Molecular Dynamics Simulation of Grain Growth of Cu Film
—Effects of Adhesion Strength between Substrate and Cu Atoms—

Takatoshi Kato1,*, Takeshiro Nagai1,*, Yasushi Sasajima2 and Jin Onuki2

1Graduate School of Science and Engineering, Ibaraki University, Hitachi 316-8511, Japan
2Department of Materials Science and Engineering, Ibaraki University, Hitachi 316-8511, Japan

The growth process of Cu polycrystal films on Si, Ti, W and Ru substrate during isothermal annealing was studied by the molecular dynamics method. We focused on the influence of the adhesion strength between substrate and Cu on crystallinity and orientational order of the film. After structural relaxation at low temperature (50 K), the movements of individual Cu atoms were calculated for different annealing temperatures using the molecular dynamics method. The crystallinity and orientational order of the film were examined by 2D-Fourier transformation of the atomic structure. We found that the system with strong adhesion strength between substrate and Cu showed higher crystallinity and orientational order for (111) oriented Cu film. [doi:10.2320/matertrans.MG200903]

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1. Introduction

In the production of LSIs, annealing is necessary to coarsen the crystal grains in the wires. Coarse crystal grains increase the resistance strength to electromigration and simultaneously decrease the electrical resistance.1–3) We investigated the growth process of Cu polycrystal films on various substrates such as Si, W, Ti and Ru during isothermal annealing by the molecular dynamics method. We focused on the influence of the adhesion strength between substrate and Cu on crystallinity and orientational order of the film. After structural relaxation at low temperature (50 K), the movements of individual Cu atoms were calculated for different annealing temperatures using the molecular dynamics method. The crystallinity and orientational order of the film were examined by 2D-Fourier transformation of the atomic structure.

2. Calculation Method

2.1 Outline of simulation procedure

At first, the area of film is divided by Voronoi polygon. Each Voronoi polygon is filled with a Cu single crystal with random grain orientation, while crystal orientation of the film is assumed to be (100) or (111). Each film dimensions is 5.41 nm x 5.41 nm x 1.88 nm and 7.14 nm x 6.18 nm x 1.80 nm. Under the Cu film, a rigid plate was placed as a substrate. The interaction between the substrate and Cu atoms mimics Cu-Si, Cu-Ti, Cu-W and Cu-Ru as described in section 2.3. Figure 1 shows the initial structure of the film.

After relaxation at a low temperature (50 K) to stabilize the structure, an annealing temperature is set. Annealing temperature is 700 K or 1300 K, and relaxation time and annealing time are 20 ps and 100 ps, respectively. After stabilizing the structure, pressure of 101 MPa is imposed on the system to suppress void generation in the film.

2.2 Velocity Verlet method

The molecular dynamics is utilized to solve the equation of motion of Cu atoms numerically.

The velocity Verlet method4) is adopted as algorithm for numerical integration:

\[
\begin{align*}
\mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{(\Delta t)^2}{2m_i} \mathbf{F}_i(t) \\
\mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \frac{\Delta t}{2m_i} \left( \mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t) \right)
\end{align*}
\]

where \( \mathbf{r}_i \) is the position of the i-th atom, \( \mathbf{v}_i \) is the velocity, \( \mathbf{F}_i \) is the atomic force, \( m_i \) is the atomic mass and \( \Delta t \) is discretized time interval. \( \Delta t \) is set to be 1 fs.

2.3 Interaction potentials

The interaction between Cu atoms is calculated by the extended Tersoff potential.5) This potential is based on the Tersoff potential,6) and can reproduce the energy of a semiconductor, metal, oxide and other compounds. The interaction between Cu atoms and a rigid substrate is

*Graduate Student, Ibaraki University

Fig. 1 Initial structure of the film.
calculated by the Morse potential to save calculation time. Therefore the effect of atomic arrangement of substrate atoms is not considered here, only the strength of the interaction between substrate and Cu atoms is considered.

Figure 2 shows the Morse potentials for Cu-Si, Cu-W, Cu-Ti and Cu-Ru interaction as a function of the distance between Cu atoms and substrates. The Morse potential parameters, \( r_0 \), \( D \) and \( \alpha / C_{11} \) were determined as follows. Firstly, the potential curves of the interaction between Cu and substrate atoms (Si, W, Ti and Ru) were calculated using the extended Tersoff potential. Then the parameters \( r_0 \) and \( D \) were determined as the equilibrium distance and the minimum of the potential curve, respectively. Finally, the rest parameter \( \alpha / C_{11} \) was determined by best fitting to the potential curve.

The equation of the Morse potential is
\[
\phi(r) = D[\exp(-2\alpha(r - r_0)) - 2 \exp(-\alpha(r - r_0))],
\]
where \( r \) is the nearest distance between a Cu atom and the substrate. The determined parameters are listed in Table 1.

### Table 1 Parameters of Morse potential.

<table>
<thead>
<tr>
<th>Surface boundary</th>
<th>Cu/Si</th>
<th>Cu/W</th>
<th>Cu/Ti</th>
<th>Cu/Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D/\text{adJ} )</td>
<td>0.194</td>
<td>0.150</td>
<td>0.112</td>
<td>0.28</td>
</tr>
<tr>
<td>( \alpha/\text{nm}^{-1} )</td>
<td>13.7</td>
<td>14.7</td>
<td>12.7</td>
<td>8.34</td>
</tr>
<tr>
<td>( r_0/\text{nm} )</td>
<td>0.25</td>
<td>0.26</td>
<td>0.27</td>
<td>0.18</td>
</tr>
</tbody>
</table>

### 2.4 Analysis method

The 2D Fourier transform was utilized for the structural analysis. The 2D Fourier transform is expressed as
\[
F = \sum_j \{\cos(k_x x_j + k_y y_j) + i \sin(k_x x_j + k_y y_j)\},
\]
where \( x_j \) and \( y_j \) are the atomic coordinates in lateral direction of the film and \( k_x \) and \( k_y \) are the wave number vectors. The intensity of the diffracted beam, \( I \), is obtained by the square of \( F \), i.e.,
\[
I = \left\{ \sum_j \cos(k_x x_j + k_y y_j) \right\}^2 + \left\{ \sum_j \sin(k_x x_j + k_y y_j) \right\}^2.
\]

The calculated results are expressed as the map as a function of \( k_x \) and \( k_y \).

### 3. Results and Discussion

#### 3.1 (100) oriented film

Figure 3 shows the final structure of Cu (100) polycrystalline film on each substrate annealed at 700 K, and Fig. 4 at 1300 K. The grains have been coarsen compared to the initial...
structure shown in Fig. 1. The grain size at 1300 K is larger than that at 700 K.

Figures 5 and 6 are the 2D-Fourier transform of the Cu film shown in Figs. 3 and 4, respectively. The light spots reflect the (100) oriented coarse grains of Cu. It can be seen that the obtained structure has good crystallinity and orientation for Si substrate. The other cases such as W, Ru and Ti substrate showed the worse crystallinity and orientational order in this sequence. For the annealing temperature 700 K showed similar results as in the 1300 K cases, but a little bit worse crystallinity and orientational order. The effect of temperature on crystallinity and orientational order was weak because of the short period of annealing time. For good quality of the film, the strength between substrate and Cu atoms should be intermediate between Cu/Ti and Cu/Ru, i.e., the $D$ value of the Morse potential should be around $0.150–0.194 \text{ aJ}$.

To examine the system size dependence, the area of the Cu(100)/Si(100) system was enlarged two times as large as the present condition, and was annealed at 700 K and for 100 ps. The Fourier transform of the obtained structure showed more diffuse pattern than the present result. It can be attributed to the increase of the number of the grains with various orientations, and the relaxation time for grain coarsening has become larger. It can be considered that much longer annealing time will lead to the similar result as the present system size.

To check the effect of the initial configuration of the system, the different grain structure was produced by changing the seed of the random number generator, and was annealed. The calculated systems were (100)Cu films on Si, Ti, W and Ru substrate and were annealed at 700 K for 100 ps. It was confirmed that the order of crystallinity and orientational order did not changed nevertheless the final structure and its 2D-Fourier transform was a little different from the present results.

### 3.2 (111) oriented film

Figure 7 shows the final structure of Cu (111) polycrystalline film on each substrate annealed at 700 K. Figure 8 is the 2D-Fourier transform of the Cu film shown in Fig. 7. For the (111) orientated Cu film, the Ru substrate leads to the best crystallinity and orientational order at 700 K among the examined substrates. Superiority of Ru to the other substrates was evident. The order of crystallinity and orientational order was different from those of the (100) case. The obtained results can be summarized in Table 2. The technological interest is how to select materials for appropriate substrate.
which achieve good crystallinity and orientational order. From the present results, Ru is found to be one of the best candidate of the substrate for (111) Cu film because of the strong adhesion strength. (see the $D$ value in Table 1, $0.28 \text{ aJ}$.)

We performed the MD calculation in which the individual substrate atoms were considered. The intentions between atoms were modeled by the extended Tersoff potential. The Fourier transform of the obtained atomic structure was compared to that of the present results obtained by utilizing the Morse potential. As the representative result, the Fourier transform of the Cu(111) film on the Si(100) substrate is shown in Fig. 9. It can be seen from the figure that the whole pattern become more diffuse and the peaks in the high wave number region become sharper (see also Fig. 8(a)). These differences, however, gave no effects on the order of crystallinity and orientational order. It has also been found that all the calculated systems formed incoherent interfaces

| Table 2 The order of crystallinity and orientation. |
|----------------|----------------|
| (100), 700 K   | Si > W > Ru > Ti |
| (100), 1300 K  | Si > W > Ru > Ti |
| (111), 700 K   | Ru > Ti > W > Si  |

Fig. 6 2D-Fourier transform of Fig. 4.

Fig. 7 Structure of Cu (111) film at 700 K.

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because of the large difference of the lattice constant at the interface. Therefore the influence of the lattice was not significant as the binding energy of the interface. From these results, it can be concluded that the assumption of the rigid-body for the substrate and the two-body approximation for the substrate—film atom interaction are effective for the system with incoherent interface.

4. Conclusion

The growth process of Cu polycrystal films on Si, Ti, W and Ru substrate during isothermal annealing was studied by the molecular dynamics method.

For good quality of the (100) orientated Cu films, the strength between substrate and Cu atoms should be intermediate between Cu/Ti and Cu/Ru, i.e., the $D$ value of the Morse potential should be around 0.150–0.194 aJ. For the (111) Cu films, the Ru substrate was the most appropriate to achieve good crystallinity and orientational order. According to the experiments of Al film, (111) orientation enhances the resistance to electromigration.7) Therefore, it can be considered that the materials with strong adhesion strength as Ru are good candidate for the substrate of the (111) orientated Cu wire in LSIs.

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Appendix: Extended Tersoff potential

Equations of the extended Tersoff potential between i and j atoms are shown in eq.

\[ U_T = \sum_{i<j} u_{ij} + \sum_i \phi_i, \]

where

\[ u_{ij} = u_{\text{REP}} + u_{\text{SHT}} + u_{\text{ION}} + u_{\text{VDW}}, \]

\[ \phi_i = [(U_{EI} + A_{EI})/(2e)]q_i + [(U_{EI} - A_{EI})/(2e)]q_i^2, \]

\[ u_{\text{REP}} = f_{\text{Sij}}A_{\text{ij}}\exp(-A_{\text{ij}}r_{\text{ij}}), \]

\[ u_{\text{SHT}} = -f_{\text{Sij}}b_{\text{ij}}B_{\text{ij}}\exp(-\mu_{\text{ij}}q_{\text{ij}}), \]

\[ u_{\text{ION}} = f_{\text{Lij}}\eta_{\text{ij}}q_{\text{ij}}/(4\pi\varepsilon_0q_{\text{ij}}), \]

\[ u_{\text{VDW}} = f_{\text{ij}}(C_{\text{VDW}}C_{\text{VDW}})/r_{\text{ij}}^6, \]

\[ \text{with} \]

\[ b_{\text{ij}} = \left[ 1 + \left( \beta \sum_k \zeta_{\text{ijk}} \right)^{-1/2(nk)} \right]^{-1/2}, \]

\[ \zeta_{\text{ijk}} = f_{\text{Sij}}\exp[m_{\text{ij}}(r_{\text{ij}} - r_{\text{ik}})^m] \times \left[ 1 + c_{\text{ij}}^2/d_{\text{ij}}^2 + c_{\text{ij}}^2/(d_{\text{ij}}^2 + (h_{\text{ij}} - \cos \theta_{\text{ijk}})^2) \right], \]

\[ f_{\text{Sij}} = f_{\text{ij}}(r_{\text{ij}}\sqrt{R_{\text{Si}}R_{\text{Sj}}}/\sqrt{S_{\text{Si}}S_{\text{Sj}}}), \]

\[ f_{\text{ij}}(r, R, s) = \begin{cases} 1, & (r \leq R) \\ 1/2 + (1/2)\cos[\pi(r - R)/(S - R)], & (R < r < S), \\ 0, & (r \geq S) \end{cases} \]

\[ A_{\text{ij}} = (A_1 + A_2)/2, \]

\[ \mu_{\text{ij}} = (\mu_1 + \mu_2)/2, \]

\[ A_{\text{ij}} = \sqrt{A_{\text{Si}}A_{\text{Sj}}}, \]

\[ B_{\text{ij}} = \sqrt{B_{\text{Si}}B_{\text{Sj}}}, \]

\[ A_{\text{Si}} = A_1\exp(A_2D_1), \]

\[ B_{\text{Si}} = B_1\exp(\mu_1D_1)[a_{\text{Bi}} - |b_{\text{Bi}}(q_{\text{Bi}} - Q_{\text{Oi}})|^{a_{\text{Bi}}}], \]

\[ D_{\text{ij}} = D_{\text{ii}} + |b_{\text{Bi}}(q_{\text{Bi}} - Q_{\text{Oi}})|^{a_{\text{Bi}}}, \]

\[ b_{\text{Di}} = (D_{\text{ii}} - D_{\text{ij}})^{1/nc}/(Q_{\text{ii}} - Q_{\text{ij}}), \]

\[ n_{\text{Di}} = \ln[-D_{\text{ii}}/(D_{\text{II}} - D_{\text{ij}})]/\ln[Q_{\text{ii}}/(Q_{\text{II}} - Q_{\text{ij}})], \]

\[ a_{\text{Bi}} = |a_{\text{Bi}}|^{1/nc}/\Delta Q_{\text{ij}}, \]

\[ a_{\text{Bi}} = 1/(1 - |Q_{\text{Oi}}/\Delta Q_{\text{ij}}|^{nc}), \]

\[ Q_{\text{Oi}} = (Q_{\text{i}} + Q_{\text{II}})/2, \]

\[ \Delta Q_{\text{i}} = (Q_{\text{ii}} - Q_{\text{ij}})/2, \]

The potential energy of the system \( U_T \) is calculated as the summation of repulsive energy \( u_{\text{REP}} \), short-range energy \( u_{\text{SHT}} \), ionic bond energy \( u_{\text{ION}} \), van der Waals energy \( u_{\text{VDW}} \) and the energy of atom i itself \( \phi_i \) and \( q_i \) is the charge of atom i, and is optimized at every step to minimize \( U_T \). The potential parameters for Cu, Ti, W, Si and Ru are listed in Table A-1.