Production method of gold single crystal with high quality and large grain size and its application to a SPM substrate

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Novel process for forming a gold crystal film with high (111) orientation on a substrate has been established using a supersaturated solution of \( \text{[AuI}_4^- \) \]. The gold crystal film has a grain size of approximately 200 \( \mu \)m and an atomically flat surface, which provides sufficient quality for the substrate of SPM observation. High resolution and accuracy AFM images for a plasmid DNA thus have been obtained using the gold crystal film.

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I. INTRODUCTION

Since the invention of the scanning probe microscope (SPM), it has been used for evaluating surface profiles and properties of various materials in nanometer-scale. In recent years, analysis of organic molecules and biomolecules with SPM is being watched with keen interest. For imaging of these molecules with SPM, it is necessary to use an atomically flat substrate. A gold single crystal especially has been employed because it forms strong bond with a sulfur atom, e.g. fixation of proteins using a thiol or a disulfide group in the molecules, and preparation of self-assembled monolayers using alkane thiol. In general, the gold single crystals for SPM are attained by evaporation of gold onto freshly cleaved mica with annealing [1], but this method has some disadvantages in respect of quality and grain size of the gold single crystals prepared. Recently, we have established liquid phase epitaxy method for the preparation of the gold single crystals with high quality and large grain size, which are available to a recording medium substrate [2]. We will present the improved preparation method of the gold single crystals and the atomic force microscope (AFM) image of a plasmid DNA using these crystals.

II. EXPERIMENTAL

A. Preparation of gold single crystals on substrate

Gold powder with a purity of 99.998% (1.87 g, 0.02 mol) was suspended to a solution of potassium iodide (39.84 g, 0.48 mol) and iodine (12.06 g, 0.10 mol) in distilled water (500 ml). The suspension stirred for a few days at room temperature. The gold powder particle gradually disappeared and changed to a homogeneous solution to form a gold complex \( \text{[AuI}_4^- \) \].

The apparatus for producing the gold single crystals, as shown in Fig. 1, was assembled in fume hood. The solution of gold complex \( \text{[AuI}_4^- \) \} \( \text{(300 ml)} \) was poured into the quartz separable flask and heated at 90°C for 3 hours. At this time it is necessary to add hot water from time to time to avoid drying up. A Ti (160 nm) / Si substrate was then dipped into the solution. The flask was put with a cover (vent size 19 mm \( \phi \) ) followed by heating at 90°C accurately for 10 hours to grow the gold single crystals on the substrate. The substrate was picked up from the solution and rinsed at distilled water.

B. Surface treatment

The compounded gold single crystals were treated with \( \text{O}_2 \) plasma (RF output 300 W, \( \text{O}_2 \) flow 50 sccm, 5 min) in order to clean the crystal surfaces. After \( \text{O}_2 \) plasma treatment, the gold single crystals on the substrate were annealed at 300°C for 30 min. Further annealing treatment enables to improve quality of the crystals and strengthen the adhesion between the crystals and the substrate. The crystals are rinsed with ultra pure water before use.

FIG. 1: A schematic view of the apparatus for producing gold single crystals.
FIG. 2: (a) The optical microscope images of gold single crystals obtained by the liquid phase epitaxy. (b) An illustration of the gold single crystal compounded by the liquid phase epitaxy. The crystal has a ratio longitudinal direction to that in the lateral direction of 1:100∼200 and plane face have the (111) orientation and side face have the (110) orientation.

FIG. 3: The tapping mode AFM image of gold single crystal without surface cleaning.

C. DNA sample preparation

A water solution of a pBR322 plasmid DNA (100 ng/ml) was dropped onto the gold single crystal surface. After incubating for a few minutes, the solution was purged by N2 gas and dried up.

III. RESULTS AND DISCUSSIONS

A. Preparation of high quality and large grain size gold crystals

The detailed reaction pathway for preparation of the gold complex [AuI4]− solution is described in Eq. (1). The gold powder is oxidized by I3− derived from KI and iodine to form [AuI4]− soluble in water. The each path is an equilibrium reaction respectively. Removal of I2 by heating of the solution reduces the concentration of I3− in situ and reform Au from [AuI4]−. The Au slowly deposit on the substance surface as random nuclei to grow the crystals.

\[
\begin{align*}
2KI + I_2 & \rightleftharpoons 2K^+ + I_3^- + I^- \\
2Au + I_3^- + I^- & \rightleftharpoons 2AuI_2^- \\
AuI_2^- + I_3^- & \rightleftharpoons AuI_4^- + I^-.
\end{align*}
\]

The optical microscope images of the gold crystals obtained by the liquid phase epitaxy are shown in Fig. 2. These crystals have triangle or hexagonal shape and their average size are approximately 200 µm with the thickness to the width ratio of 1:100∼200. The result of optical microscope observation reveals that the thus formed crystals are defect-free single crystals with the (111) orientation. The gold crystals obtained by our liquid phase
FIG. 5: The tapping mode AFM image of gold single crystal after (a) \( O_2 \) plasma treatment and (b) \( O_2 \) plasma and annealing treatment. The contamination layer can take away from the gold single crystal surface by \( O_2 \) plasma treatment. As shown in Fig. 5(b), after \( O_2 \) plasma and annealing treatment, it is often observed the triangular terrace structures corresponding to the formation of ideal gold (111) surface.

C. Application to use for the substrate of the AFM observation

We attempted to employ the produced gold single crystals as the substrate of the AFM observation. AFM observation of a pBR322 plasmid DNA with tapping mode on the crystal shows clear image of the molecules as shown in Fig. 6. The height of the plasmid DNA in air is about 0.5 nm [3], and hence it is difficult to observe the plasmid DNA on conventional evaporated gold film due to its roughness. The surface of gold single crystals obtained by our liquid phase epitaxy is extremely smooth enough to observe the plasmid DNA clearly.

IV. CONCLUSIONS

We have developed a new process for growing a crystalline gold thin film composed of a group of single crystals on the substrate. This process provides gold single crystals with high (111) orientation and large grain size, which is suitable for the substrate of the AFM observation. We will attempt the further applications of this gold single crystal relating to the molecular analysis of soft matters and their AFM imaging.

FIG. 6: The tapping mode AFM image of a pBR322 plasmid DNA on the gold single crystal surface. DNA molecules with about 0.5 nm heights are clearly observed.

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