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Photo-induced metal deposition onto a Au electrode in solution

Yoshitaka Sawai [a], Masato Suzuki [a], Kei Murakoshi [a,b,*], Yoshihiro Nakato [a]

[a] Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[b] Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Corporation, Toyonaka, Osaka 560-8531, Japan

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Abstract

The effect of photo-irradiation on metal deposition onto several Au electrodes was investigated. The metal deposition can be controlled by photo-irradiation at the metal/solution interface. Although the deposition proceeds when the ions are excited by the photo-irradiation at the electrode whose potential is maintained at an appropriate potential, the process can be accelerated by the photo-excitation of electrons in the metal electrode. The introduction of surface roughness for the excitation of surface plasmon was useful in improving the reaction efficiency. The contribution of the plasmon mode was successfully applied to construct a single metal-dot structure on the smooth Au(1 1 1) surface in the vicinity of the thin metal tip. Cu metal nano-dot 15 nm in size and 1 nm in height can be prepared by the photo-irradiation of an atomically smooth surface of the metal electrode only at a point in the vicinity of the metal tip.

Keywords: STM; Metal nano-dot; Photo-induced deposition; Plasmon; Au(1 1 1); Cu nanoparticle

1. Introduction

Recently, the importance of the structural control in a size range of less than 100 nm has been widely recognized for the construction of various functionalized units in electronic and optical devices, and molecular sensors. At present, there are several technical limits for the effective and fast construction of nano-structure. Thus, a novel method needs to be developed. This report proposes that the selective excitation of a specific surface plasmon mode of metal nanostructures can be employed as a perturbation for effective structural control. Useful effects on the particle-interaction and highly localized electrochemical reaction were found in several nanostructured metal systems [1–5]. Plasmon absorption is known to cause a highly localized electric field at the interface between the metal surface and the surrounding medium. Thus, if such a localized field could be utilized to induce electrochemical reactions, the effect can be applied to change and/or control the structure of the metal nanostructure.

Photo-induced metal deposition was also achieved by the photo-excitation of metal ions in solution. Photo-excited metal ions accept electron from metal electrode, resulting in the formation of metal thin layer on the electrode surface [6]. Localized plasmon excitation at the metal surface is expected to contribute the reaction. It should be important to study the effect of the photo-absorption of metal electrodes. For further developments as novel method of nano-structural control, coupling the phenomenon with the system in an electrochemical scanning tunneling microscope (EC-STM) [7,8] could prove interesting. Several attempts have been reported using photo-irradiation for the tunneling gap of STM systems for nanostructure fabrication [9–15]. Although some of these studies succeeded in the preparation of nano-structures on solid surfaces, several problems still remain. When light is irradiated in the STM gap, thermal expansion of the tip and the sample substrates is observed as the most prominent effect [9–11,13,16–25]. This contribution is difficult to control, and often changes the distance of the gap leading to the deformation of the prepared structures. Thus, it is important to identify the condition that minimizes the contribution of the thermal expansion. Appropriate potential control of the electrodes in EC-STM systems is expected to improve the reaction efficiency of the photo-induced metal deposition.

In the present study, the effect of photo-irradiation on the metal deposition process was investigated. Photoelectrochemical response was measured using several Au electrodes with varying roughness in an electrolyte solution containing $CuSO_4$ or $AgNO_3$. Contributions of the photo-excitation of the metal electrode and the ions in solutions were considered to explain the observed photocurrent responses. The

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* Corresponding author. Present address: Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan. Tel.: +81-6-6850-6237; fax: +81-6-6850-6236.
E-mail address: kei@chem.es.osaka-u.ac.jp (K. Murakoshi).

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effect of the photo-irradiation at the gap between the electrode surface and the tip of the electrochemical STM was also investigated. Possibilities for applying structural control of the metal nano-dot were discussed.

2. Experimental

2.1. Electrochemical measurements

All chemicals for electrolytes were of reagent grade and were used as-received. Electrochemical measurements were performed using a three-electrode cell. A polycrystalline Au plate was fixed at the bottom of the cell (apparent area = 0.28 cm^2), and then immersed in deaerated aqueous electrolyte solution containing 0.1 M $CuSO_4$ or $AgNO_3$. A platinum wire was used as a counter electrode. The potential of the Au working electrode was regulated with respect to the Ag/AgCl reference electrode. A potentiostat (Toho Technical Research, 2001) and a programmed function generator (Toho Technical Research, FG-02) were used to control the potential of the electrodes. Photoelectrochemical measurement was conducted using the same electrochemical cell. Photo-irradiation of unpolarized light on the surface of the Au electrode was performed using a semiconductor laser (830 nm; Spectra Physics OPC-H005) as a light source. Time dependent changes in the current were recorded using a digital oscilloscope (SONY Tektronix, TDS3014B).

Photoelectrochemical response was investigated using several Au electrodes with varying roughness. The roughened surface of the Au electrode was prepared by electrochemical dissolution and deposition cycles (oxidation and reduction cycles (ORC)) in 0.1 M KCl aqueous solution. The potential was swept into the potential range between 0 and 1.2 V. The roughness of the electrode surface increased by repeating this cycle.

2.2. Electrochemical STM measurements and laser light irradiation

The electrochemical STM system (NanoScope IIIa, Digital Instruments) combined with a semiconductor laser was used for the in situ structural characterization of photo-deposited metal dot on the surface of the electrode in solution. Au single crystal electrodes were used as the working electrode. Au single crystals were prepared by flame annealing of the Au wires (diameter = 0.8 mm, 99.999%, Nilaco) in a hydrogen–oxygen flame. The resulting single crystal spheres with a diameter of approximately 3 mm were annealed and then quenched in Milli-Q water just before use. They had an atomically flat Au(1 1 1) facet. Photo-irradiation was conducted on the surface of the single crystal. The diameter of the illuminated light spot was approximately 3 mm. The illuminated light intensity was controlled by the internal setting of the equipment and optical neutral density filters in the range of 100 mW–5 W/cm^2. The illuminated time can be adjusted by the internal setting of the equipment for 1–1000 ms.

3. Results and discussion

3.1. Effect of the photo-irradiation on the reductive current to the polycrystalline Au electrode in 0.1 M $CuSO_4$ or $AgNO_3$ aqueous solution

Cyclic voltammograms using the Au electrode in electrolyte solution containing 0.1 M $CuSO_4$ or $AgNO_3$ show typical bulk metal deposition and dissolution behaviors as shown in Fig. 1. The bulk deposition of Cu and Ag was apparently observed below approximately 0.15 and 0.6 V, respectively. Transient current response for the pulsed photo-irradiation was obtained after the potential step from 0.5 V to various negative potentials. After the potential was maintained at the negative potential for 5 s, the light was then illuminated for 1 s. Fig. 2(a) shows the time course of the current in the pulsed light irradiation experiment with irradiation power of 1 W/cm^2. In the 0.1 M $CuSO_4$ system, photo-irradiation increased the reduction current. At the potential of 0.4 V, the increment of the reduction current was less than a few tens of nA. This photo-induced current increased as the potential of the electrode became negative. At 0.05 V, the value of the current increased to more than 400 nA. The changes of the current at the start of the irradiation showed a slight time delay in the order of a few tens of ms. In the 0.1 M $AgNO_3$ system, the effect of the photo-irradiation was completely different to that of $CuSO_4$. Anodic current response was observed

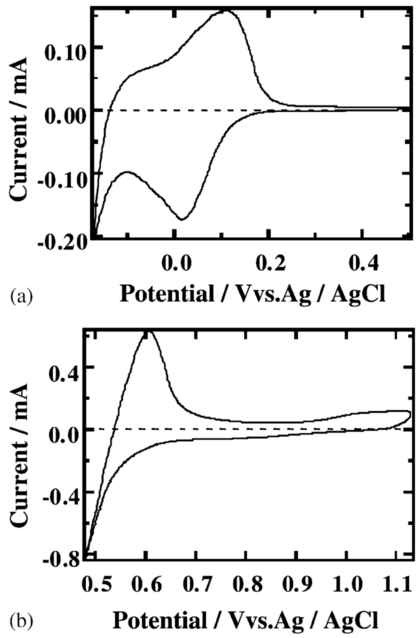

Fig. 1. Cyclic voltammograms of Au polycrystalline electrode in 0.1 M $CuSO_4$ and 0.1 M $AgNO_3$; scan rate was 100 mV/s.

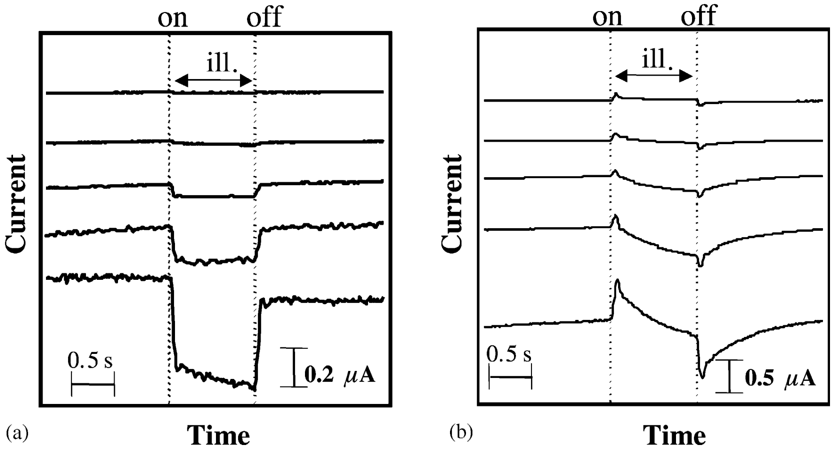

Fig. 2. Time course of current under pulsed light irradiation: (a) 0.1 M $CuSO_4$, electrode potentials were 0.05, 0.1, 0.2, 0.3 and 0.4 V (from bottom to top); (b) 0.1 M $AgNO_3$, electrode potentials were 0.54, 0.58, 0.63, 0.73 and 0.83 V (from bottom to top); irradiation power was 1 W/cm^2.

at the start of the irradiation. After a steep rise, the current decreased gradually during the photo-irradiation. At the time of light off, the current showed the opposite response to light on. Steep decline was followed by the gradual increase of the current. The changes due to the photo-irradiation became much more apparent as the potential became negative from 0.83 to 0.54 V. These results in the $CuSO_4$ and $AgNO_3$ systems prove that photoelectrochemical reactions can be induced by the irradiation of 830 nm light to the Au electrode. The photo-induced reactions were accelerated by the negative polarization of the Au electrode.

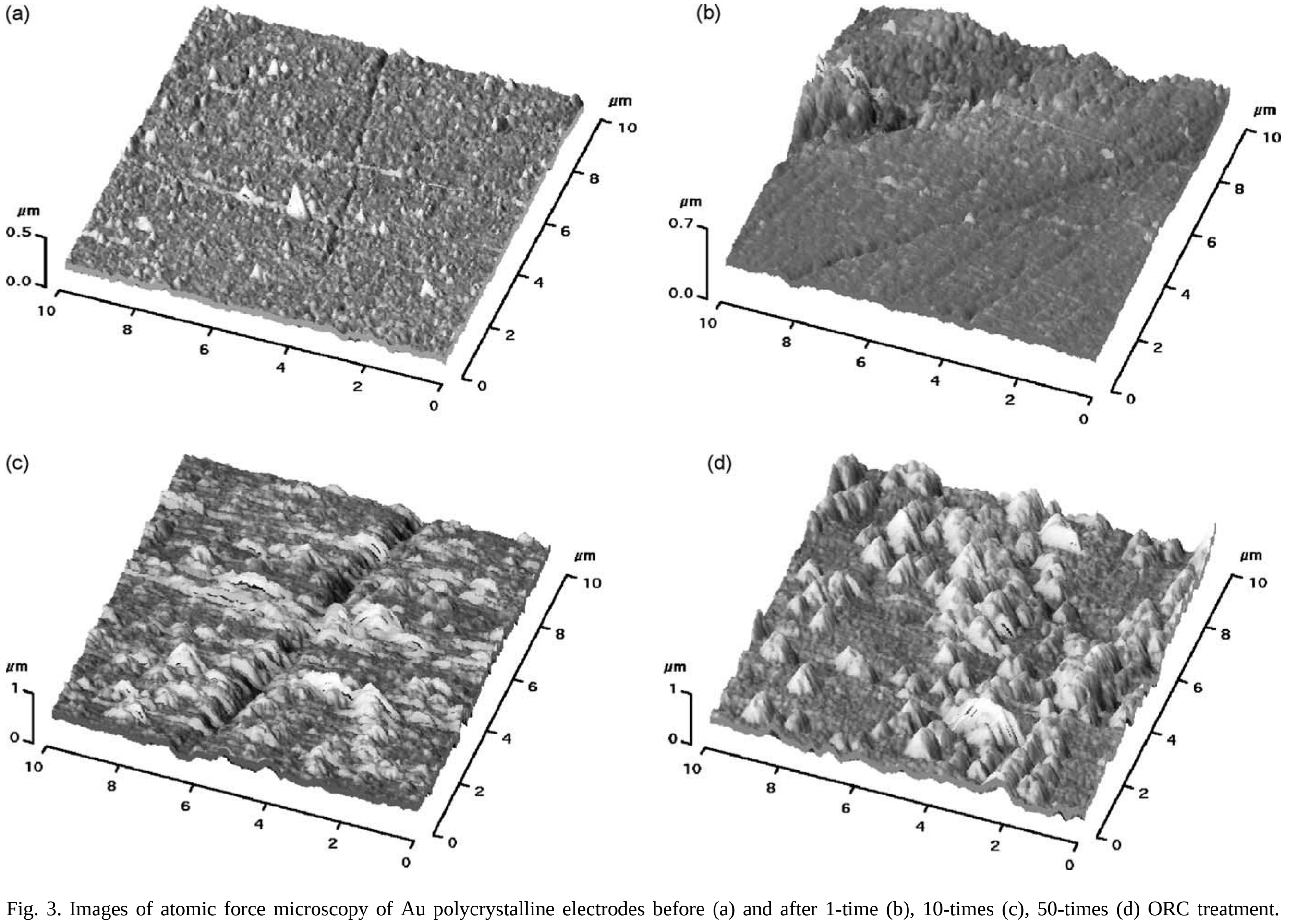

Fig. 3. Images of atomic force microscopy of Au polycrystalline electrodes before (a) and after 1-time (b), 10-times (c), 50-times (d) ORC treatment.

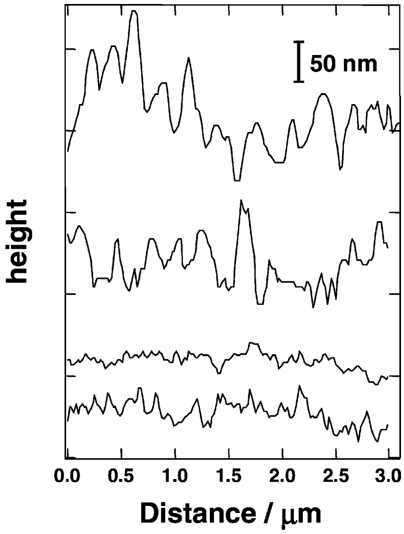

Fig. 4. Vertical sectional views of Au polycrystalline electrodes before and after 1-time, 10-times, 50-times ORC treatment (from bottom to top).

3.2. Effects of surface roughness and irradiation power on the photo-induced reductive current of the polycrystalline Au electrode in 0.1 M $CuSO_4$ aqueous solution

The effect of electrode roughness on the photo-induced reductive current was investigated using the $CuSO_4$ system. Electrode roughness was controlled by changing the number of ORC. Fig. 3 shows atomic force microscopic images of the Au electrodes before and after ORC treatments. As the number of the ORC increased, relatively large dome-like structures with less than 1 µm sizes formed on the surface. As well as this dome-like structure, structural change in the smaller size range was also recognized. Fig. 4 shows vertical sectional views of relatively flat places of the electrodes. It is clearly shown that ORC treatment changes the surface structure from that with small roughness in sizes less than a few tens of nm to that with sizes around 100 nm. As shown in Fig. 4, the ORC treatment introduced a novel roughened structure with a depth of 50 nm and a width of 100 nm (top two in Fig. 4) accompanied by the loss of initial roughness with sizes less than a few tens of nm (bottom of Fig. 4).

Transient response of the current at the pulsed photo-irradiation was measured using these electrodes with varying surface roughness. The photocurrent increased drastically as the number of ORC increased. The observed photocurrent is plotted against the number of ORC in Fig. 5. It should be noted that the increment of the current was not caused by the increments of the surface area of the electrodes. Electrochemically active areas of these electrodes were evaluated by electrochemical measurements in the dark. Current due to the double layer charging, as well as metal deposition of the electrodes in the dark using the electrodes before and after ORC treatment (data not shown here) indicated that the increments of the active area due to the ORC treatment were not apparent. The relative ratio of the active area of the electrode after 50-times ORC in the area before ORC was approximately 2. Up to 10-times ORC did not show any increments of the effective surface area. Although the formation of the dome-like structure and the roughness with sizes of 100 nm by the ORC treatment could increase the apparent surface area of the electrode, the disappearance of relatively small roughness at the initial electrode contributed to the decrease of the area. As the sum of these opposite effects, the slight increments in the active surface area of the electrode were caused in the present system. Thus, the observed significant increments of the photocurrent shown in Fig. 5 should not be caused by the increments of the surface area of the electrode.

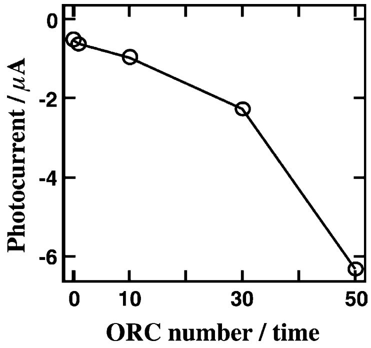

Fig. 5. Dependence of the number of ORC on photocurrent observed in 0.1 M $CuSO_4$; irradiation power was 5 W/cm^2; electrode potential was 0.35 V.

One possible effect to increase the photocurrent is to increase the photo-absorption due to the structural changes introduced by the ORC treatments. It is known that roughened metal surface structures with the periodicity of sizes around 100 nm show absorption in the infrared spectral range [26]. The present structures introduced by the ORC treatments may increase the photo-absorption of 830 nm light. Thus, increments in the photocurrent at the ORC treated electrodes should be due to the increment in the photo-adsorption of the electrode.

Irradiation power dependence was also investigated using the electrodes before and after 50-times ORC. At both electrodes, the photocurrent increased linearly as the power of the irradiation increased as shown in Fig. 6. This linearity of the photocurrent to the irradiation power proves that this photo-induced reaction obeys first-order kinetics. The slope of the electrode after 50-times ORC was approximately one order higher than that of the electrode before ORC. This difference in the slope suggests the contribution of the photo-absorption of the electrode to the observed reductive photocurrent. Slight deviation from the linearity at higher power irradiation above 4 W/cm^2 should imply the contribution of the heat effect.

These effects of surface roughness and irradiation power on the photo-induced reductive current of the polycrystalline Au electrode in 0.1 M $CuSO_4$ aqueous solution prove that

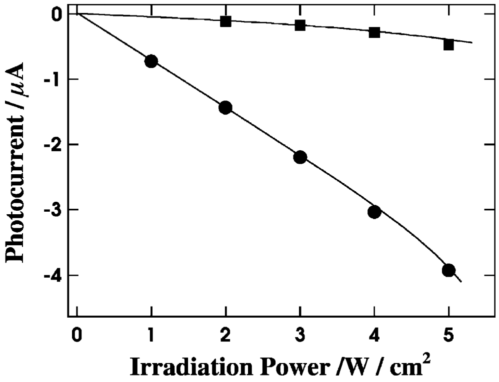

Fig. 6. Irradiation power dependence on photocurrent observed in 0.1 M $CuSO_4$ at electrode before (closed square) and after 50-times ORC (closed circle); electrode potential was 0.35 V.

the photo-absorption of the electrode should be a primary step in inducing the reductive photocurrent.

3.3. *Photo-induced metal deposition onto an atomically flat Au(1 1 1) facet surface*

The effect of photo-irradiation using an Au(1 1 1) single crystal was investigated under the comparable condition of polycrystalline Au electrodes. Structural characterization was conducted using the in situ electrochemical STM system. Fig. 7 shows in situ STM images before and after the photo-irradiation. In this experiment, when the light was irradiated on the Au(1 1 1) surface whose electrochemical potential was controlled, the STM tip was retracted. After irradiation with a power of 1 W/cm^2, the tip was engaged again to obtain the images of the irradiated surfaces. Before the irradiation, the image shows that a typical atomically flat Au(1 1 1) surface structure consists of terraces and several steps with mono-atomic height (Fig. 7(a)) on the terrace. After irradiation under potential maintained at 0.4 V, several small islands less than 10 nm in size and 0.2–0.3 nm in height were observed. The islands disappeared after the polarization at 0.6 V, indicating that the island could be a Cu metal dot formed by the photo-induced reduction of Cu^{2+} in electrolyte solution. The number of island structures increased as the electrode potential became negative. Fig. 7(b) shows the surface images maintained at 0.35 V. Relatively large numbers of islands with sizes between 10 and 20 nm were formed on the surface. The height of the island was also greater than that at 0.4 V (approximately 0.4 nm). Although several larger or smaller islands were also recognized, the size and height of the islands were quite uniform. At more negative potential, the photo-irradiation resulted in further structural changes of the surface. As shown in Fig. 7(d), small islands were formed on the surface. The size of the islands were smaller than those observed at 0.35 V. The height, however, was higher (around 0.5–0.6 nm). As well as these small structures, the flat part of the terrace also seems to be covered by a thin layer. Even with these structural changes, the mono-atomic step of Au(1 1 1) could still be recognized after the irradiation.

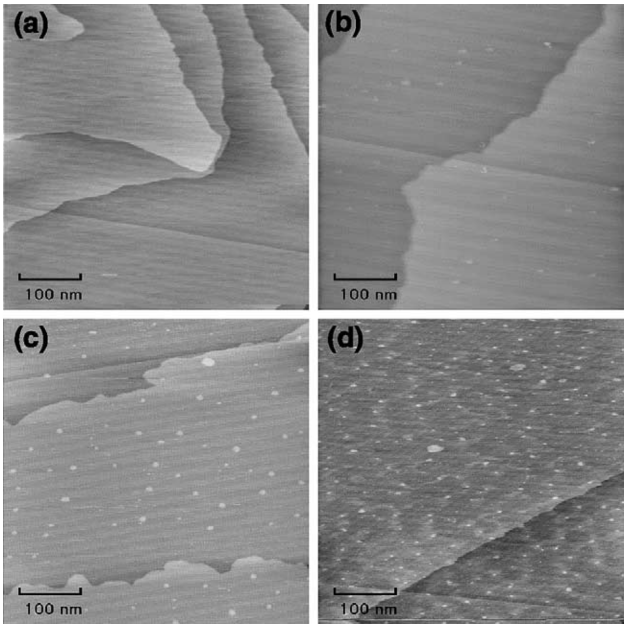

Fig. 7. Images of EC-STM of Au(1 1 1) single crystalline electrodes before photo-irradiation at 0.6 V (a), after photo-irradiation at 0.4 V (b), 0.35 V (c), 0.3 V (d); irradiation power was 5 W/cm^2; irradiation time was 10 ms.

The potentials for these observations are more positive than the potential of the bulk Cu deposition. It was confirmed that the polarization at 0.3 V in the dark did not show any island structure formation. The observed island structures could be Cu metals deposited by the photo-irradiation. Disappearance by the positive polarization of these island structures also supports that the islands are Cu metal. This result shown in Fig. 7 proves that Cu metal islands can be prepared onto an atomically flat Au(1 1 1) surface by photo-irradiation. The prepared structure was rather uniform, and was controlled by the electrode potentials.

3.4. *Position selective metal deposition onto a Au(1 1 1) surface in the vicinity of the metal tip*

The effect of the photo-irradiation on the gap between the Au(1 1 1) surface and the tip of the electrochemical STM was also investigated. Relatively weak light (100 mW/cm^2) was irradiated in the gap in the present experiment. During the irradiation for 10 ms, the position of the tip was fixed at the center part of the observed area under the constant tunneling current mode. After the irradiation, the tip was scanned again to obtain the surface image. This relatively weak light irradiation in the gap between the tip and the surface of the Au(1 1 1) electrode whose potential was maintained at 0.4 V resulted in the formation of a small island structure on the Au(1 1 1) surface in the vicinity of the tip as shown in Fig. 8. It was confirmed that irradiation with the power to the order of 100 mW/cm^2 did not form any deposit on the Au(1 1 1)

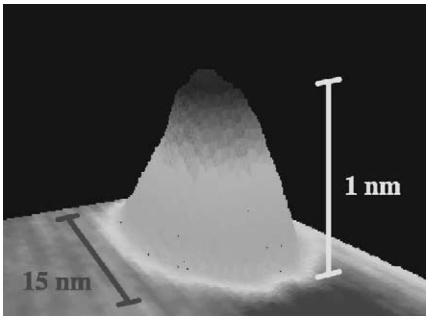

Fig. 8. Image of EC-STM of Au(1 1 1) single crystalline electrodes after photo-irradiation with power of 100 mW/cm^2 for 10 ms. Tip was fixed at the center position of the observed area during the irradiation.

surface in the absence of the tip. The island structure was formed on the surface just below the tip only when the light was irradiated at the point of the gap. The island was dissolved when the potential of the electrode was maintained at 0.6 V. This fact indicates that the Cu metal nano-dot can be prepared by the photo-irradiation of an atomically smooth surface of a metal electrode in the vicinity of the metal tip. The position of the dot can be controlled by changing the position of the metal tip of the electrochemical STM.

3.5. Mechanism of metal deposition onto electrode surface by light irradiation

Reductive photocurrent was apparently observed in the $CuSO_4$ system under 830 nm photo-irradiation. The origin of the reductive photocurrent was attributed to the reduction of Cu^{2+} on Cu metal deposited onto the electrode surface. One possible effect of the photo-irradiation on the metal/electrolyte solution interface is the photo-excitation of electrons in the metal electrode. Although it is known that the lifetime of the excited electron in metal is extremely short, the existence of an appropriate acceptor at the interface may capture these excited electrons. The heat effect caused by the irradiation also contributes to the change in the rate of the reaction. The delay time in the photocurrent around a few tens of ms and gradual increases of the photocurrent under strong light illumination (bottom of Fig. 2(a)) should be caused by the heat effect. Thus, the reductive photo-current in the system may reflect the contributions from the electronic excitation and the heat caused by the 830 nm photo-irradiation. As shown in Fig. 6, the effect of the heat became apparent under the condition of relatively strong light irradiation.

The importance of the optical absorption process at the metal electrode was supported by the significant increments in the photocurrent using roughened electrode. As shown in Fig. 5, the ORC treated electrode showed one order higher photocurrent compared to the electrode without the ORC treatment. It is known that the Au surface with roughness of about 100 nm shows optical absorption at visible and near-infrared regions due to surface plasmon excitation [26]. If the plasmon excitation can couple with the electronic excitation in metal, the photo-induced metal deposition induced by the excited electrons should be accelerated by the increments of the optical absorption by the introduction of the surface roughness. Observed increments of the photocurrent at the roughened electrodes prove the importance of the optical absorption of the metal electrode for the photo-induced metal deposition.

As well as the contribution of the excited electrons in metal, the photo-excitation of ions in the electrolyte solution should also be considered [6]. It is known that Cu^{2+} with d^9 electronic configuration has a hydrated distorted octahedral structure [27]. This Cu^{2+} complex has a broad optical absorption band at the near-infrared region, which is attributed to d–d transition. Thus, photo-excited Cu^{2+} hydrated complex can capture electrons from metal electrode to its unoccupied t_{2g} states in solution. This process should contribute to the photo-induced reduction of Cu^{2+} to Cu metal at the metal electrode/solution interface. It should be noted that the Ag^+ ion also has a hydration structure of tetrahedral coordination. The Ag^+ complex, however, does not show the optical absorption at the near-infrared region. Contribution of the photo-excitation of ions should be minor in the $AgNO_3$ system. Other processes, such as oxidation of the Au surface by photo-excited holes, and acceleration of the Ag deposition by heat caused by the irradiation, and re-oxidation of the deposited Ag on the Au electrode by the photo-excited holes, could contribute to demonstrating the observed complicated behavior caused by the irradiation (Fig. 2(b)).

The importance of the excitation of the ions for the metal deposition was shown by the results in the system using the atomically flat Au(1 1 1) electrode (Fig. 7), because external irradiation of the smooth metal surface cannot excite surface plasmon directly due to the lack of momentum. It is known that surface roughness is required for the plasmon excitation [28]. The contribution of the photo-excitation of the electrons in metal can be minimized by the use of the atomically smooth electrode. Thus, the observed photo-deposition of the Cu metal islands on the smooth surface should reflect the contribution of the excitation of the ions.

These results mentioned above prove that metal deposition can be controlled by photo-irradiation at the interface. The deposition proceeds when the ions are excited by the photo-irradiation and the substrate electrode is maintained at appropriate potential. The process can be accelerated by the photo-excitation of the metal electrode. The introduction of the surface roughness to excite the surface plasmon was a useful method for inducing the deposition effectively. The contribution of the plasmon mode was successfully applied to construct a single metal-dot structure on the smooth Au(1 1 1) surface in the vicinity of the thin metal tip. Yates et al. proposed the possibility that the tip can work as a conical antenna or a waveguide for the light under irradiation [17]. Thus, it is expected that the enhanced field was induced by the photo-irradiation in the gap between the smooth metal surface [12,29–31]. The field can induce the highly localized excitation of electrons at that point, leading to position selective metal deposition onto the electrode surface vicinity of the tip. As a result, a dot 15 nm in size and 1 nm in height was prepared on the Au(1 1 1) surface. The fact that the preparation of the dot was achieved under relatively weak light irradiation proves the effective antenna effect of the tip in localizing the excitation.

4. Conclusion

It was proven that the metal deposition process can be controlled by photo-irradiation at the metal/solution interface. Although the deposition proceeds when the ions are excited by photo-irradiation at the electrode whose potential is maintained at appropriate potential, the process can be accelerated by photo-excitation of the metal electrode. Introduction of the surface roughness to excite the surface plasmon was a useful method for inducing the deposition effectively. The contribution of the plasmon mode was successfully applied to construct a single metal-dot structure on the smooth Au(1 1 1) surface in the vicinity of the thin metal tip. Cu metal nano-dot 15 nm in size and 1 nm in height can be prepared by the photo-irradiation of an atomically smooth surface of the metal electrode only at a point in the vicinity of the metal tip. The method of position selective photo-deposition may be applied for novel structural control of the nano-dot on the solid surface.

Acknowledgements

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