gold nanoparticles on Si substrates. Using this feature, we performed transmission sections as well as smooth and rough areas: A box of 4 μm square at each corner of a window on the bottom-side surface was irradiated with a FIB. (a) Schematic diagrams of a single crystalline silicon grid with nine windows for TEM observation. This grid has 15 nm-thick membrane of polycrystalline silicon on the bottom. A box area at each corner of a window on the bottom-side surface was irradiated with a FIB. (b) An SEM image at a tilt of gold nanoparticles grown at a corner of a window [shown in (a) as the red open rectangle]. The inset is the top view [bottom view for the silicon grid in (a)]. (c) The magnified image of (b), focusing on the membrane.

With our method, gold can grow even at very thin cross-sections as well as smooth and flat top surfaces of silicon substrates. Using this feature, we performed transmission electron microscope (TEM) observations of gold nanoparticles. Figure 3(a) shows schematic diagrams of a single crystalline silicon grid with nine windows for TEM observation (TEMwindows.com Porous UltraSM). This grid has 15 nm-thick membrane of polycrystalline silicon on the bottom. The diagram also indicates FIB irradiation areas: A box of 4 μm square at each corner of a window on the bottom-side surface was irradiated with a FIB at an acceleration voltage of 30 kV, a current of 100 pA, and an ion dose of 0.67 nC/μm². Then, the FIB-irradiated substrate was exposed to a droplet of a pre-prepared suspension, and was dried at 80°C. The suspension was prepared as follows. A mixture of 42.5 μl of MPTMS and 3 ml of 0.05 M chloroauric acid aqueous solution was stirred for 2 h in a glass vial on a hot plate set to 100°C.

The latter reason was important for us because we found that amorphous silicon forms on the lines scratched weakly by a diamond-tipped pencil. The effect of amorphous silicon on gold growth is discussed later. Figure 2 shows SEM images (Hitachi S-4300) of “Gold” that grew area-selectively on a FIB-irradiated area on a silicon substrate. The procedure was as follows: An undoped Si(100) substrate of 5 mm squares was pre-cleaned by sonication in ethanol for 5 min. A local area on the silicon substrate was irradiated with a Ga⁺ FIB (FEI Strata DB235) at an acceleration voltage of 30 kV, a current of 100 pA, and an ion dose of 0.67 nC/μm². Then, the FIB-irradiated substrate was exposed to a droplet of a pre-prepared suspension, and was dried at 80°C. The suspension was prepared as follows. A mixture of 42.5 μl of MPTMS and 3 ml of 0.05 M chloroauric acid aqueous solution was stirred for 2 h in a glass vial on a hot plate set to 100°C.

To understand the mechanism of gold growth further, a silicon substrate that has a droplet of a gold-ion-containing liquid on its top surface after irradiation was rinsed with ethanol before drying of the droplet. The purpose of this experiment was to examine whether gold grows before drying or under drying at 80°C. In this experiment, an ultrashort pulsed laser (Cyber Laser Ifrit) was used instead of a FIB. The use of an ultrashort pulsed laser is discussed later. Additionally, 2-mercaptoethanol was used instead of MPTMS to examine the role of MPTMS on gold growth.
whether MPTMS plays a role of a reducing agent and/or a silane coupling agent. As the result, gold grown area-selectively on the laser-irradiated area of the silicon substrate was observed even if the substrate exposed to gold-ion-containing liquid was rinsed with ethanol and dried in air at room temperature. This result shows two things: One is that gold grows before drying. Drying at 80°C is unnecessary for the growth of gold. The other is that MPTMS does not work as a silane-coupling agent. Methoxy groups are unnecessary for the growth of gold on ultrashort pulsed laser-irradiated silicon. In fact, we subsequently found that thiol compounds, including MPTMS and 2-mercaptoethanol, are unnecessary as well. We re-examined whether gold grows on FIB-irradiated silicon substrates in response to exposure to a pure chloroauric acid solution or not, where, after exposure to the solution, we rinsed the substrates with ethanol and dried them at room temperature. Gold successfully grew both on ultrashort pulsed laser-irradiated and FIB-irradiated local silicon area-selectively in response to exposure to a pure chloroauric acid solution. Therefore, gold ions are probably reduced by such silicon. Importantly, the results enabled us to use a pure chloroauric acid solution instead of a specifically prepared gold-ion-containing suspension. This simplicity is helpful to understand the mechanism of the growth of gold. Before discussing the mechanism further, we discuss what roles MPTMS played in the growth of gold.

MPTMS, a thiol compound, can reduce gold ions through, for example, formation of the disulfide and the sulfonate as is mentioned in Section 2. A suspension, to be dropped on a FIB- or laser-irradiated silicon, was prepared by heating a mixture of MPTMS and chloroauric acid solution at 100°C for 2 h, and it is composed of ochercolored particles and a colorless transparent solution. Energy dispersive X-ray spectroscopy indicated that the particles are MPTMS-derived polymers and contain gold atoms. The colorless solution contains monovalent gold ions. This reduction of the valence and the concentration of gold ions in the solution causes a change in the volume, size and shape of the grown gold; for example, the size of gold ions in the solution causes a change in the volume, size and shape of the grown gold. The other is that it covers under a vacuum, and does not have oxidized layer on its surface at preparation. The other is that it covers a substrate of 5 mm square, and the area is large enough for the spatial resolution of conventional X-ray photoelectron spectrometers (XPS), which is an effective tool for evaluating surface oxidation. Amorphous nature of the sputter-deposited silicon thin film was identified by X-ray diffraction analysis. Fracture surfaces of a crystalline silicon substrate were used as well, since they also have dangling-bond defects. Freshly fractured crystalline silicon is different from fresh amorphous silicon: The former has dangling-bond defects just at the surface layer, but the latter has them throughout it. In the experiment, both types of silicon with a fresh surface were stored in a desiccator for varying hours. Then, they were exposed to a droplet of a gold-ion-containing suspension for one minute at room temperature. The suspension included 2-mercaptoethanol, because we thought that a thiol compound was necessary at that time. After one-minute exposure, they were rinsed with ethanol and dried in air at room temperature. To evaluate the degree of oxidation of the silicon surfaces, XPS Si 2p spectra were measured by using Mg Kα excitation (ULVAC-PHI Inc. MT-5500). Figures 5(a)–5(d) shows SEM images of gold nanoparticles that grew on the sputter-deposited amorphous silicon thin films stored in a desiccator for (a) 8 min, (b) 24 h, (c) 48 h, and (d) 96 h after preparation. Gold nanoparticles that grew on fracture surfaces of a crystalline silicon substrate are shown in Figs. 5(e) and 5(f): Storage time in a desiccator after preparation was (e) 5 min, and (f) 24 h. Gold nanoparticles grew on each surface of both types of silicon. Their number decreased as the storage time after preparation increased. Fracture surfaces of a crystalline silicon substrate, however, had much smaller numbers of gold nanoparticles than sputter-deposited amorphous silicon surfaces at the same storage time. Figure 6(a) shows Si 2p XPS spectra of sputter-deposited amorphous silicon thin films stored in a desiccator. Two peaks were observed: one is assigned to silicon and the other is assigned to oxidized silicon, SiOx.63)–65) Degrees of oxidation of silicon surfaces, including fracture surfaces of a crystalline silicon substrate, as a function of the storage time are shown in Fig. 6(b). The degree of oxidation was defined as $\Delta(\text{SiO}_x)/[\Delta(\text{Si}) + \Delta(\text{SiO}_x)]$, where $\Delta(\text{Si})$ and
A(SiOx) are the areas of the peaks assigned to silicon and oxidized silicon, SiOx, respectively. Surfaces of both types of silicon rapidly oxidized up to about 20% of XPS-detectable silicon. XPS provides chemical information of top surfaces within 3 nm depth under the experimental conditions. After that, sputter-deposited amorphous silicon surfaces slowly continued to oxidize, while fracture surfaces of a crystalline silicon substrate. Storage time in a desiccator was (e) 5 min, and (f) 24 h. The gold-ion-containing suspension was prepared by heating a mixture of a chloroauric acid solution and 2-mercaptoethanol.

As we described above, pure chloroauric acid solutions replaced heat-treated mixtures of a chloroauric acid solution and a thiol compound. This finding simplified the reaction system and allowed us to consider the mechanism further. Since silicon dangling-bond defects are energetically located at around the Fermi level of intrinsic silicon, they can reduce gold ions. We can write the chemical equation as follows:

$$3\text{Si}^* + \text{Au}^{3+} + 3\text{H}_2\text{O} \rightarrow 3\text{Si}^\text{OH} + \text{Au} + 3\text{H}^+,$$

where Si* represents a silicon atom with a single dangling bond and three covalent bonds with other silicon atoms. Equation (1) deduced that water molecules, or protic solvent molecules are essential for the nucleation of gold, since we can generalize Eq. (1) as follows.
2-propanol, 2,2,2-trifluoroethanol, and dimethyl sulfoxide (DMSO). All these solvents, except DMSO, are protic solvents. DMSO is an aprotic solvent. SEM observations revealed that, in all of the protic solvents, gold nanoparticles grew selectively on the FIB-irradiated area of silicon substrates in response to exposure to a 5 mM chloroauric acid (a) aqueous, (b) ethanol, (c) 1-butanol, and (d) DMSO solution for 1 min.29) Fig. 7.

\[ 3\text{Si} + \text{Au}^{3+} + 3\text{ROH} \rightarrow 3\text{Si} - \text{OR} + \text{Au} + 3\text{H}^+ \], (2)

where R represents a hydrogen atom or a hydrocarbon group. Thus, we investigated the dependence of growth behavior of gold on the solvents used to dissolve chloroauric acid.29) An undoped Si(100) wafer was cut into 5 mm squares and precleaned by sonication in ethanol for 5 min. A local area of 5 \( \mu \)m square was irradiated with a Ga\(^+\) FIB (JEOL JIB-4600F) at an acceleration voltage of 30 kV, a current of 1000 pA, and an ion dose of 0.5 nC/\( \mu \)m\(^2\). The FIB-irradiated silicon was exposed to a 5 mM chloroauric acid solution for 1 min followed by ethanol rinse and air-drying at room temperature. The solvents, which we used to dissolve chloroauric acid, were water, methanol, ethanol, 1-propanol, 1-butanol, 2-methyl-2-propanol, 2,2,2-trifluoroethanol, and dimethyl sulfoxide (DMSO). All these solvents, except DMSO, are protic solvents. DMSO is an aprotic solvent. SEM observations revealed that, in all of the protic solvents, gold nanoparticles grew on the FIB-irradiated surface. In contrast, as shown in Fig. 7, no gold grew in DMSO, as Eqs. (1) and (2) deduced [for other results supporting Eqs. (1) and (2), see Ref. 29].

Estimates of the total numbers of grown gold atoms and FIB-induced dangling-bond defects allow us to understand the quantitative contribution of the dangling-bond defects to the amount of grown gold through Eq. (1).31) The former was obtained through estimation of the total volume of grown gold. The area used for FIB irradiation, 5 \( \times \) 5 \( \mu \)m\(^2\), was multiplied by the mean thickness of gold. The mean thickness was obtained as follows. A cross-section of a gold aggregate, covering the FIB-irradiated area, was prepared by FIB irradiation, and was observed at a 55° tilt with an SEM (see Fig. 8). Using the SEM image, thicknesses of the cross-section were measured at 10 points equally spaced, and the mean thickness was calculated. With our gold growth procedure, gold almost covers 5 \( \times \) 5 \( \mu \)m\(^2\) of FIB-irradiation area just after 1 s exposure to a 50 mM chloroauric acid aqueous solution, but incompletely covers the area. To estimate the gold volume at 1 s exposure, we firstly obtained the area ratio of gold on the FIB-irradiated area by image processing of the top-view SEM images (Wavemetrics Igor Pro 5), and multiplied it by 5 \( \times \) 5 \( \mu \)m\(^2\). The resultant gold area was, then, multiplied by the gold thickness, which was measured using SEM images at a 55° tilt through the space without gold. Thus, we estimated the total numbers of grown gold atoms; for example, 2.2 \( \times \) 10\(^{10}\) at 1 s exposure and 1.0 \( \times \) 10\(^{11}\) at 60 s exposure, where we used 19.3 g/cm\(^3\) as the density of gold. Then, we need the total number of dangling-bond defects, induced by FIB irradiation, to understand the quantitative contribution of the dangling-bond defects to the amount of grown gold through Eq. (1); however, we could not estimate or measure the total number of dangling-bond defects. Instead, we overestimated an upper limit of the total number of dangling-bond defects using an imaginary structure: each silicon atom has one dangling-bond defect in a FIB-induced effective surface volume. The volume was defined as the product of the FIB-irradiated area, 5 \( \times \) 5 \( \mu \)m\(^2\), and the penetration depth of a 30 keV Ga\(^+\) ion into silicon, 27 nm. This depth was obtained by the Stopping and Range of Ions in Matter (2008 version) based on a Monte Carlo simulation method. The number of silicon atoms in the FIB-induced effective surface volume was then estimated using a crystalline silicon model, although such region was amorphized in fact. The resultant number of the overestimated silicon dangling-bond defects is 3.3 \( \times \) 10\(^{10}\). Since Eq. (1) requires silicon dangling-bond defects three times as many numbers as gold atoms, the number of gold atoms even at 1 s exposure was not explained by Eq. (1). This indicates that the growth reaction of gold after nucleation is different from the nucleation reaction shown by Eq. (1) (for the growth of gold on SiC surfaces, see Ref. 30).

To confirm the difference, we used double exposure.31) The FIB-irradiated silicon substrates were first exposed to a 50 mM chloroauric acid aqueous solution for 30 s,
followed by an ethanol rinse and air drying. Then, the substrate was observed using an SEM, and the growth of gold was confirmed. After that, the substrate was exposed to a 50 mM chloroauric DMSO solution for 1 h, followed by an ethanol rinse and air drying. Note that single exposure of FIB-irradiated silicon to DMSO solution of chloroauric acid did not result in the growth of gold as shown in Fig. 7. Thus, DMSO solution cannot be used for the first exposure of the double exposure experiment. We found that gold further grows at the second exposure even in a DMSO solution of chloroauric acid (see Fig. 9). This result proved that the growth reaction of gold after its nucleation is different from the nucleation reaction shown in Eqs. (1) and (2).

Since the overestimated upper limit of the number of dangling-bond defects explains only 10% of the number of gold atoms grown at 60 s single exposure as mentioned above, the growth reaction of gold after its nucleation determines the amount of resultant gold. The mechanism of the growth of gold after its nucleation can be as follows. Soon after silicon/gold interfaces form via gold nucleation, electrons in crystalline silicon flow into the solution and reduce gold ions through the interfaces and the growing gold. The electron transfer is driven by the difference in the Fermi level, that is, chemical potential of electrons. The Fermi level decreases in the order silicon > gold > chloroauric solution in the isolated form.

\[ \text{Si}_n \rightarrow \text{Si}_n^+ + e^- \]  
\[ [\text{AuCl}_4]^- + 3e^- \rightarrow \text{Au}^0 + 4\text{Cl}^- \]

where \( n \) is the number of silicon atoms. The positive charge of \( \text{Si}_n^+ \) is delocalized in \( n \) atoms of silicon. This reaction should forms space-charge layers of silicon/(growing gold)/(chloroauric acid solution) under electron-neutrality. As predicted by the mechanism, copper, silver, palladium, and platinum grew and nickel does not grow with our method. However, details of the mechanism of gold growth after the nucleation are unclear yet and is still under research; for example, whether Si–O bonds form under the reaction or not. The depth of the FIB-irradiated area from the non-FIB-irradiated surface level changed little after the growth of gold, which was measured by atomic force microscopy (AFM). For the measurement after gold growth, gold was removed in a similar manner described in Ref. 29 before the measurement. The result indicated that the FIB-irradiated silicon did not dissolve during the growth of gold. A tentative analysis of time-of-flight secondary ion mass spectra have indicated that Si–O bond formation in the depth direction under the FIB-irradiated area was within a few nanometers, which can explain only a fraction of a total amount of grown gold. Although we need further experiments, a slight increase in Si–O bonds everywhere on a very wide unirradiated surface around FIB-irradiated area may also contribute to electron supply to the interfaces of silicon/(growing gold)/(chloroauric acid solution). Since our reaction system is very simple, it is useful to further understand the phenomena at the interface between semiconductors and solutions.

To remove the native oxide layer area-selectively from silicon surfaces, we can use an ultrashort pulsed laser instead of a FIB. Figure 10 shows SEM images of gold nanoparticles that grew on the laser irradiation spot of a silicon substrate in response to exposure to a 1 mM chloroauric acid solution. Laser irradiation was performed with a single pulse: the pulse width, 100 fs; the wavelength, 800 nm (Coherent Inc., Mira-RegA9000). By using electric trigger, we changed the repetition rate from 250 to 1 kHz, and extracted a single pulse. This figure also shows the dependences of the growth of gold on the laser power and on the irradiation atmosphere, that is, in air or in a vacuum. The laser power at the position before entering the objective lens, 10× and numerical aperture of 0.3, was changed from 2 to 20 mW. In the SEM images, white-colored structure is gold. In air, gold nanoparticles grew on the laser-irradiated spot at 2 mW, but grew only on the outer edge of the laser-irradiated spot at the laser power of 10 and 20 mW, whereas, in a vacuum, gold nanoparticles grew on the laser-irradiated spot at each laser power. This difference in growth behavior of gold is probably owing to reoxidation of silicon in the laser-irradiation in air. A key procedure of our method is to remove the native oxide layer locally so that the electrons of silicon go to the chloroauric acid solution through the local area and reduce gold ions in response to exposure to it. Thus, reoxidation prevents the growth of gold. Laser irradiation not only ablates the native oxide surface layer but also causes heat in the relaxation process. This heat probably accelerates reoxidation of the silicon surface in air. Considering the laser beam profile, the intensity decreases outwards. In other words, the local temperature in the laser-irradiated spot also decreases outwards. Thus, in laser irradiation in air at higher power, reoxidation accelerates at the inner areas in the laser-irradiated spot, resulting in growth of gold only on the outer edge of the laser-irradiated spot. In the laser irradiation in a vacuum, gold grew over the laser irradiation spot, since reoxidation did not occur even at the center of the laser irradiation spot owing to the absence of oxygen around silicon. Therefore, in the laser irradiation in air, the laser power must be regulated for ablating the oxide surface layers on silicon.
4. Fabrication of probes for tip-enhanced Raman spectroscopy

Tip-enhanced Raman scattering (TERS) is an option for scanning probe microscopy, and provides chemical information at nanoscale spatial resolutions.\(^{68) - 74}\) Thus, TERS has attracted much attention of material researchers since its first experimental realization.\(^{75) - 78}\) However, TERS is still not a common technique and is used only by the limited research groups. In TERS, extremely enhanced electric fields of incident and scattered light at the surface of the metal apex of a probe tip allow us to detect otherwise undetectably weak Raman signals from nanoscale volumes including a single molecule. Typical probes used for TERS are, currently, chemically-etched metal probes for scanning tunneling microscopy (STM) and metal-coated silicon probes for AFM. Round robin studies indicated that TERS using STM systems showed higher reproducibility of TERS spectra than TERS using AFM systems.\(^{79}\) Since STM requires conductive samples and since AFM can measure both conductive and non-conductive samples, TERS using AFM must be improved so that TERS become a more popular and powerful method. Improvement in probes for AFM-based TERS is a key issue.

We reported a new option to fabricate TERS probes using commercially available AFM probes.\(^{80}\) Our method of selective growth of metal nanostructures on a local area of silicon substrates, described in Section 3, was applied to growth of gold and silver at the tip apex of AFM probes. AFM probes are commonly made of silicon, and uneven surfaces or tip apexes as well as smooth and flat surfaces are potential targets of our method. Figure 11 is an example of gold grown at the apex of AFM probes (Mikromasch, HQ:NSC14/No Al). Upper three images, (a)–(c), are tip appearance at each step of the gold growth process: (a) before FIB irradiation, (b) after FIB irradiation, and (c) after immersion to a pure 50 mM chloroauric acid aqueous solution for 60 s. Lower three images, (d)–(f), are magnified images of (a)–(c). We can modify the size and shape of gold by concentrations of chloroauric acid solutions, immersion time, additives into solutions, FIB irradiation conditions, and so on. Figure 12 is another example of gold grown at the apex of AFM probes (Olympus, OMCL-AC160TN-R3). Our current interest is in further control of the size and shape of gold and silver, improvement of their reproducibility, and TERS measurements using our probes. In fact, we successfully demonstrated TERS measurements of carbon nanotubes using our probes. The results will be reported soon.

5. Conclusions

We demonstrated area-selective growth of gold, silver, copper, palladium, and platinum on silicon. Our method is effective in area-selective local deposition of metal nanoparticles, and not effective in covering the whole surface of a silicon substrate. For the latter purpose, usage of hydrofluoric acid is preferable within electroless deposition.

Although we first thought that MPTMS was necessary for our area-selective metal growth method, we found that we can use a pure chloroauric acid solution instead of an MPTMS-containing chloroauric acid solution. This finding/simplicity not only allowed us to understand the
mechanism of the area-selective metal growth further, but also expanded the potential of our method. Using our method, we, for example, grew gold at the tip apex of silicon AFM probes. The resultant probes can be used as probes for TERS, a nanoscale Raman spectroscopy.

Acknowledgements The author wishes to thank all the co-workers and the students who supported him. Especially, the author is deeply grateful to the following ones: Prof. K. Hirao (Kyoto Univ.) for his kind support; Dr. H. Itasaka, and Dr. T. Matsuoka, who were the students at that time, for their experimental support and fruitful discussions; Prof. M. Watanabe and Prof. H. Jain (Lehigh Univ.) for their support in TEM observation; Prof. K. Miura and Prof. Y. Shimotsuwa (Kyoto Univ.) for their support in laser irradiation. This research was supported in part by Ministry of Education, Culture, sports, Science and Technology (MEXT) of Japan: Global COE Program “International Center for Integrated Research and Advanced Education in Materials Science” (No. B-09), KAKENHI Grant Number 18750181, 25288107, 15J07791, 16K05933, administrated by the Japan Society for the Promotion of Science; the Center of Innovation Program from Japan Science and Technology Agency, JST. This research was also supported in part by the National Science Foundation for initiating and supporting our international collaboration through the International Materials Institute for New Functionality in Glass (IMI-NFG: NSF Grant No. DMR-0844014).

References


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