Two Dimensional Nucleation Process by Monte Carlo Simulation

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Two Dimensional Nucleation Process by Monte Carlo Simulation

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Two dimensional nucleation process on substrate is investigated by Monte Carlo simulation, and the critical nucleus size and its waiting time are measured with a high accuracy. In order to measure the critical nucleus with a high accuracy, we calculate the attachment and the detachment rate to the nucleus directly, and define the critical nucleus size when both rate are equal. Using the kinematical nucleation theory by Nishioka, it is found that our obtained kinematical two dimensional critical nucleus size are about ten percent smaller than the thermodynamically defined one. The dependence on the chemical potentials for the critical nucleus size is good agreement with the classical nucleation theory.

For the surface diffusion dependence of the critical nucleus size, it is found that the critical nucleus size increases as the surface diffusion length to long distance.

KEYWORDS: surface diffusion dependence of the critical nucleus size, two dimensional nucleation, critical nucleus size, Monte Carlo simulation

1. Introduction

When we control the early stages of the crystal growth such as the forming of the nano structure on the substrate, there must be to understand the nucleation process by the atomic level. For its purpose, the computer simulations by the molecular dynamics or Monte Carlo method are an effective means. To get a critical nucleus size and the waiting time until where it is formed, a lot of samples must be taken and in the ability of the present computer, it seems that it is difficult to use the molecule dynamics. Therefore, we computed precisely as straight as possible using Monte Carlo method (Paragraph 2).

The nucleation process which is given by the simulation is kinematics, and it may be different from the one which is defined by the thermodynamics in the critical nucleus size, the waiting time to the nucleation. Nishioka[1,2] shows recently that the critical nucleus size defined by kinematics is less than the one defined by thermodynamics generally. We estimated the critical nucleus size which is defined by the thermodynamics from the critical nucleus size which was given by the simulation using this theory and estimated step free energy. Also, we examined the influence of the surface diffusion, too, because there was supposed not to be an influence of the surface diffusion to the critical nucleus size in the nucleation process but it was not an obvious thing (Paragraph 3). Moreover, because the MBE (the molecular beam epitaxy) growth, too, is important as the way of growing, it makes a characteristic in case of the nucleation clear.

2. Simulation method

2.1. Monte Carlo simulation

We simulated the absorption of atom, the evaporation and the surface diffusion process on the surface of the simple cube lattice (001) (on the substrate), using Gilmer and Bennema model[3,4]. Each frequency of the absorption, the evaporation, the surface diffusion as K^+, K_i^-, K_i^D are as follows,

$$K_i^-/K^+ = \exp[(2-i)\phi/kT - \Delta\mu/kT] \quad (1)$$

$$K_i^D/K^+ = (\lambda_s/a)^2 \exp[(2-i)\phi/kT - \Delta\mu/kT]. \quad (2)$$

Here, ϕ is nearest neighbor bond energy, i is the number of the bond which is combining with nearest neighbor atom, $\Delta\mu$ is a chemical potential difference between the crystal and the vapor, λ_s is a surface diffusion distance a is lattice constant, k is Boltzmann's constant and T is a temperature. In the computation after that, we suppose that substrate atoms don't evaporate but we add beforehand that a hole is hardly made in the temperature (ϕ/kT) range we used, in the equilibrium condition even if it permits the evaporation of substrate atom.

2.2. Critical nucleus size and the waiting time of the nucleation

We sometimes examine the coverage of the partial molecule layer to estimate the waiting time of the nucleation and the critical nucleus size approximately[5].

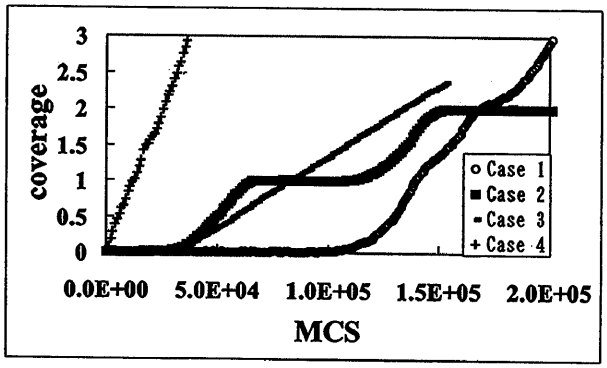

Figure 1. Time development of the total number of atoms (coverage) ; case1, 2, 3:$\phi/kT = 3, \Delta\mu/kT = -.5$, lattice size:64 × 64(case1,2), 256 × 256(case3),case 4: $\phi/kT = 1.5, \Delta\mu/kT = 0.05$,lattice size: 64 × 64.

Figure 1 shows the time change of the coverage. Case 4 goes at $\phi/kT = 1.5$, $\Delta\mu/kT = 0.05$ and the simulation

size is 64 × 64. The step energy is small, because it is near the roughening temperature in this case. Therefore, it finds that it doesn't need the heat excitation process of the nucleation. Cases 1, 2, 3 are the one which was simulated in 64×64 (cases 1, 2) and 256×256 (case 3), at $\phi/kT = 3\Delta\mu/kT = 0.5$ In these case, the heat excitation process is needed (The coverage doesn't stand up readily). In this way, in the nucleation, it finds that there are sample dependence and simulation size dependence.

We estimated a direct critic nucleus size and waiting time in the following way. Because the fluctuation of maximum cluster size n can be monitored in simulation, the counter N_n^+ or N_n^- can be increased in 1. And, we monitor the waiting time τ_n when the size changes at the same time. Then, the increase frequency (the transfer frequency of $n \rightarrow n+1$) P_n^+ and decrease frequency (the transfer frequency of $n \rightarrow n-1$) P_n^- of the n body cluster are found as follows,

$$P_n^+ = N_n^+/\tau_n, P_n^- = N_n^-/\tau_n. \tag{3}$$

With this, the increase rate R_n of the n body cluster becomes

$$R_n = P_n^+ - P_n^-. \tag{4}$$

Therefore, n_k^* is the critical nucleus size which satisfies

$$R_{n_k^*} = 0. \tag{5}$$

n_k^* is decided in the kinematics according to the Nishioka's theory and it distinguishes it from the critical nucleus size n^* which is defined by the thermodynamics.

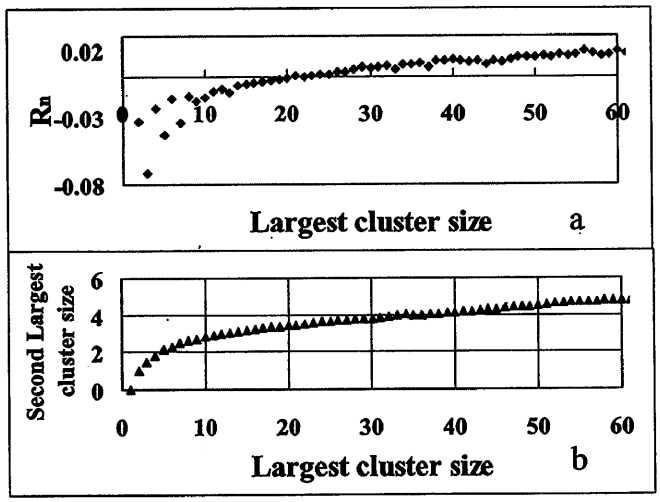

Figure 2. (a) increasing rate of the cluster size n and (b) the 2nd cluster size when the maximum cluster size is n; $\phi/kT = 3, \Delta\mu/kT = 0.55$.

Figure 2a is the size dependence of the increase rate (The average of 10000 sample) Zero point of R_n in this case is between 20 and 21, we call a critical nucleus size as 21 ,because of the place to have taken an un-negative value for the first time. In case of the comparison with the thermodynamics, we regard as the continues value. Because a simulation is done in square lattice, R_n vibrates at equal to or less than 10 , it is the effect of the size and unisotropic of bond of the cluster. Also, we monitor the waiting time $\tau_w(n)$ which reaches n body cluster first and decide the waiting time of the nucleation, and moreover monitor the average length of the edge of the cluster (the number of the broken bond) . Incidentally, for P_n^+ and P_n^- to be right, it is necessary to pay attention to one cluster.

Figure 2b shows relation with maximum cluster size and the 2nd large cluster size, and shows that $n \geq 5$ pays attention to one cluster. Moreover, there is a process of the transfer, $n \rightarrow n \pm m(m \neq 1)$, too, in the simulation, but it is a negligible process.

3. Result and discussion

3.1. Simulation size dependence and the influential range of nucleus

In waiting time $\tau_w(n_k^*)$, there is simulation size dependence because it is proportional to area A reverse like the (6).

$$\tau_w(n_k^*) = 1/I_n A \tag{6}$$

Here, I_n is a nucleation frequency. When the simulation size is too large, more than one nucleus sometimes generates in it.

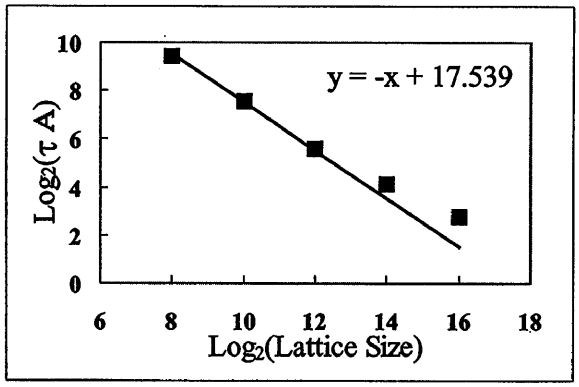

Figure 3. Lattice size dependence on the waiting time of nucleation on the surface; $\phi/kT = 3, \Delta\mu/kT = 0.55$.

Figure 3 shows relation between the simulation size and the waiting time with bond energy $\phi/kT = 3$, chemical potential difference $\Delta\mu/kT = 0.55$. The solid line is the straight line of the inclination -1 which passes being $\log_2$ in the waiting time at simulation size $32\times32(=2^{10})$. Within simulation size 64 × 64, the critical nucleus is one but it finds that more than one (not two) is made in above 128 × 128 because the waiting time becomes long. That is, it finds that the influential range per nucleus is between 64 × 64 and 128 × 128 in estimating the beginning of the difference from the straight line in the waiting time.

3.2. Supersaturating dependence and step free energy

The critical two dimensional nucleus size is given as (8) as the maximum condition with free energy (7).

$$\Delta G = -n\Delta\mu + f\sqrt{n}\gamma, \quad (7)$$

$$n^* = (f\gamma/2\Delta\mu)^2. \quad (8)$$

Here, n is the atomicity which composes the cluster to have formed in on the crystal surface, γ is step free energy and $f\sqrt{n}$ is the length of the edge of the n body cluster. As the critical nucleus size given by the simulation looks for the critical nucleus size which was decided in the kinematics, it is different from n^* which can be given in (8). Therefore, we transform n_k^* in n^* using probabilities P_n^- and P_n^+ by the simulation and (9)[1,2] with a fitting parameter $f\gamma$.

$$P_n^-/P_n^+ = \exp[-\Delta G(n-1)/kT - \ln[P_{n-1}^+] + \Delta G(n)/kT - \ln[P_n^+] = 1 \quad (9)$$

Incidentally, a critical nucleus size decided by kinematics is supposed to have a stable nucleus size (called the 2nd critical nucleus) but it is very difficult to confirm it by our simulation. Because, it is easy to find the 2nd critical nucleus at high temperature according to the theory, but the large cluster generates in the equilibrium condition and we are not able to distinguish between the 2nd critical nucleus at high temperature.

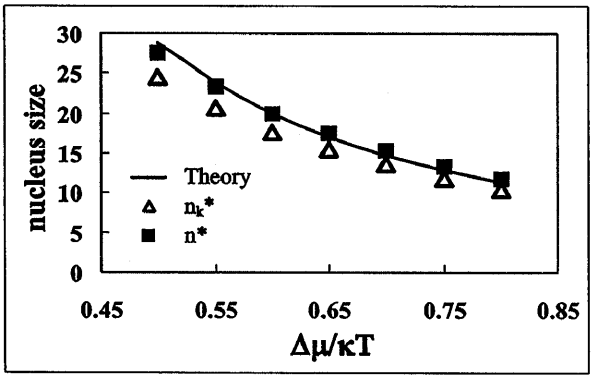

Figure 4. Chemical potential dependence of the nucleus size n_k^* and n^*; $\phi/kT = 3$. Solid line is the theoretical value adjusting at $\Delta\mu/kT = 0.6$.

Table 1
Mean value of the step free energy and form factor

ϕ/kT	γ/kT	f	γ/kT(BCF's)
2.6	0.71	5.64	0.74
3.0	1.01	5.37	1.05
3.5	1.39	5.10	1.40

Figure 4 is the chemical potential dependence of the critical nucleus size n_k^* which is given by the simulation and n^* which applied theory, and the solid line does $f\gamma$ in the fitting in the finding (8) in $\Delta\mu/kT = 0.6$. It finds that about 10

Table 1 shows the theoretical value[6] of the step free energy given by BCF, and the mean value of the step free energy and form factor obtained by simulations. The simulation result has good agreement with the theory.

3.3. The surface diffusion dependence

Because it is possible to estimate a critical nucleus size in the very good precision in our simulation, it thinks that there is surface diffusion dependence in the actual phenomenon if there is surface diffusion dependence in the critical nucleus size in the simulation.

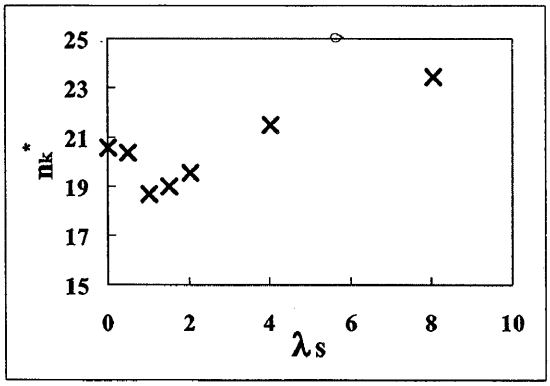

Figure 5. Surface diffusion dependence of the nucleus size n_k^*; $\phi/kT = 3$, $\Delta\mu/kT = 0.55$.

Table 2
Step free energy and form factor with surface diffusion at $\phi/kT = 3$.

	Δμ \ λs	0	1	2	4	8	12
γ	0.55	0.961	0.9	0.907	0.967	1.036	1.07
	0.65	0.956		0.935	1.018		
f	0.55	5.367	5.329	5.285	5.337	5.307	5.343
	0.65	5.269		5.205	5.264		

Figure 5 is the relation with critical nucleus size and surface diffusion distance. It shows that the nucleus size becomes large, i.e. $f\gamma$ becomes large if the surface diffusion distance becomes long without short surface diffusion distance range. Because it is permitted to suppose that there is not surface diffusion dependence in step shape factor f, the step free energy γ becomes large if the surface diffusion distance becomes long. (Table 2) Also, because there is not surface diffusion dependence in the bond energy, γ becomes large if the entropy becomes small. Therefore, it is possible to say that the critical nucleus size becomes large when the surface diffusion distance becomes long generally, because the entropy becomes small when the surface diffusion distance becomes long and the step energy becomes large. Qualitatively, the form of the cluster seems to become a good symmetrical form , breaking a distorted form when the surface diffusion distance becomes long, and the variety of the form seems to become small. On the other hand, the nucleus size seems to become small because the good symmetrical form is low as the energy, because it is near the equilibrium form. However, in the actual nucleation, the entropy effect seems bigger.

3.4. The stable nucleus with the MBE growth condition

In the situation as the evaporation of the absorption atom from the substrate can be ignored like the MBE growth condition, above-mentioned theory can not be adapted[7]. As the absorption atom concentration on the substrate increases in the time, the nucleation is cannot describe only in the chemical potential of vapor atom. Therefore, in case of application, it is to estimate "how many cluster sizes are stable?" and also "what time is it made?" from the incident flux.

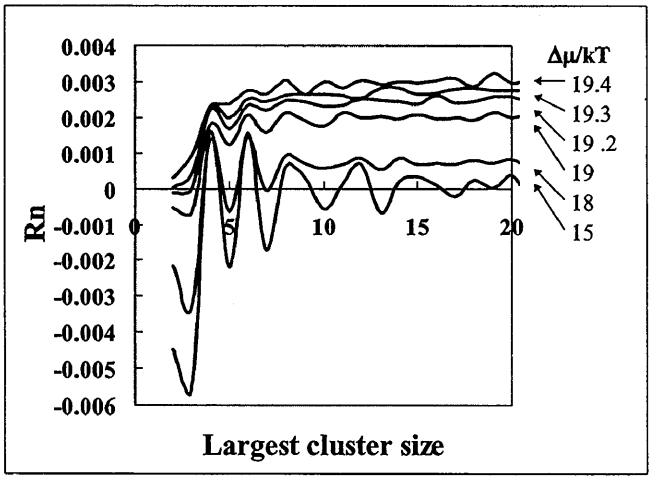

Figure 6. Increasing rate of the cluster size n under MBE growth condition (no evaporation occurs):$\phi/kT = 5$, $\lambda_s/a = 20000$, $\Delta\mu/kT = 15, 18, 19, 19.219.3, 19.4$.

Figure 6 shows the increase rate R_n of the n body cluster when the chemical potentials (the incident flux) are $\Delta\mu/kT = 15, 18, 19, 19.2, 19.3, 19.4$ with $\phi/kT = 5, \lambda_s/a = 20000$. In $\Delta\mu/kT \geq 19.3$, the stable nucleus size is (the cluster shape becomes a DLA type) two and in $\Delta\mu/kT \leq 19.2$, it is four. It finds that the range where the stable nucleus size is three is very narrow range[4] (there are no figure) . Also, when $\Delta\mu/kT$ is small, the cluster size that the increase rate is a positive value emerges discretely. This means that it reflects lattice structure, and that the cluster structure with long lifetime emerges discretely. This thing should be able to be experimentally observed, and the contrast between the energy computation and the experiment on the small cluster is waited for. Incidentally, be careful, this stable nucleus is different from the 2nd critical nucleus pointed out the Nishioka theory.

4. Conclusion

Two dimensional nucleation process on substrate is investigated by Monte Carlo simulation, and the critical nucleus size and its waiting time are measured with high accuracy from the attachment and detachment rate. Using the kinematical nucleation theory by Nishioka, it is found that our obtained kinematical two dimensional critical nucleus size are about ten percent smaller than the thermodynamically defined one. Also, the chemical potential dependence of this nucleus size ha good agreement with the conventional theory.

It is found that there are surface diffusion dependence in the critical nucleus size, and the critical nucleus size become large when the surface diffusion distance becomes long. This is because the entropy of the step forming by the nucleus becomes small. The reason is not clear about why the critical nucleus size becomes small when the surface diffusion distance is about $2a$, comparing when the surface distance is zero.

In the MBE growth condition, when the incident flux (chemical potential) is small, it is found that the splash occurred to the stable nucleus size with the shape of the cluster and the influence of the lattice structure. Be careful that these stable nucleuses are not the 2nd critical nucleus pointed by Nishioka.

Now, in this paper, we transformed the critical nucleus size given by the simulation into the critical nucleus size which is defined by thermodynamics, and evaluated the step free energy and so on. However, the result changes hardly even if we directly use the size which is obtained from the simulation.

5. References

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