Crystal growth study using combination of molecular dynamics and Monte Carlo methods

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Abstract. Molecular dynamics method although provides details of energies of the system as a function of time, is not suited to simulate the processes involving activation processes. Therefore, we attempted to combine the molecular dynamics and Monte Carlo methods. Using molecular dynamics, the energies of the system were calculated which were subsequently combined with Monte Carlo method using random numbers, epitaxial growth of (111) plane of copper, silver, and gold. While surface adsorption and surface diffusion for copper, silver, and gold were simulated by use of molecular dynamics method, the relation between the growth rate of thin films and the packing density of atoms were obtained using Monte Carlo simulation. Thus, by combining the results of the molecular dynamics method and the Monte Carlo method the growth process of thin films at elevated temperatures were obtained, which is too tedious to be calculated by molecular dynamics alone.

Keywords. Homoepitaxial growth; thin films; embedded-atom method.

1. Introduction

Crystal growth is becoming increasingly important in diverse industries, particularly in the electronics industries. Molecular dynamics method is often used to simulate elemental process of surface diffusion (Takano *et al* 1998). In molecular dynamics studies, the energies of the system, including surface, is calculated as a function of time. The temperature of a specimen with the average kinetic energy is adjusted to an aiming temperature. For the surface diffusion simulation, a diffusing atom is held at a position, the stress is released (the positions of atoms are moved toward resultant force) and the energy of the system is calculated. However, the time step in the molecular dynamics normally used is of the order of 10^{-15} sec. Therefore, even in the case wherein one million time steps were calculated, the total elapsed time was only of the order of 10^{-9} sec. Normally surface diffusion occurs by the activation process, and therefore 10^{-9} sec is not long enough to simulate many activation processes. In an activated process, usually many attempts are required before the saddle point of the activated process can be overcome. The molecular dynamics method, involving activation process, requires a long time of computations, and hence here is an attempt to combine the molecular dynamics and Monte Carlo methods. Using molecular dynamics, the energies of the system are calculated and subsequently combined with Monte Carlo method using random numbers, epitaxial growth of (111) plane of copper, silver, and gold.

Choice of the jumping sites for diffusing atoms is given by Monte Carlo method. In this study the energies of surface diffusion are calculated by molecular method and from this calculation the frequency of the diffusing atom

is calculated from the curvature near the stable point. The next jumping position is selected by using random numbers.

2. The potential used

In metals, the conducting electrons travel from one atom to another atom and the interaction between atoms cannot be represented by a pairwise potential but by many body potentials. The interaction between the *i*th atom and the *j*th atom depends not only on the distance between them but also on other factors. By the embedded function (Foiles 1986; Ackland *et al* 1987; Oh and Johnson 1988, 1989; Baskes 1992), surface problems can also be treated. By the N-body embedded function used in Baskes (1992), the total energy is given by

$$E_{\text{total}} = \sum E_i, \quad (1)$$

$$r_{ij} = [r_i - r_j], \quad (2)$$

$$E_i = (1/2) \sum \phi(r_{ij}) + F(\rho_i), \quad (3)$$

$$F(\rho_i) = D \rho_i \ln \rho_i, \quad (4)$$

$$\rho_i = \sum f(r_{ij}). \quad (5)$$

Here, E_{total} is the total internal energy of a crystal. E_i the internal energy associated with atom *i*. ρ_i is the electron density at atom *i* due to all the other atoms. $F(\rho_i)$ is the embedding energy of an atom into electron density ρ_i . $\phi(r_{ij})$ is the two-body central potential between atoms *i* and *j* separated by r_{ij} and is repulsive if (r_{ij}) is the

contribution to the electron density at atom *i* due to atom *j* at the distance *r_{ij}* from atom *i*. *F*(*ρ_i*) is an attractive term. For the functional forms

$$\phi(r_{ij}) = A_1 (r_{c1} - r_{ij})^2 \exp (- C_1 r_{ij}), \tag{6}$$

$$f(r_{ij}) = A_2 (r_{c2} - r_{ij})^2 \exp (- C_2 r_{ij}), \tag{7}$$

are assumed. $\phi(r_{ij})$ and $f(r_{ij})$ are smoothly truncated at *r_{c1}* and *r_{c2}*, respectively. *r_{c1}* was chosen to be 1.65 *d* (*d* is the nearest neighbour distance), $f(r_{ij})$ was cut off between the next nearest neighbour and the third nearest neighbour for

a perfect crystal. *r_{c2}* was chosen to be 1.95 *d*, i.e. $\phi(r_{ij})$ was cut off between the third nearest and the fourth nearest neighbours. The parameters of the potential are given in table 1.

3. Molecular dynamics

The following results have been obtained using molecular dynamics. Figure 1 shows some of the motion and conversion of adatoms and adatom clusters.

Table 1. Potential parameters.

	Cu	Ag	Au
A ₁	8.28945997705 × 10 ³	9.10810768184 × 10 ³	5.18021878920 × 10 ⁵
A ₂	1.83251035107 × 10 ⁻²	5.25514178418 × 10 ⁻²	1.83065797788 × 10 ⁻²
C ₁	10.72729128641	10.817215101079	15.57704835828
C ₂	3.19759369823 × 10 ⁻¹	1.38555356572	1.28671308081 × 10 ⁻⁵
D	13.07921251628	11.28152486706	11.93177438785

Figure 1. Configuration of adatom and adatom clusters on (111) plane of an fcc metal. A. a single adatom, B. motion of a di-adatom, C. one of dissociation process of tri-adatom, $E_3^{60} \rightarrow E_3^{120}$, D. conversion of a tri-adatom, $E_3^{120} \rightarrow E_3^{60}$, E. $E_3^{180} \rightarrow E_3^{120}$, F. $E_3^{120} \rightarrow E_3^{180}$, G. motion of a vacancy on (111), H. motion of a divacancy on (111).

(i) A single adatom on (111) plane is very easy to move. The activation energies of the motion of a single adatom in copper and silver from an fcc site to a hcp site are 0.055 eV and 0.058 eV, respectively. Here an fcc site means that an adatom forms an fcc structure and an hcp

site means an adatom forms an hcp structure. The activation energies of the motion of a single adatom in copper and silver from an hcp site to an fcc site are 0.042 eV and 0.054 eV, respectively. The difference is due to the elemental stacking fault.

Figure 2. Motion of a trapped adatom to a step on (111). **a.** Atom A can move $a1 \rightarrow a2 \rightarrow a3 \rightarrow a4 \rightarrow a5$, **b.** atom A can move through $a1 \rightarrow a2 \rightarrow a3$.

(ii) The activation energy of the motion of a di-adatom was found to be 0.12 eV in copper, which is much higher than that of a single adatom. A di-adatom is much more difficult to migrate on (111) plane.

(iii) The activation energies of conversion of tri-adatoms in silver are $E_3^{60} \rightarrow E_3^{120}$, $E_3^{120} \rightarrow E_3^{60}$, $E_3^{180} \rightarrow E_3^{120}$ and $E_3^{120} \rightarrow E_3^{180}$ and 0.41, 0.08, 0.16, 0.17 eV, respectively. The potential used was as described by Oh and Johnson (1988). The conversion is not very easy.

(iv) A vacancy on (111) is much harder to move.

(v) A single adatom is very easy to move on (111).

4. Growth of a step on (111)

Figures 2a and b show atom A sticks to a flat step. Figure 2b shows atom A sticks to a jog of a step. To move the atom A, it has to partially be dissociated from the flat step. For example, the movement of atom A from $a1 \rightarrow a2 \rightarrow a3 \rightarrow a4 \rightarrow a5$. However, the motion of atom A shown in figure 2b is different in that the atom A can move without dissociating from the step. Figure 3 shows the crystal energy vs position for copper and silver for the case of figure 2a. This indicates that when an adatom diffuses near the step on (111), the adatom is attracted by the step and it is pulled by the step without an activation energy. In the case of figure 2a, a trapped adatom at the step cannot move easily.

When a step on (111) has a jog (figure 4), a trapped adatom A is rather difficult to move along the step as shown in figure 4a from $a1 \rightarrow a2 \rightarrow a3 \rightarrow a4 \rightarrow a5$, or as shown in figure 4b from $a1 \rightarrow a2$. It is also more difficult to climb up the jog on (111) as shown in figure 4a, i.e. from $a1 \rightarrow a2 \rightarrow a6 \rightarrow a7 \rightarrow a8$ or as shown in figure 4b from $a1 \rightarrow a2 \rightarrow a4 \rightarrow a5 \rightarrow a6 \rightarrow a7 \rightarrow a8$. Figures 4a and

b show the motion of an adatom. The jog has more attractive force to atom A compared with the case without jog.

5. Monte Carlo simulation of epitaxial growth

We took a closed packed plane of (111) in an fcc metal. We assumed that atoms of a metal arrive from vacuum at a constant flowing rate. Let an atom's arriving rate at the (111) surface be τ_2 . The atom adsorbed on (111) can easily diffuse with a low activation energy. Let the mean jumping time from a site to one of the nearest neighbour sites of a single adatom be τ_1 . τ_1 can be expressed as:

$$\tau_1 = \nu_1 \exp(E_1/(kT)), \quad (8)$$

where ν_1 is the frequency of the jumping adatom, E_1 the activation energy of diffusion of a single adatom on (111) plane. k is the Boltzmann constant, and T the absolute temperature. Here we take τ_1 as a time unit. Each atom arriving randomly at (111) plane ($7d$ in x direction and $6(3)^{1/2}d$ in y direction, where d is the nearest neighbour distance). The periodic boundary conditions are used in x and y directions. Each atom is arriving every τ_2 second. In our simulation, two arriving rates are taken, i.e. $\tau_2 = \tau_1$ (case 1); and $\tau_2 = 20\tau_1$ (case 2).

In case 1, while all the single adatoms on (111) make jumps once a new atom arrives on (111), in case 2, all the single adatoms on (111) make 20 jumps before a new atom arrives on (111). Furthermore, in case 2 there is more time to diffuse before the arrival of another atom. The arrived adatom is put at the fcc site closest to the position given by the random numbers. At every τ_2 , all single adatoms are moved to one of the nearest positions by using a random number. As soon as a single adatom forms an adatom cluster, the adatom cluster is frozen and stay at the closest fcc position. All adatoms pass fcc and hcp sites alternately. Figure 5 shows the stacking of atoms on (111). While figure 5a depicts the elapsed time as $600\tau_1 = 30\tau_2 = 30$ atoms (slow deposition), figure 5b depicts the elapsed time as $30\tau_1 = 30\tau_2 = 30$ atoms (fast deposition) although the deposited atoms are the same as figure 5a. The completeness of the deposition is higher in a slow deposition. Figure 5c depicts the elapsed time as $110\tau_2 = 2,200\tau_1 = 110$ deposited atoms (slow deposition) and figure 5d depicts the elapsed time as $110\tau_2 = 110\tau_1 = 110$ deposited atoms (fast deposition rate). With a slower deposition rate, the packing density (perfectness) of a deposited film is higher. There is more time to rearrange the crystal for a slower deposition.

6. Calculation of mean time for an adatom to diffuse on (111)

The mean jumping time τ_1 from a site to one of the nearest neighbour sites of a single adatom is given by

Figure 3. Energy diagram of the motion of a single adatom near a step on (111) for silver and copper.

Figure 4. Motion of a trapped adatom to a step with a jog on (111). **a.** Atom A can move $a1 \rightarrow a2 \rightarrow a3 \rightarrow a4 \rightarrow a5$. **b.** Atom A can move through $a1 \rightarrow a2 \rightarrow a3$. To climb a jog is more difficult. Climbing of a trapped adatom to a step on (111). **a.** Atom A can move $a1 \rightarrow a2 \rightarrow a4 \rightarrow a5 \rightarrow a6 \rightarrow a7 \rightarrow a8 \rightarrow a9 \rightarrow a10$ and **b.** Atom A can move through $a1 \rightarrow a2 \rightarrow a4 \rightarrow a5 \rightarrow a6 \rightarrow a7 \rightarrow a8$.

Figure 5. a-b.

Figure 5. a–d. a. is for the elapsed time = $600\tau_1 = 30\tau_2 = 30$ atoms (slow deposition), b. is for the elapsed time = $30\tau_1 = 30\tau_2 = 30$ atoms (fast deposition), the deposited atoms are the same as in a. The completeness of the deposition is higher in a slow deposition, c. is for the elapsed time = $110\tau_2 = 2,200\tau_1 = 110$ deposited atoms (slow deposition), d. is for the elapsed time = $110\tau_2 = 110\tau_1 = 110$ deposited atoms (fast deposition rate).

$$\tau_1 = \nu_1 \exp(E_1/(kT)), \quad (9)$$

where ν_1 is the frequency of the jumping adatom, E_1 the activation energy of diffusion of a single adatom on (111) plane. k is the Boltzmann constant, and T the absolute temperature. Here we take τ_1 as a time unit. ν_1 can be calculated from the energy scheme. ν_1 for copper was of the order of 10^{11} s^{-1} , and τ_1 was of the order of 10^{-10} s at room temperature. At 600 K, τ_1 was of the order of 10^{-11} s .

7. Conclusions

We have attempted to combine molecular dynamics and Monte Carlo methods. Molecular dynamics simulates a time sequential phenomena as a function of elapsed time. However, this method is not suited for a problem involving activation processes.

The motion of an adatom along a flat step and with a jog was studied. We observed a relationship between the rate of growth and the packing density of atoms. It was observed to be more suitable for a slow-growth process

than for a fast-growth process to obtain a near-perfect single-crystal thin film. The deposition temperatures and the figures based on probability of the crystal growth process have been studied.

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