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Fabrication of gold microstructures using negative photoresist doped with gold ions through two-photon excitation

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The fabrication of gold microstructures was investigated using a mixture of SU-8 and gold ions with two-photon excitation induced by a femtosecond laser. Energy dispersive X-ray spectrometry, micro-X-ray diffraction and X-ray photoelectron spectroscopy were performed to analyse the resulting microstructures. Electrical conductivity was also measured. The elemental analysis showed that the fabricated structures consisted of triangular, reduced gold crystals and small amounts of cross-linked SU-8. The conductivity of the fabricated structures was four orders of magnitude lower than that of pure gold because of the cross-linked SU-8 present in the material.

1. Introduction

In recent year, one-photon excitation process has been employed to control the formation of silver and gold crystals[1-4] and fabricate the patterned structures on a polymer surface.[5] These techniques achieved the fabrication of silver and gold nanoplate and patterned 3D structures on the polymer surface.

On the other hand, multiphoton excitation processes have attracted attention in many fields. In particular, the use of direct laser writing (DLW) through two-photon excitation for the creation of intricately patterned structures has been studied in the fields of microelectromechanical systems (MEMS)[5] and micro-optics[6] because high-resolution, three-dimensional (3D) structures can be fabricated using this technique. A femtosecond laser combined with a microscope and a high-magnification, high-numerical-aperture objective lens are commonly used to fabricate patterned, 3D structures on a micron or submicron scale; two-photon excitation can be easily induced by a femtosecond laser due to high peak intensity.

An advantage of DLW through two-photon excitation is that one can fabricate microstructures at specific points. Thus, in recent years, DLW has been used to fabricate many types of 3D structures out of various materials.[7-12] In particular, Maruo's group achieved the fabrication of complex 3D structure using photo-resist and gave a mechanical function to the fabricated structures.[13] The fabrication of conductive metal structures has also been studied[14,15] because these structures can provide a unique function.[16] Among other metals, silver and gold ions have been used to create this type of structure mainly because they are sensitive to light. However, few reports have included analyses of the fabricated structures. The analysis of a fabricated structure is important to demonstrate its conductivity.

Previous studies[17-19] have demonstrated the successful fabrication of a structure made of photo-reduced silver. However, the oxygen dissolved in the sample oxidized the fabricated silver structure to form a silver oxide structure and the conductivity of the fabricated structure was six orders of magnitude lower than that of the pure silver because of the formation of silver oxide (i.e., oxidation). Thus, we think that a structure with conductivity close to that of the pure metal can be obtained using gold ions because elemental gold is more stable than elemental silver. The chemical reaction between SU-8 and tetrachloroauric (iii) acid has been previously reported[20] and is shown in Scheme S1. This report describes not only the fabrication of gold microstructures via this reaction but also the analysis of the resulting structures by energy dispersive X-ray (EDX) spectrometry, micro-X-ray diffractometry (μ-XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Base on these analysis, we clarify the mechanism for the fabrication of the gold structures. We think that the understanding of the mechanism is important for the refinement of the fabrication methods and the enhancement of characteristics, such as conductivity, of the fabricated structures.

2. Experimental

A mixture of SU-8 (Microchem Co.), which includes a photo-acid generator (Ar_2ISbF_6) as a polymer matrix and cyclopentanone (Nacalai Tesque Inc.) as a solvent, and tetrachloroauric (iii) acid ($HAuCl_4$) (Sigma-Aldrich Co. Ltd) was used. In addition, styrene (Nacalai Tesque Inc.) and pentaerythritol triacrylate (PETA) (Sigma-Aldrich Co. Ltd) as a monomer, and 2,2'-asobis(isobtyronitrile) (AIBN) (Nacalai Tesque Inc.) and 2-isopropylthioxanthone (ITX) (Sigma-

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Aldrich Co. Ltd) as an initiator were used. As described in Electronic Supplementary Information, SU-8 monomer gave the favourable and preferred results. Therefore, in this paper, SU-8 monomer is employed to fabricate the gold structures. $HAuCl_4$ (0.042 g) was added to 1 ml of cyclopentanone, and the mixture was stirred for 15 min. SU-8 (1.25 g) was added to the mixed solution in ice-cold water to prevent a side reaction between the SU-8 and the gold ions occurring from the heat of dissolution. The prepared solution was used to fill a 5-mm hole in a 500-μm-thick silicone film on a slide glass, and a cover glass was placed over the sample. All procedures were carried out in the dark at room temperature. The absorption spectrum of the solution shown in Figure 1 indicates that the sample solution absorbs wavelengths under 400 nm and does not absorb 800 nm light.

An 800 nm femtosecond laser was employed to reduce gold ions through two-photon excitation. First, the 800 nm laser beam directly excited photo-acid generators in SU-8 through two-photon excitation, and then gold ions were reduced through SU-8 cross-linking. A schematic of the laser irradiation system is illustrated in Figure S2 (a). The light source was a Ti:Sapphire laser system (Spectra Physics MaiTai) with an operating wavelength of 800 nm, repetition rate of 80 MHz, and pulse width of 130 fs. A detailed illustration of the sample configuration under the microscope is shown in Figure S2 (b). Femtosecond pulses of 800-nm light were passed through an optical microscope (Olympus BX51WI) and focused on the samples using an oil-immersion objective lens (Olympus UPlan FLN, 100X, NA=1.3). The samples in which the Au structures

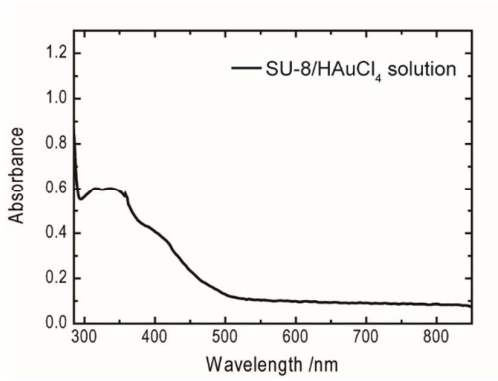

Figure 1. UV-Vis absorption spectrum of the mixture.

were fabricated were on a 3D stage controlled by ALPS3861 software. A laser scan speed of 50 μm s^{-1}, a laser power of 50 mW and a laser diameter of approx. 3 μm were used. To analyse the profiles and properties of the fabricated structures, linear and planar structures were fabricated by single laser scans and by arranging the linear structures, respectively.

After being irradiated by the laser, the sample was thermally treated at 95 °C for 15 min. SU-8 monomer was reacted with photo-acid generated by the laser irradiation under this thermal treatment. Then, the sample was developed and rinsed to remove the photo-acid generator from the sample, as well as the unreacted resist and gold ions. Note that only small amount of the reduction of gold ions occurred by only thermally treatment.

The resulting structures were analysed using an EDX at an acceleration voltage of 20 kV and a μ-XRD at a tube voltage of 40 kV, tube current of 30 mA and step speed of 0.1 degree min^{-1}, as well as a XPS and an AFM. A gold electrode was evaporated to measure conductivity, as illustrated in Scheme S2, and the resistance of fabricated structures of various lateral widths was measured using a digital multimeter (DMM) (KENWOOD, DL-97).

3. Results and Discussion

3-1. Elemental analysis

To investigate the elemental composition of the fabricated structures, EDX measurements were obtained from the planar structures, and the results are shown in Figure 2. Characteristic X-ray spectrum illustrated in Figure 2 (a) gives the concentration of the fabricated structures. From this spectrum, the ratio of CK and Au (AuMa and AuLa) is calculated 34/66 by wt. As shown in Figures 2 (c) and (d), no carbon signals can be observed, and gold signals are visible in the fabricated planar structure. In addition, the Si and O signals of the glass substrate cannot be observed in the fabricated planar structure, as illustrated in Figure 2 (e) and (f). Thus, the EDX results indicate that the fabricated structure mainly consists of gold. Furthermore, μ-XRD was performed to analyse the elements in detail, and the diffraction pattern is shown in Figure 3.

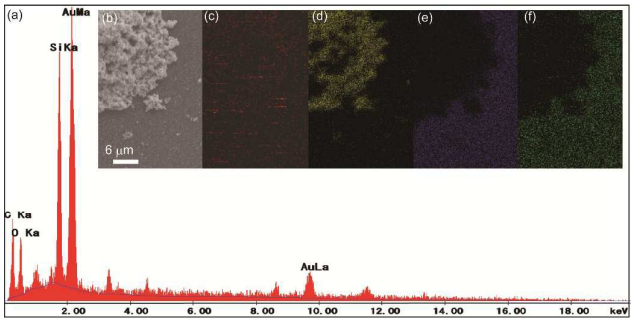

Figure 2. (a) Characteristic X-ray spectrum of the fabricated structure, (b) SEM image of surface of the fabricated structures and colour mapping of (c) C, (d) Au, (e) O and (f) Si detected by EDX.

The μ-XRD pattern of a gold thin film (50 nm) that was evaporated is also shown as a reference. A clear Au diffraction pattern can be observed in the μ-XRD signals of the fabricated structures, as shown in Figure 5. The μ-XRD results show peaks at 38.1° and 44.3°, which were attributed to Au (111) and Au (200),[21] respectively. Compared with the XRD pattern of monocrystalline gold shown as a reference, the results indicate that the orientation of the gold crystal grain in the fabricated structures is random and that many gold microcrystals generated by the two-photon reduction gather to form the gold structures.

XPS was performed to analyse the chemical state of the samples. Figure 4 shows the C (1s), Cl (2p) and gold ($4f_{7/2}$ and

$4f_{5/2}$) XPS spectra. Figure 4 (c) includes the XPS spectrum of the pure gold as a reference. Figure 4 (a) shows the XPS peak derived from carbon, which can be separated into two peaks by multiple Gaussian curve fitting. The peak at 285.0 eV can be attributed to C (1s), and the peak at 286.5 eV can be attributed to C-O- bonds, which are derived from the cross-linked SU-8. The EDX results showed that a small amount of cross-linked SU-8 is incorporated into the fabricated gold structures. The absence of a peak in Figure 4 (b) indicates that chloride is not a component of the fabricated structures. The Au (Au $4f_{7/2}$ and Au $4f_{5/2}$) spectra are shown in Figure 4 (c). Compared with the gold reference spectrum, the peaks of the samples are at a lower binding energies. In general, chemical shifts to lower binding energies occur when samples are negatively charge. Here, the gold atom interacts with oxygen atoms, such as those in the carbonyl groups of poly(N-vinylpyrrolidone).[22] These results indicate that the gold atoms in the fabricated structures interact with the oxygen atoms of the cross-linked SU-8.

If the chemical reaction occurs as previously described,[15] the amounts of cross-linked SU-8 and grown gold are considered equal. However, in this case, the results indicate the existence of a small amount of cross-linked SU-8 and a large amount of grown gold. This result suggests that although the main chemical reaction was the photo-reduction of gold ions, photo acid was generated, simultaneously cross- linking of a small amount of SU-8. AFM was used to measure the height profiles of the linear and planar structures, and the results are shown in Figure 5. Figure 5 (d) is an enlarged view of the planar structure, and a 3D image of a linear structure is also shown in Figure 5. The AFM results showed that the height and the linewidth of the fabricated structures were 1.67 μm and 4.19 μm and that the planar structures were 0.76 μm in height. The linewidth of the fabricated structures is wider than the diameter of the laser beam. Because the photo-acid diffused in liquid state until it started the photopolymerization under thermal treatment, the area of the reduction of gold ions widened beyond the focal spot and thus the linewidth grew more than 3 μm. As shown in the enlarged view of the planar structures, the photo-reduced gold crystals are triangularly shaped,

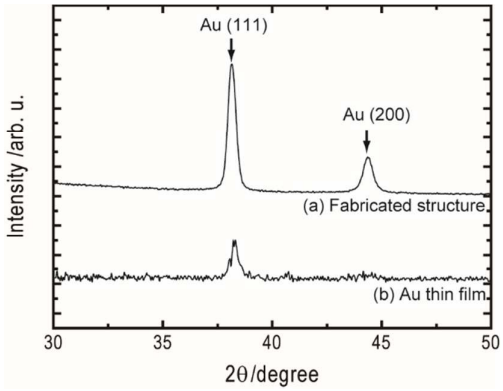

Figure 3. XRD patterns of the structure fabricated by femtosecond laser and a pure gold thin film, shown as a reference.

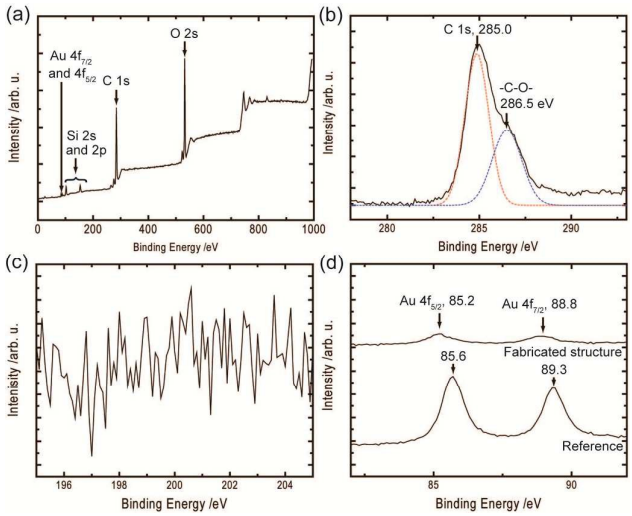

Figure 4. XPS spectra of the fabricated planar structures (a) over the whole range, (b) C (1 s), (c) Cl (2p) and Au ($4f_{7/2}$ and $4f_{5/2}$). The spectrum shown in (b) can be separated into two peaks by multiple Gaussian curve fitting.

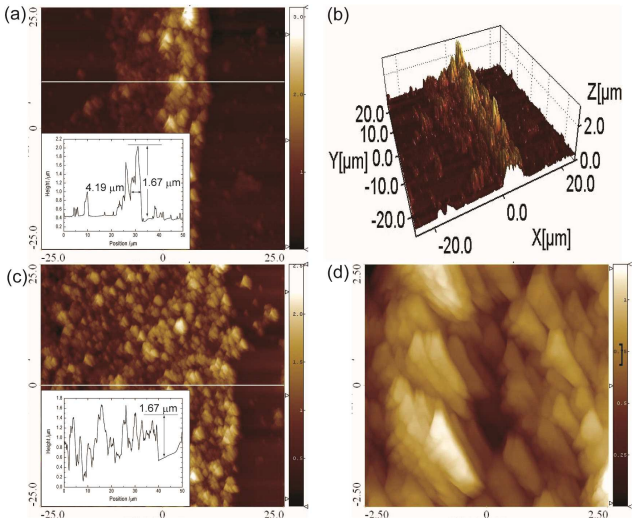

Figure 5. AFM images of the fabricated gold structures. (a), and (c) planar structures and height profiles (insets). (b) 3D image of the fabricated structures; (d) is an enlargement of (c).

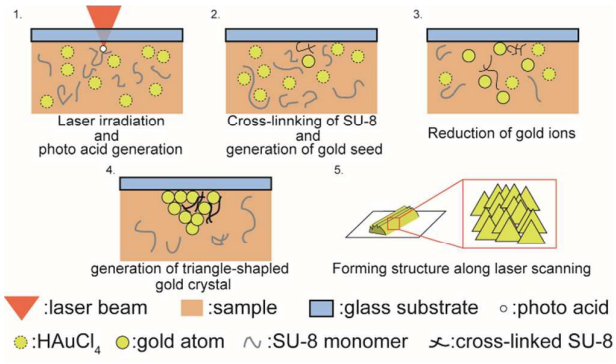

Figure 6. Schematic view of the fabrication mechanism of the gold structures.

and the structures are composed of the triangular gold crystals. Although gold trough structures generated by laser ablation have been previously reported,[23] the structures fabricated in the present study are mountain-like in shape, and damage from the femtosecond laser was not observed. In the context of this previous report,[24] these results indicate that this method can prevent generation of the trough structures generated by laser ablation.

Considering the results of the analyses, the fabrication mechanism for the gold structures is illustrated in Figure 6. First, the laser beam excites a photo-acid generator to generate photo acid. Then, the photo acid reacts with the SU-8 monomer, which cross-links. The cross-linking SU-8 reduces $HAuCl_4$, thereby reducing gold ions. Subsequently, the reduced gold ions assemble into triangular gold crystals, which eventually form linear or planar structures.

3-2. Structure width dependency of conductivity

In a previous study,[14] the conductivity of a fabricated silver structure was very low because oxidization resulted in an oxidized silver structure. In the present study, the conductivity of the fabricated structures was expected to be essentially equal to that of pure gold because the stability of elemental gold is high, preventing it from reacting with other elements. To assess conductivity, the electrical resistance of fabricated gold structures of various lateral widths was measured using a DMM. The resistivity calculated from the obtained resistances using the following equation:

$$\rho = R\frac{A}{L} \quad (1)$$

where ρ is the resistivity, R is the resistance, A is the cross-sectional area of the fabricated structure, i.e., lateral width $\times$ height, and L is the distance between the electrodes.

Table 1. Electric conductivity and resistivity of the fabricated planar structure

Lateral width /μm	Resistance /Ω	Resistivity /Ω m
100	116	5.8×10^{-5}
300	111	1.67×10^{-4}
600	135	4.05×10^{-4}

The calculated values are summarized in Table 1. As shown in Table 1, the fabricated gold structures were conductive; in addition, the resistivity of the fabricated gold structures was lower than that of the previously reported silver structure, which was approximately 2.0×10^{-2} Ω m. However, the resistivity of the gold structures was four orders of magnitude higher than that of the pure gold reference material. As described above, cross-linked SU-8 is incorporated into the fabricated structure, and interfaces among the photo-reduced gold crystals and cross-linked SU-8 are generated.

We expected that the resistivity would be reduced by the small amount of cross-linked SU-8, structural defects occurring during electrode preparation, and interfaces developing among the reduced gold crystals and cross-linked SU-8. Furthermore, the resistance of the structure with a lateral width of less than 10 μm could not be obtained because the structure was broken at the time the samples were developed and rinsed.

4. Conclusions

In this study, the fabrication of gold structures using a mixture of the negative photo-resist SU-8 and gold ions through two-photon excitation was investigated. The EDX analysis and μ-XRD patterns show that the structures are mainly composed of elemental gold and that the orientation of the gold crystal grain in the fabricated structures is random. The XPS results indicate that there is a small amount of cross-linked SU-8 present in the structures and that the gold atoms interact with oxygen atoms derived from the cross-linked SU-8. These results suggest that the main chemical reaction is the photo-reduction of gold ions and that the generated photo acid simultaneously cross-links a small amount of SU-8. The AFM results showed the fabricated structures to be approximately 1 μm in height. The structures were determined to be conductive based on DMM measurements; however, the resistivity of the fabricated gold structures was four orders of magnitude higher than that of pure gold. This discrepancy was caused by the small amount of SU-8 present in the fabricated gold structures, which formed structural defects that reduced conductivity. We believe that the conductivity of fabricated metal structures can be improved and by selecting a matrix without oxygen atoms.

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