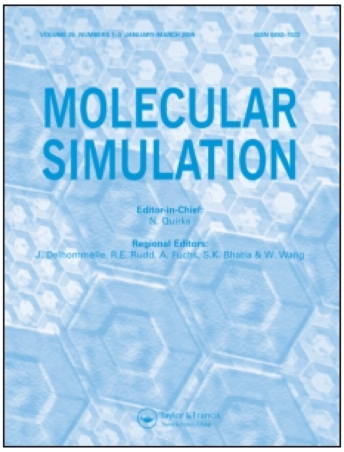

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Molecular Dynamics Study of the Thin Film Formation Process

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MOLECULAR DYNAMICS STUDY OF THE THIN FILM FORMATION PROCESS

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The initial stage of thin film formation process was studied by the molecular dynamics method. The Morse function was assumed as the interaction potential between the substrate-substrate, substrate-deposited and deposited-deposited atoms. The interfacial structure of the calculated system was restricted to be coherent, i.e. the structures of the substrate and the deposited atoms were both fcc and had the same lattice constants. The depth of the potentials for the three types of interaction was changed to study its effects on the film structure. The substrate temperature was also varied to see the temperature dependence of the relaxation process of the film structure.

Two kinds of structure of the deposited films were considered; three atomic layers of fcc(111) and a monolayer of fcc(111). Both consisted of 19 atoms. They were considered as the nucleus of the film at the initial stage of the deposition process. The deposited nuclei were relaxed into equilibrium shapes such as the monolayer, the 3 dimensional island and the intermediate structure, which were determined by the ratios of the depths of the potentials for the deposited-deposited atoms D_{ff} and the deposited-substrate atoms D_{fs}. The relaxed structures were dependent upon the initial structure, but roughly speaking, $D_{ff}/D_{fs} > 2$ made the 3 dimensional island structure, $D_{ff}/D_{fs} < 1$ produced a monolayer and $1 < D_{ff}/D_{fs} < 2$ the intermediate structure. The appropriate substrate temperature was necessary to accomplish such structural transitions. A low substrate temperature kept the film in the initial structure.

KEY WORDS: Thin film formation, molecular dynamics, growth mode, depth of potential, substrate temperature.

INTRODUCTION

It is helpful to simulate the thin film formation process in order to obtain information useful for the atomic level control of thin film structure. The equilibrium shape of the nucleus determines the film structure. Three types of film structure have been experimentally observed [1,2]; the first is the stacking of monolayers, Frank-van der Merwe type (FM), the second is the three dimensional (3D) island, Volmer-Weber type (VW), and the third is the 3D island on a few monolayers, Stranski-Krastanov type (SK). These growth modes are considered to be determined by the interatomic potentials because the observed film structures are energetically metastable. Especially at the early stage of the deposition process, the nuclei of the film are relaxed under the strong influence of the substrate potential and finally show the equilibrium shape leading to one of the three types of the film structure, FM, VW or SK. The relaxation process of the deposited nucleus is the key to understand the thin film structure. Recently, the film formation process at a homogeneous solid/vapor interface has been studied by the molecular dynamics method [3–6], but the details of its mechanism are not evident as yet. In this paper, the relaxation process of the deposited nucleus on the fcc(111) substrate was simulated by the molecular dynamics method. The calculated equilibrium shapes were related to the growth mode, the effects of the potential parameters and the substrate temperature.

METHODS OF CALCULATION

Initial Structure

Six planes of fcc(111) which contained about 100 atoms each were set up as the substrate. Two types of nucleus comprising 19 atoms were deposited on the substrate; one was the partial monolayer and another was the three atomic layers of fcc(111). It is not always true that the nuclei generated at the initial stage of film formation are composed of 19 atoms. However, the present simulation gives a typical example of the structural relaxation process of the nuclei, which is crucial to determine the growth mode. The structure of the film atoms was assumed to be the same as the substrate atoms, i.e. fcc with the same lattice constant.

Interatomic Potential

The Morse function,

$$\phi_{ij}(r) = D_{ij}[\exp(-2\alpha(r - r_0)) - 2\exp(-\alpha(r - r_0))], \qquad (1)$$

was assumed as the interaction potential, where ij represents the three kinds of pair interaction between substrate-substrate (ss), film-susbstrate (fs) and film-film (ff) atoms. D_{ij}, α and r_0 are the potential parameters. α and r_0 were fixed through the three types of interaction, $\alpha = 6.0$ and $r_0 = 1.01640$. Within the 5-th neighbor interaction, r_0 was determined so that the equilibrium nearest neighbor distance of the fcc lattice gave unit length in this simulation. The value of α was taken from those of Cu–Cu and Ni–Ni interactions as the typical value of the metal–metal combination. D_{ij} is the only parameter which represents the difference of atomic interaction, $ss(D_{ss})$, $fs(D_{fs})$ and $ff(D_{ff})$ types. It can be considered that the ratio D_{ff}/D_{fs} is an essential factor which determine the equilibrium shape of nucleus of film atoms. Therefore D_{ff}/D_{fs} determines the growth mode if the mobility of the film atom is high enough with appropriate substrate temperature T_{sub}.

Molecular Dynamics Simulation

The two types of nucleus, the monolayer and the three atomic layers of fcc(111), were relaxed by the molecular dynamics method. The uppermost layer of the substrate was also relaxed but the rest of the layers and the rim of the uppermost layer were fixed. Therefore the fixed boundary and free boundary conditions were taken for the substrate and deposited systems, respectively. Concerning the film morphology, the thermal vibration of the substrate atoms does not play an important role in the calculation. The same conclusion would be obtained even if all the substrate atoms were fixed while the film atoms were allowed to move with the corresponding thermal energy to the substrate temperature. This tendency was already found in the fcc deposits on the bcc(110) substrate [6]. Because of the short range interaction of the

Morse potential with $\alpha = 6.0$, the atomic layers without the uppermost layer do not affect the relaxation process of the deposited nucleus. If the value of α is lowered, the long range effects of the potential can be observed in the film formation process [7]. We found that the transition of the growth mode occurred if α was lowered from 6 to 2 with $D_{ff} = 0.1$ eV and $D_{fs} = 0.4$ eV. It should be pointed out that this simulation was performed by the solid on solid model, i.e. all the substrate atoms were fixed at the lattice point. The velocities of the substrate atoms which are allowed to move were reset periodically according to the Boltzmann distribution with the given substrate temperature. The substrate temperature T_{sub} was varied from 500 to 1000 K.

Since the temperature was calculated from the kinetic energy of the film atoms at the observed time step, it showed the rather high variance as shown in Figure 8. But the substrate temperature is meaningful in an averaged sense. The depth of potential parameters, D_{ff} and D_{fs} were set from 0.05 to 0.4 eV, where $D_{ss} = D_{ff}$. With these conditions, the equilibrium shape of the nucleus was calculated and related to the growth modes.

RESULTS AND DISCUSSION

At first, the results for the monoatomic system with $D_{ff} = D_{fs} = D_{ss} = 0.2$ eV are shown. Figure 1 shows the trajectories of the deposited atoms at $T_{sub} = 1000$ K. This figure shows the relaxation process where the shape of nucleus of the film atoms was changed from the 3D island to the monolayer structure. This structural change is more clearly seen in Figure 2 which represent the initial and final structures by the ball and stick model. This result suggests that this system will show the layer by layer growth mode, FM, under the appropriate substrate temperature. However, if the substrate temperature T_{sub} was 500 K, which was not high enough to give the high mobility of the film atom, the equilibrium shape of the nucleus remained the 3D island structure and could not change to the monolayer structure during the simulation time, 5000 MD steps (1.25×10^{-11} sec). Figure 3 shows the circumstances: the 3D island cluster was relaxed and its shape was changed, but it could not change into the monolayer structure. If the relaxation calculation was performed for the monolayer cluster, the shape of the deposited system did not change even at $T_{sub} = 1000$ K, because the monolayer is the stable structure of this system. The molecular dynamics simulation of the vacuum deposition process confirms the present results [4]. The calculated system was monoatomic and the interacting potential was assumed to be the Lennard–Jones potential. The obtained film structure showed the well ordered layers for all substrate temperature but it contained some defects and voids at very low temperature.

Next the calculation was performed varying the ratio D_{ff}/D_{fs}. In the higher value region of the ratio, $D_{ff}/D_{fs} > 2.0$, the three atomic layers of fcc(111) were relaxed into the 3D island structure like an isolated cluster. Figure 4 shows the initial and final structures of the deposited 3D cluster with $D_{ff} = 0.4$ eV, $D_{fs} = 0.05$ eV and $T_{sub} = 1000$ K. The final structure contained the 13 atoms icosahedral cluster which was energetically stable. Compared to the result of Figure 3, it can be found that this cluster is free from the effects of the substrate potential because the interaction energy of the substrate and the deposited atoms is very small (0.05eV) while that of the deposited-deposited atoms is fairly large (0.4eV). Contrary to this condition, the effect

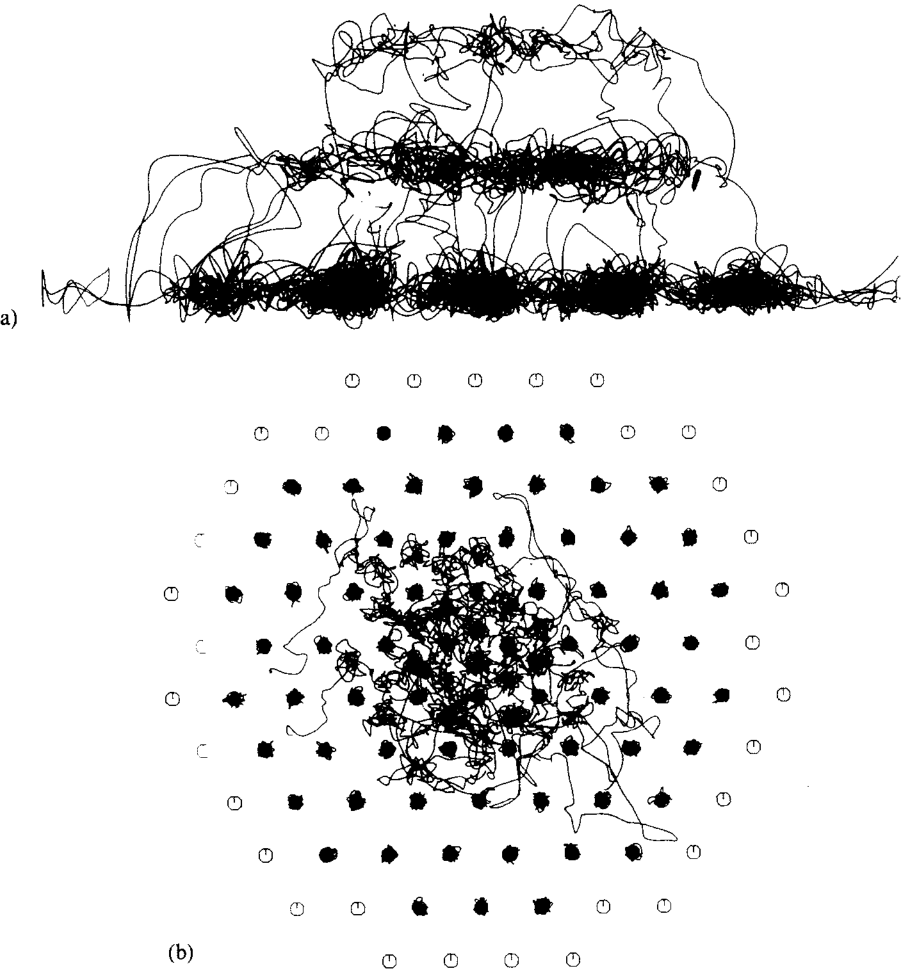

Figure 1 (a) The side view and (b) the top view of the trajectories of the deposited atoms with $D_{ff} = D_{fs} = D_{ss} = 0.2$ eV and $T_{\mathrm{sub}} = 1000$ K.

of the substrate potential can be seen for the system with $D_{ff} = D_{fs} = 0.2$eV as shown in Figure 3. Strictly speaking, the calculated equilibrium structures were different from each other under the different substrate potential and/or the substrate temperature. However, these shapes of nuclei were classified into the 3D island, the monolayer and the intermediate structures like Figure 4(b), Figure 2(b) and Figure 3(b), respectively. These classification would be enough for the present purposes *i.e.* the prediction of the growth modes. The classification for the two different initial structures as a function of D_{ff}/D_{fs} as and the substrate temperature T_{sub} are shown in Figure 5. If the appropriate substrate temperature is given, the equilibrium shape of the nucleus can be predicted from the ratio D_{ff}/D_{fs} regardless of the initial structure; $D_{ff}/D_{fs} > 2$ leads to the 3D island, $D_{ff}/D_{fs} < 1$ a monolayer, and $1 < D_{ff}/D_{fs} < 2$ the intermediate structure. This classification is consistent with the results obtained by

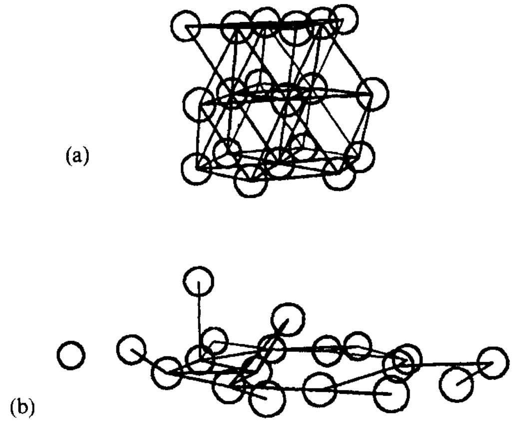

Figure 2 (a) The initial and (b) the final structures of the film cluster. The data were the same as in Figure 1.

Grabow and Gilmer [8]. When the substrate temperature is low, the nucleus remained the initial structures. The difference between the initial conditions was evident. It should be noted that the presented results were obtained from the simulation of 5000 MD steps. For the longer simulation, the boundary between 3D island and monolayer would be shifted. An interesting demonstration was obtained for the system with $D_{ff}/D_{fs} = 8.0$ and initial monolayer structures. Figure 6 shows the structural change of the deposited atoms with $D_{ff} = 0.4\,\mathrm{eV}$, $D_{fs} = 0.05\,\mathrm{eV}$ and $T_{\mathrm{sub}} = 1000\,\mathrm{K}$. The

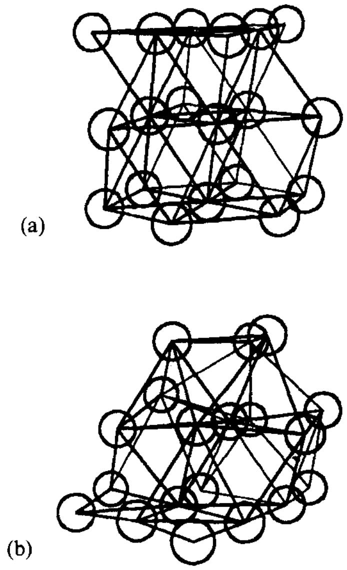

Figure 3 (a) The initial and (b) the final structures of the film cluster with $D_{ff} = D_{fs} = D_{ss} = 0.2$ eV and $T_{\mathrm{sub}} = 500\,\mathrm{K}$.

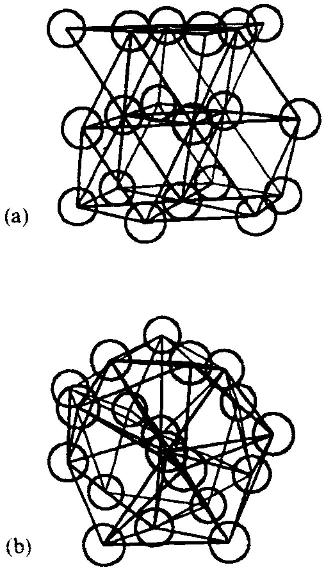

Figure 4 (a) The initial and (b) the final structures of the deposited 3D cluster with D_{ff} = 0.4 eV, D_{fs} = 0.05 eV and T_{sub} = 1000 K.

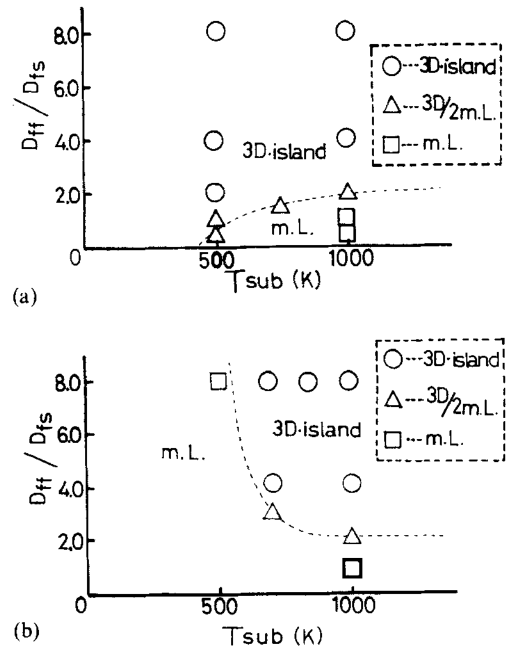

Figure 5 The obtained classification of the equilibrium shapes of the deposited nuclei as a function of D_{ff}/D_{fs} and T_{sub} for (a) the 3D island and (b) the monolayer initial structures.

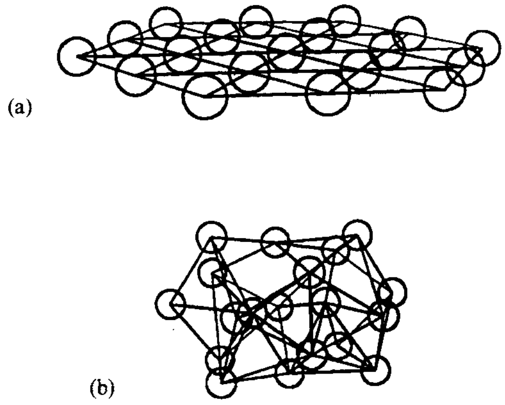

Figure 6 (a) The initial and (b) the final structures of the deposited monolayer with $D_{ff} = 0.4$ eV, $D_{fs} = 0.05$ eV and $T_{sub} = 1000$ K.

initial monolayer structure changed into the 3D island structure. However, the same system but with $T_{sub} = 500$ K did not show the structural change as presented in Figure 7. Still there is the possibility of the structural change if the long period simulation is performed. Figure 8 shows the changes of the potential energy, the substrate temperature and the sum of absolute value of forces acting on each atom during the structural change. From the abrupt change of the potential energy, the transition time was estimated. For the three different temperatures, 1000, 850 and 750 K, the logarithm of the estimated transition times were plotted against the inverse of absolute temperature. They were able to be fit by the Arrhenius's law, therefore it was predicted that the structural change would occur with $T_{sub} = 500$ K at 7500 MD steps. It was confirmed by the calculation and the result is shown in Figure 9. These structural changes can be modeled by the thermal activation process.

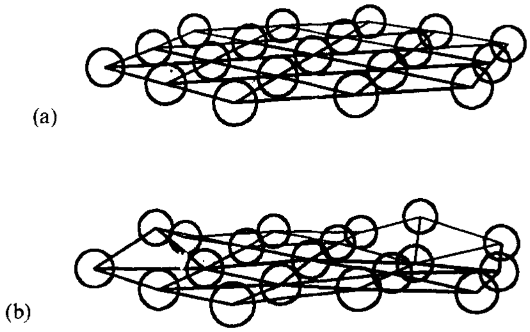

Figure 7 The same as Figure 6 but with $T_{sub} = 500$ K.

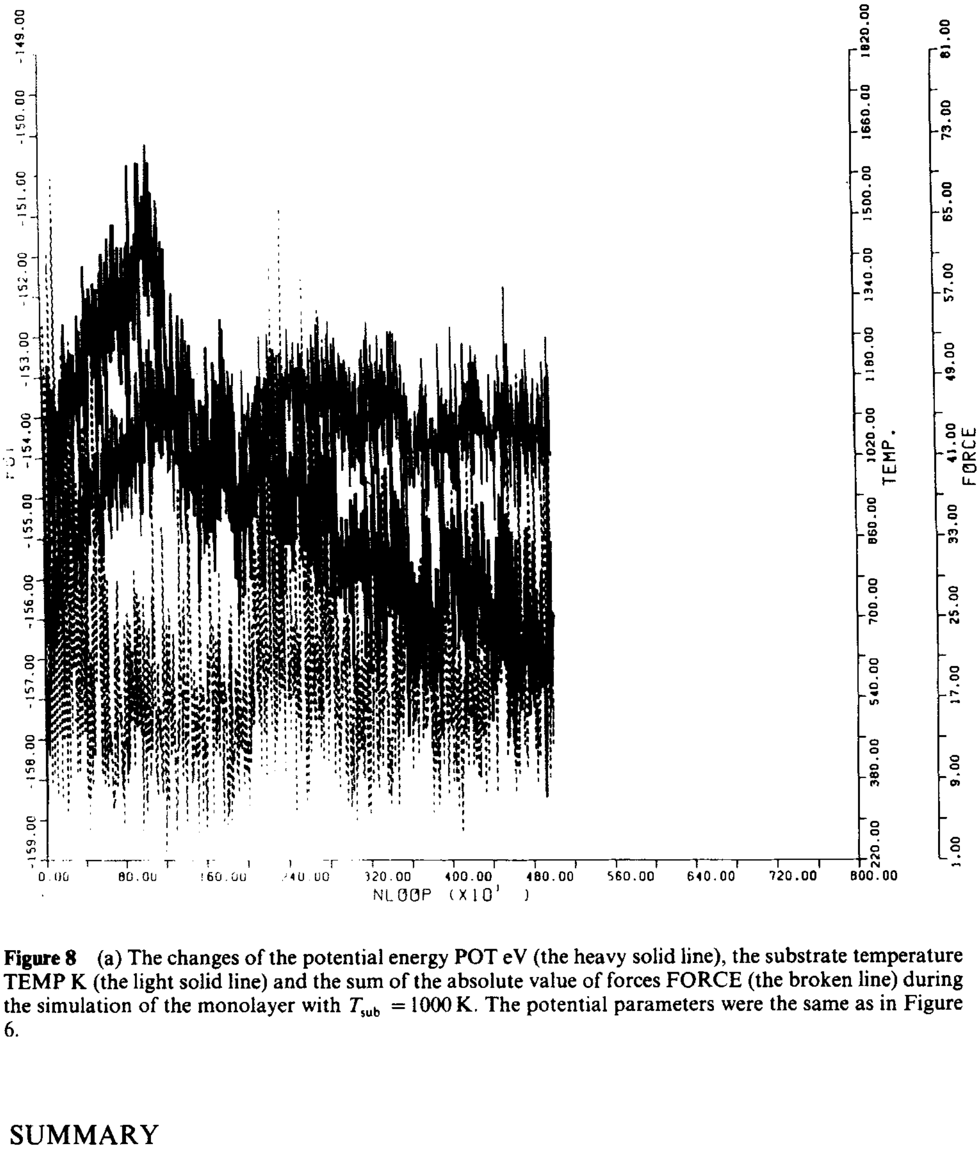

Figure 8 (a) The changes of the potential energy POT eV (the heavy solid line), the substrate temperature TEMP K (the light solid line) and the sum of the absolute value of forces FORCE (the broken line) during the simulation of the monolayer with $T_{sub} = 1000$ K. The potential parameters were the same as in Figure 6.

SUMMARY

The deposited fcc clusters on the fcc substrate were relaxed by the molecular dynamics method. The initial structures of the deposited atoms were the three layers and the monolayer of fcc(111) which contained 19 atoms. The relaxed structures were classified into the three types of shapes; 3D island, monolayer and the intermediate 3D/2D monolayer structures. The 3D island and the monolayer nuclei lead to the VW and FM types of growth modes respectively. However, SK mode could not be detected in the present simulation. If the appropriate substrate temperature (about 750–1000 K) is given, the equilibrium shapes can be determined by the potential depth ratio, D_{ff}/D_{fs}; $D_{ff}/D_{fs} > 2$ leads to the 3D island, $D_{ff}/D_{fs} < 1$ a monolayer, and

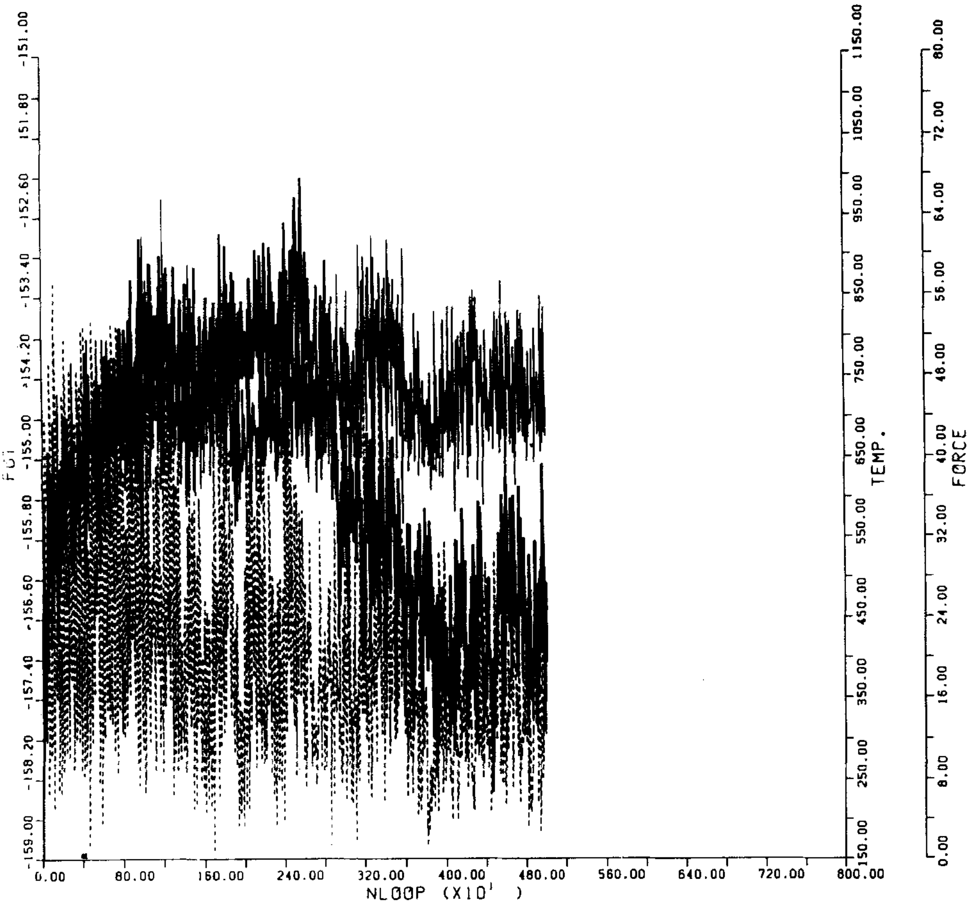

Figure 8 (b) The same as (a) but with T_{sub} = 750 K.

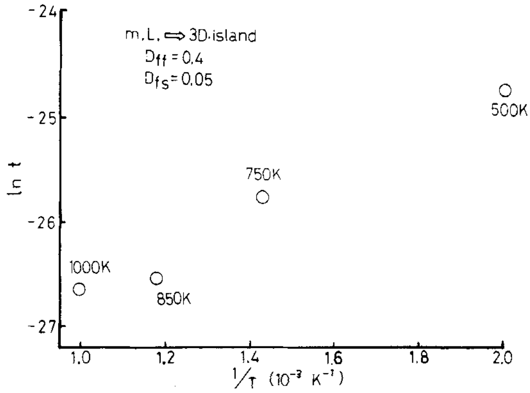

Figure 9 The Arrhenius plot of the estimated transition time and the absolute temperature for the structural change of the deposited monolayer.

$1 < D_{ff}/D_{fs} < 2$ the intermediate structure. With the low substrate temperature ($< 500\,\mathrm{K}$), the relaxed shape of the deposited atoms did not change from the initial structure. The structural change of the deposited cluster could be modeled by the thermal activation process, so the activation energy and the transition time could be estimated. The present simulations allow us to understand the difference of the growth modes in thin film formation.

Acknowledgment

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References

[1] E. Bauer and H. Poppa, "Recent advances in epitaxy", *Thin Solid Films*, **12**, 167 (1972).

[2] J.A. Venables, "Capabilities and limits of nucleation theories", *Thin Solid Films*, **32**, 135 (1976); "Nucleation calculations in a pair-binding model", *Phys. Rev.* **B36**, 4153 (1987).

[3] J.E. Black and P. Bopp, "Orientation of small rafts of xenon atoms physisorbed on Pt(111): A molecular-dynamics study", *Phys. Rev.* **B34**, 7410 (1986).

[4] M. Schneider, A. Rahman and I.K. Schuller, "Role of relaxation in epitaxial growth: A molecular-dynamics study", *Phys. Rev. Lett.* **55**, 604 (1985).

[5] M. Schneider, I.K. Schuller and A. Rahman, "Epitaxial growth of silicon: A molecular-dynamics simulation", *Phys. Rev.* **B36**, 1340 (1987).

[6] Y. Sasajima, S. Nakagawa, E. Miyamoto and M. Imabayashi, "Computer simulation of relaxation process of deposited films", *J. Crystal Growth*, **99** 496 (1990).

[7] S. Ozawa and Y. Sasajima, "Computer experiments of initial growth kinetics of vacuum-deposited thin films", *Vacuum*, **41**, 1109 (1990).

[8] M.H. Grabow and G.H. Gilmer, "Molecular dynamics studies of semiconductor thin films and interfaces", *Mater. Res. Soc. Sym. Proc.*, **94**, 15 (1987).