MONTE-CARLO SIMULATION STUDY OF VACUUM DEPOSITION PROCESS

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ABSTRACT

The initial stage of the vacuum deposition process was simulated by the Monte-Carlo (MC) method. Lennard-Jones potential was assumed as the atomic interaction. Varying the binding energy of the film-substrate atom pair and the atomic size of film atoms, the change of the critical misfit strain of the coherent interface and the difference of the growth mode were studied. The critical misfit strain of the coherent interface was 4% for the case where the binding energies of the constituent atoms were all equal. Change of the growth mode occurred when the misfit strain of the interface was increased while the strength of the potential was kept constant. The value of the critical misfit strain and the boundary between the 2D (dimensional) and 3D growth modes were shifted sensitively with change of the strength of the potential.

INTRODUCTION

Thin film technology has developed remarkably in the prodution making, controlling and evaluation techniques. Accuracy in controlling film thickness has reached atomic level through the use of molecular beam epitaxy (MBE) with a feedback control system. Recently lattice-mismatched epitaxy, which is the crystalline film growth phenomenon on the substrate with a large difference in the lattice constant, has attracted considerable attention. Superlattices constructed of two different materials with a large mismatch contain the strain force field which greatly influences the band structures. A typical example of the strained superlattice is the combination of Si and Ge with a 4% mismatch. In the present study, we performed a Monte-Carlo simulation of the initial stage of the film formation process, varying the experimental conditions and potential parameters. From the obtained structure, the difference in the growth mode and the coherent-incoherent transition at the heterogeneous interfaces are studied in continuous space and related to the combination of binding energies and the misfit strain of the system.

METHODS OF CALCULATION

MONTE-CARLO METHOD

The calculated system was restricted to two dimensions for simplicity and to save the CPU (central processing unit) time. The deposition process was simulated as follows. First, four layers of a triangular structure, of which each layer contained

twenty atoms, were set as a substrate. The periodic boundary condition was imposed on the system in the lateral direction (which was perpendicular to the growth direction) while in the growth direction, it was kept free. Then deposition atoms were adhered one by one onto the substrate for every fixed period of Monte-Carlo steps. The potential energy was calculated using the Lennard-Jones potential,

$$\phi(r) = E_{ij}\left[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}\right], \qquad (1)$$

where r is the distance between an atom pair of i and j, and E_{ij} and σ_{ij} are the parameters of the binding energy and atomic size of the i-j interaction, respectively. The subscripts i and j represent the kind of constituent atoms, i.e., substrate or film atoms (hereafter, they are denoted by subscripts s or f). Thus the parameters E_{ij} and σ_{ij} have three values which represent the three types of interactions: substrate-substrate, adatom-adatom, and adatom-substrate interactions. Here we denote E_{ss} and σ_{ss} as the parameters of the substrate-substrate interaction, E_{ff} and σ_{ff} as those of the adatom-adatom pair and E_{fs} and σ_{fs} as those of the adatom-substrate combination. For the parameter of atomic size, σ_{ss} was fixed to be $2^{1/6}$ which is considered to be a unit distance in this simulation. σ_{ff} was varied from $0.90\times\sigma_{ss}$ to $1.10\times\sigma_{ss}$, and σ_{fs} was determined as the arithmetic mean of σ_{ff} and σ_{ss}. For the parameters of binding energy, E_{ss} and E_{ff} were taken to be one unit of energy, 1, and E_{fs} was varied as 0.5, 1, 2 and 4 to study the effects of the heterogeneous interaction. The algorithm of the present simulation can be summarized as follows [3].

① A new adatom is generated at a random position on the growth front.

② Using a random number generator, a virtual displacement is given to every film atom on the substrate in order to move it in continuous space. The maximum displacement is restricted to be within 2.5% of the nearest-neighbor distance of the substrate. The accuracy of the position of the film atoms is about one hundred times higher than that of the solid-on-solid model which has been frequently used in the ordinary MC simulation.

③ The change of the potential energy between the initial and the virtually moved configurations of the film, ΔE, is calculated using the Lennard-Jones potential while the cutoff distance of the interaction is assumed to be three scaled distance units.

④ If ΔE is negative, the virtual displacement is accepted and the adatom is moved.

⑤ If ΔE is positive, Boltzmann's factor $\exp(-\Delta E/T^*)$ is calculated from the change of energy associated with the movement ΔE and the system temperature T^* in reduced units. Then a random number R is generated and the virtual displacement is accepted only if R is less than Boltzmann's factor. The system temperature is set as the substrate temperature T_{sub}, but for a newly adhered adatom, it is set as the deposition beam temperature T_{beam} in order to introduce the dynamical effects. When the generated random number R is larger than Boltzmann's factor, the virtual displacement is rejected.

⑥ Go to ② while IR [MC steps/atom] is spent for the relaxation of the film structure. Note that the decision to move the film atoms in ②-⑤ above is performed individually.

⑦ Go to ① until the number of the film atoms reaches 80, which construct about four layers when they grow in layer-by-layer mode.

RESULTS AND DISCUSSION

Changing the experimental conditions such as substrate temperature (T_{sub}), temperature of the deposition beam (T_{beam}) and the inverse of deposition rate (IR), the appropriate conditions for smoothing the film surface were studied. It was found that the appropriate conditions to obtain a smooth surface were T_{sub}= 0.05, T_{beam}=0.10 and IR=10000 [MC steps/atom]. The film structure obtained under such conditions is shown in Fig.1 (a). In the present study, temperature is represented as dimensionless. The relationship between the real temperature T_R and the reduced temperature T^* is

$$T^*=k_B \cdot T_R/E_{ss} \ , \qquad (2)$$

where k_B and E_{ss} are Boltzmann's constant and the binding energy of the substrate atom pair, respectively. Namely, the reduced temperature is the thermal energy of the system measured by E_{ss}, i.e., the unit of energy in the present simulation. We performed the Monte-Carlo simulation for the substrate only and found that the substrate began to melt at T_{sub}=0.09, while the melting point of the bulk is 0.12 [4]. The lower melting point of the substrate is attributed to surface melting. Sarma et al. [5] investigated epitaxial growth of the Lennard-Jones system on the fcc(111) orientation using the molecular dynamics (MD) method, and found that the best epitaxial growth was achieved at around one-half the melting temperature of the substrate. The result of our simulation agreeds fairly well with that obtained by the MD method. The time interval between the arrival of a newly generated adatom onto the substrate, IR=10000 [MC steps/atom], roughly corresponds to one hundred periods of atomic vibration. If the experimental parameters (T_{sub}, T_{beam} and IR) were less than the above mentioned values, it was found that 3D disorder was enhanced in the film structure. Hereafter, only the results are presented for the above mentioned experimental parameters. We checked the effects of the movements of the substrate atoms on the film structure performing the MC simulation in which the both film and substrate atoms are allowed to move. We found that it did not alter the film structure signifficantly although it enhanced the mobility of film atoms to some extent.

In the next stage of our simulation, the influence of the interface mismatch on the film structure was studied. In the present study, the interface mismatch is defined as

$$\delta \ =100\times(\sigma_{ff}-\sigma_{ss})/\sigma_{ss} \ [\%], \qquad (3)$$

where σ_{ff} and σ_{ss} are the size parameters of the Lennard-Jones potentials for film-film and substrate-substrate atom pairs, respectively. Fig.1 (b) shows that the obtained atomic configuration for δ=2(%) and $E_{ss}=E_{ff}=E_{fs}=1.0$. It can be seen from the figure that the interface is coherent and that the film morphology is a 3D cluster on a few atomic layers, i.e., Stranski-Krastanov (SK) type. Increasing the lattice mismatch, it was found that the roughness in the growth front was enhanced up to 4% because of high strain energy at the coherent interface, while at δ=5%, the interface was changed to incoherent and the surface roughness was reduced significantly (see Fig.1 (c)). The growth mode for $0<\delta\leqq 4\%$ is considered to be SK type while that for δ=5%, Frank-vander Merve (FM) type. Fig.1 (d) shows the calculated structure of the system with 10% mismatch

which indicates the Volmer-Weber(VW) growth mode, i.e., 3D nucleus formation directly on the substrate. The change of the growth mode can be attributed to the strain energy accumulated in the deposited film. In order to discuss the strain effects qualitatively, we calculated the potential energies of the deposited atoms with various δ's. Table 1 shows the difference in the potential energy between the systems with and without lattice mismatch, ΔE_{ff} and ΔE_{fs}. Here it is noted that the values of ΔE_{fs} for δ=0% to δ=4% are in the same order and are smaller than those for δ=5% to δ=10% by an order of magnitude. From this table and Fig. 1, the correlation between the film morphology and the interface strain can be easily seen. It is energetically favorable to form 3D islands on the strained film layers in order to release the strain energy contained in the coherent interface; hence, SK-type growth occurs for $0<\delta\leqq 4\%$. Increasing the lattice mismatch further, the growth mode changes into the VW-type. The 5% mismatch is a special situation such that ΔE_{ff} is small according to the release of the surface strain energy. Its interface is incoherent, and the smoothness of the film surface indicates that the growth mode is FM. Dodson and Taylor [4] simulated the film formation process by continuous-space MC techniques based on the same motivation as ours. They investigated the growth mode as a function of the interface mismatch and substrate temperature. They reported that a coherent interface was obtained up to δ=2% and incoherent interface for $\delta>2\%$ at T_{sub}=0.09. Concerning the value of critical mismatch, there is some discrepancy from our result. It can be considered that the high substrate temperature caused the improvement of adatom mobility, which allows the system to overcome the activation energy to release the coherent strain energy in the system with $2<\delta\leqq 4\%$. However, it should be noted that surface melting wil occur at such a high temperature, so the interface will be more roughened if the substrate atoms are allowed to move. Dodson and Taylor[6] also performed the same kind of simulation using the MD method and reported that the critical misfit strain was 4% with $T_{sub}<0.5T_m$ and that the incoherent interface contained many defects between film atoms and the substrate with $T_{sub}>0.5T_m$, where $0.5T_m$ is 0.06, which is less than the case of their MC simulation. The MD method provides trajectories of the individual atoms deterministically, whereas the MC method does stochastically. It is noteworthy to mention that the MD simulation contains the dynamics of the deposition beam but the MC method in general cannot. Our result of the simulation agrees fairly well with that obtained by the MD method rather than that by the MC method because the deposit beam temperature was incorporated into our calculation.

In the case of E_{fs}=2, it is confirmed that the smoothness of the interface is improved and that the film growth mode is layer-by-layer, i.e., FM. In the case of E_{fs}=0.5, 3D nuclei were directly formed on the substrate, i.e., VW. Ozawa and Sasajima [7] performed Monte-Carlo simulations of the vacuum-deposition process based on a solid-on-solid model assuming Morse potential as the atomic interaction. They found that the film growth mode can be determined essentially by the depths of the interaction potentials, E_{ff}, E_{ss} and E_{fs}; the film growth mode is FM for $E_{fs}>E_{ff}$, while VW for $E_{fs}<E_{ff}$, which is consistent with the result of the present studies. They pointed out that the SK mode without coherent strain appears if $E_{fs}>E_{ff}$ and if substrate temperature is high. This SK mode is considered to be unstable. The calculated system contained no strain

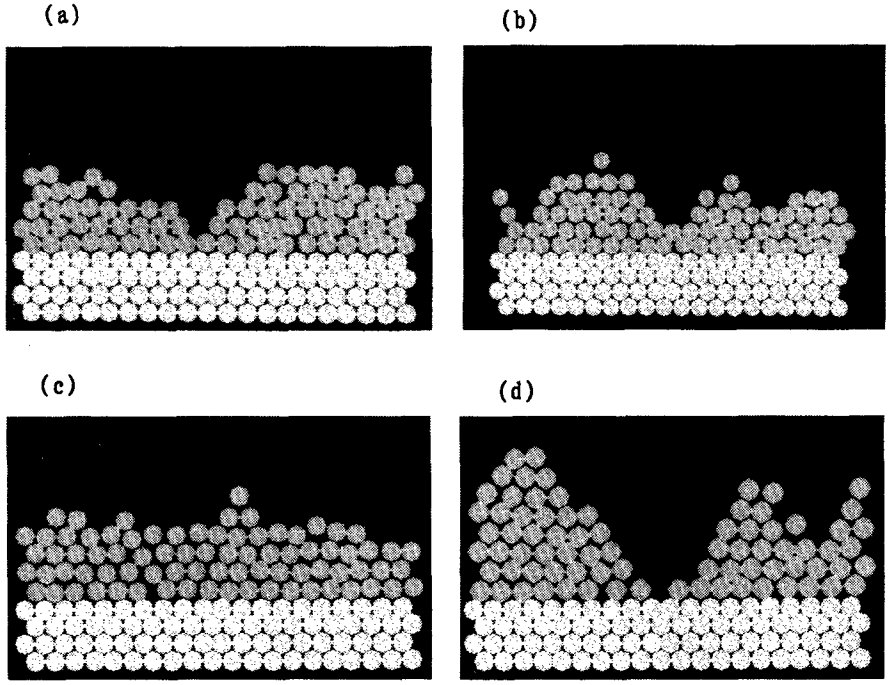

Fig.1 The film structures obtained by 2D MC simulation: (a) δ=0%, (b) δ=2%, (c) δ=5% and (d) δ=10%. The other simulation parameters are $E_{ff}=E_{ss}=E_{fs}=1.0$, $T_{sub}=0.05$, $T_{dep}=0.10$, IR=10000 [MC steps/atom].

Table 1 The difference in the potential energies of the deposited atoms, ΔE_{ff}, and that in the film-substrate atom combination, ΔE_{fs}, between the systems with and without interface mismatch δ.

mismatch δ (%)	difference of energies ΔE_{ff}	difference of energies ΔE_{fs}
0	0	0
2	0.052	−0.0038
3	0.001	−0.0002
4	0.054	0.0013
5	0.004	0.0194
7	0.050	0.0162
8	0.055	0.0148
10	0.088	0.0119

energy, so the FM mode is much stable under the appropriate temperature. Under the SK mode codition, the film atoms at the growth front are in liquid because of the high system temperature and they preferably aggregate in 3D islands. We also calculated the film structures with various sets of the potential parameters of binding energy and atomic size. Fig.2 (a) shows the map of the coherent-incoherent structure as a function of the ratio of the binding energies E_{ff}/E_{fs} and lattice mismatch δ. In the case that all binding energies are equal, the interface structure was coherent up to δ=4%. It was found that the critical value of lattice mismatch of the coherent interface increased to 8% when the ratio of the binding energies E_{ff}/E_{fs} was decreased to 0.5. In the case that E_{ff}/E_{fs} was doubled, the 3D cluster was preferentially formed on the substrate. For these systems, the determination of the interface structure, either coherent or incoherent, was made from the heterogeneous interface between the cluster and substrate. For $\delta < 0$% (hereafter, we call this condition minus mismatch), a coherent interface was obtained until δ=-10%. This is because the strain energy accumulated in the film interface is considerably smaller for minus mismatch than for plus mismatch. The energy gain of the coherent interface exceeds the loss of strain energy for the large mismatch systems if $\delta < 0$%. We calculated the strain energy of the Lennard-Jones dimolecule to discuss the above consideration quantitatively. We assume that the dimolecule system interacts via the dimensionless Lennard-Jones potential,

$$\phi(r) = 1/r^{12} - 2/r^{6} . \qquad (4)$$

The equilibrium distance is taken to be a unit distance, at which the binding energy is -1. In the case that bond length is elongated to +10% strain, the potential energy changes from -1.0 to $\phi(1.1)$=-0.81, while in the case of -10% strain, $\phi(0.9)$ =-0.22. Noting that +10% strain arises when the deposited film with δ=-10% is strained to be coherent, the coherency strain energy can be estimated to be 0.19 per bond. While for the case that the system with +10% mismatch is coherent, the strain energy is estimated to be 0.78 per bond. From this simple estimation, it is easy to understand why the interface structure of the system with large minus mismatch is coherent but that with plus mismatch is not. To discuss the effect of potential function upon the critical value of the strain of a coherent interface, we performed a similar estimation using the Morse potential,

$$\phi(r) = \exp[-2\alpha(r-r_0)] - 2\exp[-\alpha(r-r_0)], \qquad (5)$$

where r_0 is the equilibrium distance of a dimolecule which gives the potential minimum of -1. Here α was fixed to be 6.0, which was the representative value of metallic atoms. For +10% strain of the bond length, the potential energy changed from -1.0 to $\phi(1.1)$=-0.79, while for -10% strain, $\phi(0.9)$=-0.79. Therefore, it can be estimated that the strain energy accumulated in the coherent system with -10% mismatch is 0.21, while that with +10% mismatch is 0.68. It is shown that asymmetry in the strain energy is reduced compared with the case of Lennard-Jones potential. If Morse potential is assumed as the atomic interaction, it can be predicted that the critical values of the strain of a coherent interface are shifted to be less than those calculated using Lennard-Jones potential, especially for minus mis-

match. Sarma et al. [5] calculated strain energies for the cases of positive and negative misfit using overlapping anisotropic Morse potentials. They reported that strain energy for the case of negative misfit is less than that for the case of positive misfit, and this is due to anharmonic forces in the adsorbate film. Consequently, pseudomorphic growth (i.e., film growth with a coherent interface) can be more easily achieved if the lattice constant of the adsorbate is less than that of the substrate. This result is consistent with our consideration mentioned above.

Fig.2 (b) shows the phase diagram which classifies the growth modes as a function of the ratio of the binding energies, E_{ff}/E_{fs} and the lattice mismatch δ. In the case that the ratio of binding energies E_{ff}/E_{fs} are 1, increasing the lattice mismatch, the film growth mode changes from FM (δ=0%) to SK (0%< $\delta \leqq$ 4%), FM(δ=5%) to SK (5%< δ <10%) and finally to VW ($\delta \geqq$ 10%). In the case of E_{ff}/E_{fs}=0.5, with increasing positive mismatch, the growth mode varies from FM type (δ=0%) to pseudo-FM type (0< $\delta \leqq$ 6%) and finally to SK type (δ > 6%). The pseudo-FM mode is defined as growth of three atomic layers and at that time, 3D clusters nucleate on the layers. The distinction between SK and pseudo-FM mode was the number of the preformed atomic layers; pseudo-FM mode for three atomic layers and SK mode for one or two atomic layers. It is remarkable that the growth mode of the δ=10% system changes from VW type with E_{ff}/E_{fs}=1 to SK type with E_{ff}/E_{fs}=0.5. The above result is consistent with the classical phenomenological consideration that the SK mode appears preferentially in the system which has both a strong interaction between the substrate and deposited film and large lattice mismatch. Fig.3 shows the change of coverage as a function of Monte-Carlo steps for the representative systems. The coverageis a parameter which characterizes the progression of the filmgrowth; the coverage takes a value from 0 to 1 during the formation of an atomic layer. Fig.3 (a) shows the coverage change for the system with δ=0% and E_{fs}=2. It can be seen from this figure that the first three atomic layers grow at a fast rate, and then the growth rate decreases from the fourth layer, because the strong film-substrate interaction disappears. Since the coverage change indicates layer-by-layer formation, this growth mode is consideraed to be FM. Fig.3 (b) shows the coverage change for δ=10% and E_{fs}=0.5. Since a 3D cluster is formed before the completion of the first atomic layer, this growth mode is considered to be VW. Carson et al. [8] performed MC simulation based on the two kinds of lattice models, i.e., IL(interpenetrating lattice) and PM (potential minimum) models, using Lennard-Jones potential. They investigated the growth mode and the interface structure, varying lattice mismatch, substrate temperature and deposition rate. They reported that the substrate-film interface is coherent up to 4% mismatch, while beyond 6% mismatchs the interface structure is incoherent. The growth mode was FM at 2% mismatch, but at greater mismatch, VW growth was preferred. As for the critical value of misfit strain for a coherent interface, their result is consistent with ours, but there are some difference for the boundary of the growth modes. The appearance of FM at 2% mismatch was determined from the results of the film growth within only two layers. Therefore, it does not contradict our results because the SK mode will appear after the completion of the first two atomic layers.

Finally, comparison between some experimental results [7]

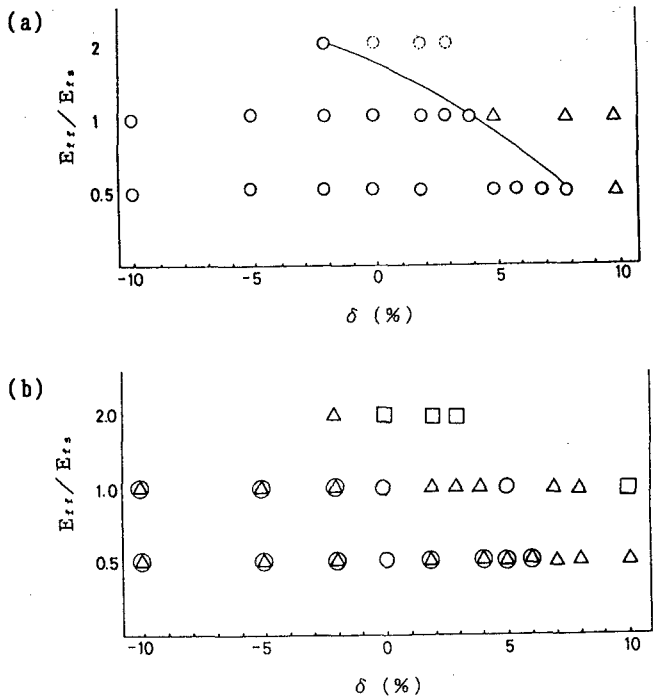

Fig.2 The map of (a) coherent-incoherent structures and of (b) growth mode obtained as a function of the binding energy ratio, E_{ff}/E_{fs}, and interface mismatch, δ. The symbols in the figures are as follows;

(a) ○ : coherent interface △ : incoherent interface
◌ : coherent interface
(The film morphology is 3D island)

(b) ○ : FM mode ⓐ: pseudo-FM mode △ : SK mode □ : VW mode

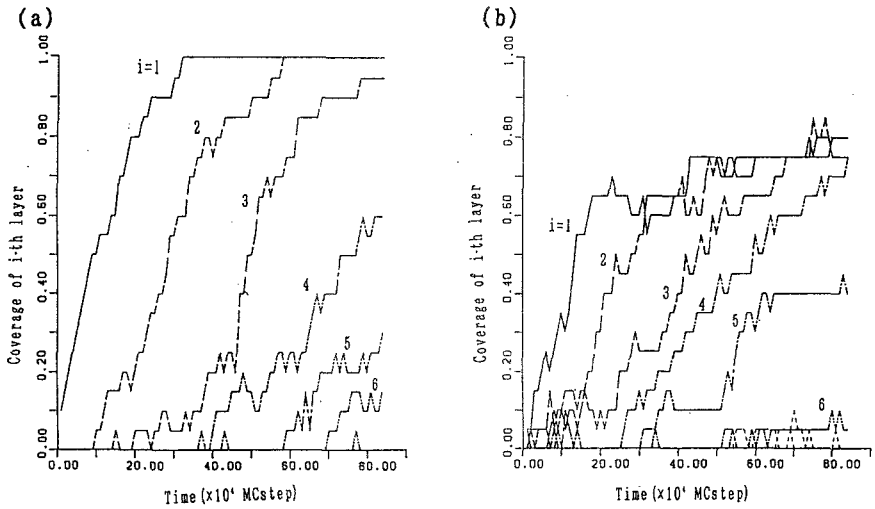

Fig.3 The coverage changes of the individual layers as a function of time for the representative cases of (a) Frank-van der Merwe mode (δ=0%, E_{fs}=2.0) and (b) Volmer-Weber mode ((δ=0%, E_{fs}=0.5)

and the present simulations was made in Fig.4. The ratios of the binding energies were estimated from the experimental values of dissociation energy [8]. The simulation results explain the experiments fairly well. Therefore, there is a possibility that the growth mode of any combination of metal can be determined from the (E_{ff}/E_{fs}-δ) map shown in Fig.2. However, how to determine the binding energy of E_{fs} still remains as an open question.

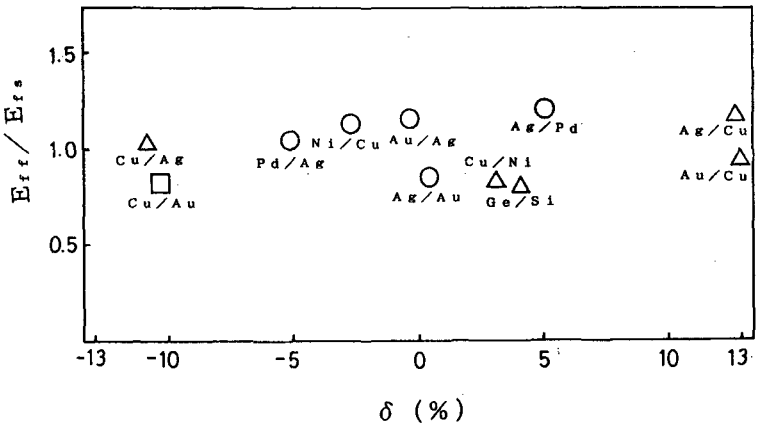

Fig.4 Comparison between the experimental results and vacuum deposition simulations. The symbols in the figures are as follows; ○: FM mode, △: SK mode, □: VW mode

CONCLUSIONS

Using the 2-dimensional Lennard-Jones potential model, we performed Monte-Carlo simulation in order to examine the influence of experimental conditions and potential parameters on the initial stage of film growth. The experimental conditions appropriate for obtaining smooth film structure were T_{sub} =0.05, T_{beam}=0.1 and IR=10000 [MCstep/atom], where T_{sub}, T_{beam} and IR represent the substrate temperature, the deposition beam temperature and the inverse of the gowth rate, respectively. Under these experimental conditions, the film formation process was simulated, varying the potential parmeters. The obtained results are as follows.

① In the case that all of the binding energies are the same ($E_{ss}=E_{ff}=E_{fs}=1$), a coherent interface is obtained up to 4% mismatch. If the binding energy between the adatom-substrate pair E_{fs} is strenghened to be two times larger than the other energies, E_{ss} and E_{ff}, the critical mismatch of the coherent interface is changed to 8%.

② In the case that the ratio of binding energies E_{ff}/E_{fs} are 1, increasing the lattice mismatch, the film growth mode changes from FM (δ=0%) to SK (0%< $\delta \leqq$ 4%), FM (δ=5%) to SK (5%< δ <10%) and finally to VW ($\delta \geqq$ 10%). In the case of E_{ff}/E_{fs}=0.5, increasing the lattice mismatch, the growth mode changes from FM(δ=0%) to pseudo-FM (0%< $\delta \leqq$ 6%) and finally to SK (6%< $\delta \leqq$ 10%).

③ When the heterogeneous interaction was weakened, the growth mode was VW in a wide range of mismatch, regardless of increase of the mismatch.

④ As for plus and minus mismatch of adatoms on the substrate,

match, the SK mode preferentially appeared as compared with the plus mismatch case.

In the present study, it was demonstrated that the binding enegies of constituent atoms and the lattice mismatch play crucial roles in film growth formation.

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