Fabrication of Ordered Gold Nano-dots Array using Nano Plastic Forming and Self-assembly

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INTRODUCTION
Nano-scale ordered dots arrays of semi-conductor and metallic material are of interest for application in high performance electronic, optic and magnetic devices [1-2]. Therefore, various fabrication techniques of the nano-dots array have been actively studied. In particular, the electron beam lithography, the ultraviolet lithography and the focused ion beam milling are well-known as popular fabrication methods [3-6]. However, these top-down fabrication methods generally require expensive equipments and complicated processes. Also, size of the nano-dots produced by above top-down methods is limited by beam and ion resolutions. On the other hand, fabrication of the nano-dots array using self-assembly is also drawn attention as an alternative bottom-up approach. For example, several fabrication processes with thermal-annealing, epitaxial growth and sputter redeposition with porous alumina templates are proposed [7-14]. Although the self-assembly enables us to produce many small nano-dots in a short time, to control the size and alignment of the nano-dots is difficult.

In this study, we propose a new fabrication method of ordered nano-dots array by using the nano plastic forming (NPF) technique which is direct imprinting method, and the self-assembly of thin film during high-temperature annealing.

EXPERIMENTAL PROCEDURE
In this study, two different fabrication processes shown in Fig. 1 are examined. Process A is a conventional fabrication process of the Au nano-dots and is expected to produce randomly distributed nano-dots. On the other hand, Process B is the proposed process and consists of three steps, that is, coating, the NPF and the high-temperature annealing. From the following section, these three steps are explained according to Process B.

COATING
The size of the quartz glass substrate is 10 mm in width, 12 mm in length and 1 mm in thickness. Before the coating, the substrate is cleaned by ultrasonically degreasing in acetone. The Au thin film is deposited with thickness of 10 nm on the substrate using a DC spatter coater (IB-3, Eiko Co. Ltd.). The coating process is conducted in Argon atmosphere. The base pressure for the spattering is 10 Pa and the distance between the substrate and the Au target is 35 mm.

NANO PLASTIC FORMING (NPF)
Figure 2 shows the overall view of the NPF equipment developed by the authors [15-16]. This equipment has computer controlled X, Y, Z and Tilt stages. Feed resolution of the X, Y and Z stages is 10 nm. A specially designed single crystal diamond tool shown in Fig. 3 is mounted at the top of a load cell on the Z stage. The diamond tool is directly imprinted on the Au-coated substrate under load control. The edge angle, edge radius and width of the tool are 60 degrees, 50 nm and 600 µm, respectively. By controlling movement and rotation of the stages and the imprinting load, arbitrary surface pattern can be fabricated on the substrate and the film. In this study, to produce ordered Au nano-dots array, lattice-patterned grooves are fabricated on the surface of the Au film coated on the substrate.

HIGH-TEMPERATURE ANNEALING
After the deposition of the Au film on the quartz glass substrate and the NPF, the specimen is annealed in air at 973 K for 10 minutes. Then, the specimen is cooled down to room temperature slowly.

After the annealing, the size and distribution of the obtained Au nano-dots are evaluated by using field-emission scanning electron microscope (FE-SEM).

Fig. 1: Fabrication processes of Au nano-dots alloy.
Fig. 2: Schematic figure of nano plastic forming equipment.

Fig. 3: Knife-edge type diamond tool.

Fig. 4: SEM micrographs of (a) Au thin film before annealing and (b) random Au nano-dots produced by Process A.

Fig. 5: Diameter and frequency of the Au nano-dots fabricated by Process A.

Fig. 6: SEM micrographs of (a) grooves on the Au thin film and (b) ordered Au nano-dots array produced by Process B.

Fig. 7: Diameter and frequency of the Au nano-dots fabricated by Process B.

EXPERIMENTAL RESULTS

EFFECT OF NPF ON ORDERING OF AU NANO-DOTS ALLOY

Figure 4 (a) and (b) show SEM micrographs of the surface morphology of the Au thin film and the Au nano-dots produced by Process A. The morphology of the film is changed to many small dots due to the annealing so as to decrease the total energy of the system, which is sum of the surface energy, the interfacial energy and the elastic strain energy. However, the size and distribution of the Au nano-dots are quite random.
Fig. 8: SEM micographs of grooves on the Au filmy for different pitch setting at (a) 250 nm, (b) 500 nm and (c) 1000 nm.

Figure 5 shows histograms of frequency and distribution of the nano-dot diameter. It is seen that the distribution of the dot diameter shows a wide range. The mean diameter of the Au nano-dot is 131 nm and relative standard deviation is 55.2%. In the Process A, since initial surface fluctuation of the spatter-coated film triggers the morphological change of the film during the self-assembly, ordering of the nano-dots cannot be realized by Process A.

Figure 6 (a) shows SEM micrograph of the grooves imprinted on the Au thin film. The Au thin film is divided into small square film array. Here, the indentation load is 0.5 N, the depth and pitch of the lattice-patterned grooves are 48 nm and 500 nm, respectively. However, the variation in the distance between the grooves due to the feed error of the X and Y stages is occurred. Also, in this condition, although the tip of the tool reaches the quartz glass substrate, no chipping is occurred [16].

Figure 6 (b) shows SEM micrograph of the ordered Au nano-dots array produced by Process B. The square film array shown in Fig. 6(a) transforms into the ordered nano-dots array. Furthermore, it is found that a small square film corresponds to a single nano-dot. Compared to the Au nano-dots shown in Fig. 5 (b), it is clearly shown that the size and location of the nano-dots are regularly-arranged. According to Fig. 7, the mean diameter of the ordered Au nano-dot array is 221 nm and, interestingly, the relative standard deviation is largely decreased to 13%.

Fig. 9: SEM images of Au nano-dots array for different pitch setting at (a) 250 nm, (b) 500 nm and (c) 1000 nm. White dotted lines indicate the location of the grooves.

Fig. 10: Relationship between pitch setting and mean diameter of Au nano-dot.

Thus, the uniformity of the nano-dots array can be improved by surface patterning of the film with the NPF. From these experimental results, we obviously demonstrate that the proposed method with the NPF is quite effective way to fabricate the ordered Au nano-dots array.

**EFFECT OF PITCH SETTING ON SIZE OF AU NANO-DOT**

For Process B, the controllability of the nano-dot size by changing the pitch setting of the grooves is investigated. Figure 8 shows SEM micrographs of grooves on the Au thin film on the substrate for different pitch setting at (a) 250 nm,
(b) 500 nm and (c) 1000 nm. For all pitch setting, the small square film array can be formed. Figure 9 shows the SEM micrographs of the Au nano-dots array obtained by annealing the samples shown in Fig. 8. In the case of Fig. 9(a) and (b), the size and alignment of the Au nano-dots can be regularized. However, in the case of Fig. 9(c), a square film separated by the lattice grooves changes to some small nano-dots. Figure 10 shows the relationship between the pitch setting, the mean diameter and the relative standard deviation. It is found that the size of the nano-dot and the relative standard deviation can be decreased with decreasing the pitch of the groove. Whereas, when the pitch setting exceeds some critical value, the ordered nano-dots array cannot be fabricated. From these results, it can be said that the size of the Au nano-dots can be controlled by changing the pitch setting of the groove and the thickness of the film.

NUMERICAL SIMULATION

In the annealing process, the morphological change of the Au thin film is driven by diffusion of Au atom on the substrate and can be understood as the minimization process of the total energy of the system. In this section, to verify above mechanism and to investigate the effects of the NPF on the ordering of the nano-dots array, the self-assembly of the Au thin film during the annealing is simulated with the multi-phase-field method.

MULTI-PHASE-FIELD METHOD

In the multi-phase-field method [17], it is assumed that the total free energy of the system is monotonically decreased with the morphological change of the Au thin film. In this study, the total energy of the system $G$ is defined as follows [18]:

$$G = \int \left\{ g_{\text{gradient}}(\nabla \phi(x,t)) + g_{\text{elastic}}(\phi(x,t)) \right\} dV \tag{1}$$

Here, $g_{\text{gradient}}$ is the gradient energy density corresponding to the interfacial and surface energies of the system and $g_{\text{elastic}}$ is the elastic strain energy density due to the misfit strain between the film and the substrate. These energy densities are the function of phase-field variables $\phi(x,t)$ ($i = 1, 2, 3$). Here, $x$ and $t$ represents coordinates and time. In this study, $\phi_1, \phi_2, \phi_3$ represent the local existence probability of air, Au and the substrate, respectively. For example, $\phi_1$ takes a value of 1 in air, 0 in Au and the substrate and changes from 0 to 1 gradually in the boundary region. Therefore, the relation $\phi_1 + \phi_2 + \phi_3 = 1$ must be satisfied at all coordinate.

For the elastic strain energy density in Eqn.(1), $C_{ijkl}$ is the elastic coefficient of the substrate and film. In this study, we assume the isotropic elasticity. $\varepsilon_{ij}$ is total strain tensor. $\varepsilon_{ij}^0$ is eigen strain tensor representing the misfit strain between the substrate and the Au film.

In Eqn.(1), $a_{ij}$ and $W_{ij}$ are the gradient coefficients and the height of energy barrier, respectively. These parameters are related to the interfacial energy $\gamma_{ij}$ and the interfacial thickness $\delta$ as follows:

$$a_{ij} = \sqrt{\frac{3\delta \gamma_{ij}}{b}},\quad W_{ij} = \frac{6b \gamma_{ij}}{\delta} \tag{2}$$

The morphological change of the Au film can be simulated by calculating the time evolution of $\phi_i$. The time evolution of $\phi_i$ can be calculated by solving the following time-dependent Ginzburg Landau (Cahn-Hilliard diffusion) equation.

$$\frac{\partial \phi_i(x,t)}{\partial t} = \nabla \cdot \left( M(T) \nabla \left( \frac{\delta G}{\partial \phi_i(x,t)} \right) \right) \tag{3}$$

Here, $M$ is a mobility of the phase-field $\phi_i$ which is related by the self-diffusion coefficients of Au atom $D(T)$ as follows:

$$M(T) = \frac{D(T)v_m}{RT} \tag{4}$$

Here, $v_m, R$ and $T$ are the molar volume, the gas constant and temperature, respectively.

SIMULATION MODEL AND CONDITION

Figure 11 shows two-dimensional simulation model for self-assembly of the Au thin film during the annealing. The size of the computational domain is $DX \times DY = 2.25 \times 0.625 \, \mu m^2$. The substrate is set at the bottom of the computational domain. In the substrate, the value of $\phi_1$ is set to be constant at 1. The thickness of the substrate is chosen as $t_{\text{sub}} = 0.5 \, \mu m$. In the simulation of Process A, the initial Au film is set on a flat substrate. On the other hand, in Process B, the initial film is set on the surface of the substrate excluding V-shaped grooves. In this simulation, since we intend to study effects of the NPF on the dot ordering, the thickness of the film $t_{\text{film}}$ is set to be 20 nm. The initial surface of the film is fluctuated by small sinusoidal waves. The maximum fluctuation is 0.1% of the film thickness. The pitch of the grooves $p$ is chosen as 204 nm and 375 nm. Depth of a groove $d$ is set to be constant at 50 nm.

The morphological change of the Au film (the time evolution...
Fig. 12: Formation process of Ordered Au nano-dots array in Process A.

<table>
<thead>
<tr>
<th>Energy [J]</th>
<th>Time [s]</th>
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<tr>
<td>0</td>
<td>0</td>
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<tr>
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<tr>
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<td>1</td>
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Fig. 13: Variations of total energy, elastic strain energy and surface (interfacial) energy during Process A.

Fig. 14: Formation process of Ordered Au nano-dots array for the pitch of the grooves $p = 375\text{nm}$.

Fig. 15: Formation process of Ordered Au nano-dots array for the pitch of the grooves $p = 204\text{nm}$

SIMULATION RESULTS

Figure 12 shows the simulated morphological change of the Au thin film during the annealing in Process A. In this case, since random fluctuation of the initial surface of the film triggered the self-assembly of the film, random Au nano-dots are formed. Thus, similar to the experimental results shown in Fig. 4, the size and location of the nano-dots is not uniform.

Figure 13 shows the change of the total energy, the elastic strain energy and the interface (surface) energy in Process A. When the morphology of the film changes to some dots, the surface energies of the film and the substrate are increased.

The self-diffusion coefficient of the Au atom $D(T) = 1.07 \times 10^{-5} \exp(-177 \times 10^{3}/RT) \text{m}^2/\text{s}$, the molar volume $v_m = 7.0 \times 10^{-6} \text{m}^3/\text{mol}$, Young’s modulus $E = 88.3 \text{GPa}$, Poisson’s ratio $\nu = 0.3$, the interfacial energy for all interface $\gamma_{ij} = 0.5 \text{J/m}^2$, the interfacial thickness $\delta = 20\text{nm}$, the magnitude of the misfit strain $\varepsilon_{\text{mis}} = 0.025$ and the annealing temperature $T = 973 \text{K}$. 

For the boundary condition of the multi-phase-field simulation, the zero Neumann condition is assumed at top and bottom of the domain and the periodic boundary condition is adopted at the right and left ends of the domain. The following parameters and physical values are used in the simulation: the self-diffusion coefficient of the Au atom $D(T) = 1.07 \times 10^{-5} \exp(-177 \times 10^{3}/RT) \text{m}^2/\text{s}$, the molar volume $v_m = 7.0 \times 10^{-6} \text{m}^3/\text{mol}$, Young’s modulus $E = 88.3 \text{GPa}$, Poisson’s ratio $\nu = 0.3$, the interfacial energy for all interface $\gamma_{ij} = 0.5 \text{J/m}^2$, the interfacial thickness $\delta = 20\text{nm}$, the magnitude of the misfit strain $\varepsilon_{\text{mis}} = 0.025$ and the annealing temperature $T = 973 \text{K}$. 

The stress field is solved by the finite element method as a plane strain problem. Since the morphology of the substrate does not change during the annealing, the misfit strain $\varepsilon_{\text{mis}}$ is applied to the substrate. That is, the eigen strain is set to be $\varepsilon_{ij}^0 = -\varepsilon_{\text{mis}}$ only in the substrate.

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However, since the elastic strain energy and the interfacial energy between the film and the substrate are largely decreased, the total energy of the system is resulted in decrease.

Figure 14 shows the simulated morphological of the Au thin film grooves in Process B for the pitch of the groove \( p = 375 \) nm. As shown in Fig. 9 (c), for the large pitch setting, a small film separated by the grooves changes to some small nano-dots. However, in the case of the pitch \( p = 204 \) nm shown in Fig. 15, a small Au thin film separated by the grooves becomes a small dot in the initial stage of the annealing. As a result, the ordered Au nano-dots can be fabricated on the surface of the substrate. According to these results, it is confirmed that the groove on the Au-coated substrate formed by the NPF plays an important role in ordering of the Au nano-dots array in Process B.

**CONCLUSION**

In this study, the fabrication method of the ordered nano-dots array by combining the coating, the NPF and the self-assembly due to the annealing was proposed. With the proposed method, we demonstrated that the ordered Au nano-dots array can be fabricated on the quartz glass substrate. Furthermore, the self-assembly process of the ordered Au nano-dots array were investigated by using the multi-phase-field method. From the experimental and simulation results, the feasibility of the proposed process and the effectiveness of the NPF on the ordering of the nano-dots arrays were demonstrated.

**REFERENCES**


