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THE COMPUTER SIMULATIONS OF THE INITIAL STAGE OF THE THIN FILM GROWTH ON THE NANO-FACETED SUBSTRATE

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The thin film growth of model elements on the nano-faceted substrate is simulated up to 3 monolayers (ML) changing the substrate temperature and the ratio of the interatomic interactions between the film atoms and between the film and the substrate atoms in order to reveal the growth mode on the faceted substrate. We limit the simulations to the cases with no lattice mismatch between the film and the substrate at a terrace though the ridge and the valley of the surface seem to cause defects in the neighborhood. In order to perform realistic growth simulations we have developed the Molecular Dynamics (MD) Aided Stochastic Monte Carlo (MC) method. In the method MD deals non-equilibrium structural relaxation of the surface clusters and MC deals thermally activated adatom migrations. The film height near the ridge becomes higher than that near the valley when the interaction between the film atoms is less than or equal to that between the film and the substrate atoms where the layer-by-layer growth mode is expected on a flat substrate. On the other hand more atoms stay near the valley than near the ridge, which smoothens the faceted surface consequently, when the interaction between the film atoms is larger.
Key words: faceted substrate, growth mode, MD Aided Stochastic MC method

1. INTRODUCTION

The faceted substrate refers to the one of which surface consists of unidirectional periodic grooves like a ridge-and-valley grating. Shinjo et al. have fabricated a Si grating by electron beam lithography and selective etching and have grown a magnetic multilayer on it to measure giant magnetoresistance with more current component in the stacking direction of the multilayer than ever [1]. The faceted structure can be also produced by utilizing a sort of self-organization phenomena. Regular facets of thermally stable planes appear by annealing a non-equilibrium surface. The advantage of this method is that the periodicity of the structure can be smaller than the smallest size achievable by the lithography techniques so far. Annealing a (110) oriented single crystal NaCl substrate produces regular grooves running along the [001] direction with alternating (100) and (010) facets in the $[1\bar{1}0]$ direction with the periodicity down to 10nm depending on the annealing temperature and time [2]. Similar structures with even smaller periodicity, which could be considered as kinds of surface reconstruction because the periodicity becomes as small as several lattice spacings, have been reported for some NaCl type transition-metal carbides, e.g., TaC [3-4], HfC [5], NbC [6]. The faceted surface is interesting not only from the point of view of pure surface science but also in terms of applications to nano-technologies. The faceted substrate of NaCl(110) has been applied to fabricating magnetic nano-wires and clusters in plane recently [7].

Although the faceted substrates have already been applied to producing some artificial structures in meso- and nano-scales, the thin film growth process on the faceted substrate has never been studied so far. It is important to know the growth process in order to insight the resulting film structures and to develop a method to fabricate the well-defined fine structures. We perform computer simulations in order to classify the growth modes on the faceted substrate which should depend on the substrate temperature, the atomic interactions between the film atoms and between the film and the substrate atoms, and the lattice mismatch between the film and the substrate as is known for the film growth on the flat substrate. The growth on a substrate with monatomic steps seems to provide hints to understand the growth on the faceted substrate. The bottom of the groove is considered to trap adatoms and to be a probable candidate of a nucleation site of a growth island. The ridge should give an excess diffusion barrier to adatoms to jump over it, as a potential barrier at a step edge (the so-called Ehrlich-Schwoebel barrier) suppresses the downward diffusion to the lower terrace.

Monte Carlo (MC) method is one of the standard method to simulate the thin film growth. The most simple simulation model is the so-called solid-on-solid model in which atom positions are restricted to the lattice points. The model deals with the surface migration of adatoms easily and is successful in the system where the possible sites atoms occupy are known. It is, however, difficult to reproduce the film structures when the film contains defects such as misfit dislocations and grain boundaries and/or when the film growth accompanies phase transitions or changes of the growing surface plane.

Molecular dynamics (MD) is also a useful method to simulate the film structure during the film growth. As the time interval between the successive calculating steps (MD step) is usually set to the order of femto-seconds, simulating phenomena of microseconds is very difficult with the computational power of the state of the art. The MD cannot deals with the thin film growth when surface diffusion plays a significant role. The deposition rate in the simulation becomes unrealistically high. Recently the accelerated MD has been developed to deal with microseconds order phenomena with the surface migration [8-9], though the

number of atoms in the simulated system is still limited.

We have developed the MD Aided Stochastic MC method in order to perform realistic growth simulations where non-equilibrium structural relaxation of the surface clusters are dealt by the MD and thermally activated adatom migrations are dealt by the MC method. The simulation method is described in the next section.

We simulate the thin film growth on the nano-faceted substrate up to 3 ML and discuss the dependence of the variation of the growth modes on the substrate temperature and the ratio of the interatomic interactions between the film atoms and between the film and the substrate atoms.

2. SIMULATION METHOD

In this section we will describe the simulation procedure of the MD Aided Stochastic MC method first and other simulation conditions afterward.

The procedure of the MD Aided Stochastic MC method is as follows. (i) Create an atom above the substrate and move it down till it interacts with any atoms deposited previously. (ii) Perform MD of 1000 MD steps (1 MD step = 2.5 fs) to relax the position of the newly deposited atom and the film structure. The number of MD steps is chosen so that the simulation ends in reasonable time; each growth simulation presented here takes about a week. (iii) Make the event list finding movable atoms and their possible kinds of events and moving directions. The simulation program automatically judges what kinds of sites the atoms sit. (iv) Determine the time interval Δt to the next event according to the equation,

$$\Delta t = \left(\frac{1}{r_{tot}}\right) \ln\left(\frac{1}{1-R}\right) \qquad (1)$$

where r_{tot} is the total rate of all the possible events on the list, R is a random number between 0 and 1 [10]. (v) Select an event from the event list with the selecting probability proportional to the factor exp(-Ei/kT), where Ei is the activation energy of the event i, k is the Boltzmann constant and T is the substrate temperature. The activation energy of an event is determined beforehand by making a potential map near the site where the event can take place. The calculated activation energies are shown in Tables I and II. (vi) Relax the local position of the moved atom adiabatically for fear that the atom has come too close to others by the movement because the moving direction and distance are determined automatically by the simulation program. (vii) If the event makes the number of the nearest neighbors of the selected atom larger, relax the film structure by MD of 1000 MD steps. (viii) Repeat the procedure from (iii) to (vii) until the sum of Δt exceeds the average time interval of the arrival of the deposition atom. In order to prevent enormous consumption of the computational time the events with activation energies smaller than the smallest one on the event list will not be taken onto the list before the next MD when the system is judged to have fell into a steady state, for instance, repetitional movements along a step with no kink site. We judge that the system is in a steady state when the configuration of the film atoms and the atoms on the event list become the same as those 20 events before. (ix) Repeat the procedure from (i) if the sum of Δt exceeds the average time interval of the atom arrival or no event is on the event list.

Table I. Activation energies (eV) for diffusion events on the substrate surface that are used in the simulations for D_{fs} =0.375, 0.250, 0.125.

event	activation energy (eV) D_{fs} = 0.375, 0.250, 0.125		
diff. on terrace	0.60	0.40	0.20
diff. on terrace to make dimer	0.39	0.20	0.05
diff. over ridge	0.75	0.50	0.25
diff. to valley	0.20	0.15	0.05
diff. from next to valley to terrace	0.65	0.45	0.20
diff. along valley	0.84	0.55	0.26
diff. along film step	0.40	0.20	0.08
diff. along film step to kink	0.38	0.17	0.01

Table II. Activation energies (eV) for diffusion events on the film surface that are used in the simulations. They are only related to D_{ff} and are independent on D_{fs}. (A) and (B) indicates the diffusion parallel to the two different steps, A and B of the (111) surface [12].

event	activation energy (eV)
(100)	
diff. on terrace	0.45
diff. on terrace to make dimer	0.25
diff. along step	0.38
diff. along step to kink	0.35
descending step	0.50
descending step at kink	0.48
(110) only in <110> direction	
diff. on terrace	0.60
diff. on terrace to make dimer	0.57
diff. along step	0.50
diff. along step to kink	0.50
descending step	0.63
descending step at kink	0.63
(111)	
diff. on terrace	0.10
diff. in dimer (A)	0.13
diff. in dimer (B)	0.20
diff. along step (A)	0.38
diff. along step (B)	0.50
diff. along step to kink (A)	0.35
diff. along step to kink (B)	0.50
descending step	0.25
descending step at kink	0.24

In the present study atoms with more than 5 nearest neighbors are assumed to be immovable. The events by which the number of the nearest neighbor atoms of the selected atom decreases are forbidden, that is, the following events are forbidden for example: dissociation of a dimer, detaching from a step to the terrace, detaching from a kink to the step, ascending a step, etc. Only the film atoms are movable and the substrate is rigid in the MD. We assume the substrate has the NaCl type structure and has 16 atoms in the $[1\bar{1}0]$ or periodic direction and 12 atoms in the [001] direction parallel to the ridge. The periodic boundary condition is applied in the both directions. The atomic

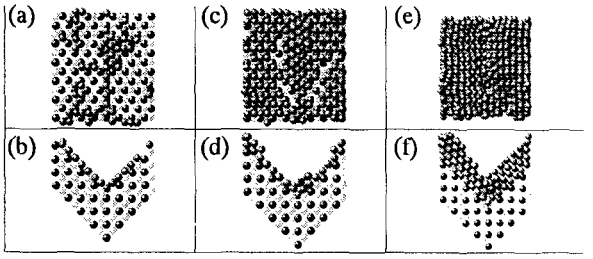

Fig. 1. Snapshots of the film structures at 0.3ML (a)(b), 1ML (c)(d), 3ML (e)(f) for D_{fs}=0.375 and the substrate temperature at 300K. (a), (c), and (e) are the plan views and (b), (d), and (f) are the side views. The substrate atoms are in black or light gray. The film atoms are in dark gray.

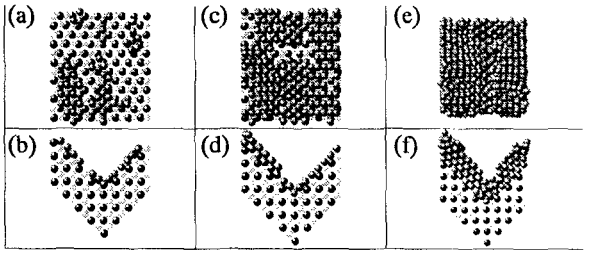

Fig. 2. Snapshots of the film structures at 0.3ML (a)(b), 1ML (c)(d), 3ML (e)(f) for D_{fs}=0.250 and the substrate temperature at 300K. (a), (c), and (e) are the plan views and (b), (d), and (f) are the side views. The substrate atoms are in black or light gray. The film atoms are in dark gray.

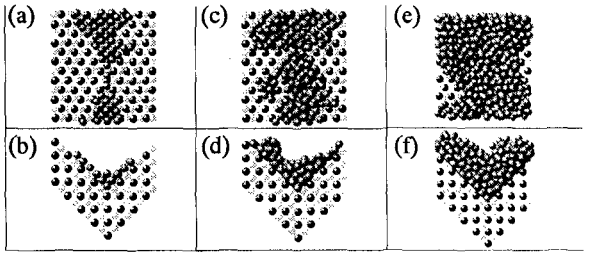

Fig. 3. Snapshots of the film structures at 0.3ML (a)(b), 1ML (c)(d), 3ML (e)(f) for D_{fs}=0.125 and the substrate temperature at 300K. (a), (c), and (e) are the plan views and (b), (d), and (f) are the side views. The substrate atoms are in black or light gray. The film atoms are in dark gray.

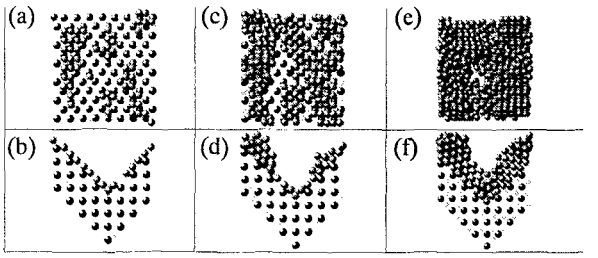

Fig. 4. Snapshots of the film structures at 0.3ML (a)(b), 1ML (c)(d), 3ML (e)(f) for D_{fs}=0.375 and the substrate temperature at 200K. (a), (c), and (e) are the plan views and (b), (d), and (f) are the side views. The substrate atoms are in black or light gray. The film atoms are in dark gray.

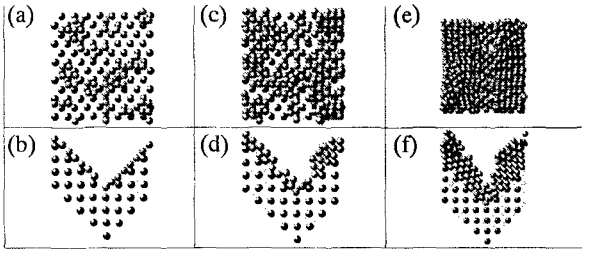

Fig. 5. Snapshots of the film structures at 0.3ML (a)(b), 1ML (c)(d), 3ML (e)(f) for D_{fs}=0.250 and the substrate temperature at 200K. (a), (c), and (e) are the plan views and (b), (d), and (f) are the side views. The substrate atoms are in black or light gray. The film atoms are in dark gray.

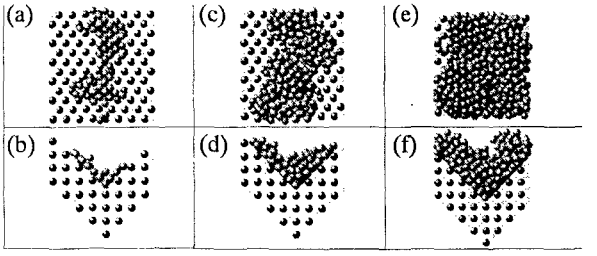

Fig. 6. Snapshots of the film structures at 0.3ML (a)(b), 1ML (c)(d), 3ML (e)(f) for D_{fs}=0.125 and the substrate temperature at 200K. (a), (c), and (e) are the plan views and (b), (d), and (f) are the side views. The substrate atoms are in black or light gray. The film atoms are in dark gray.

potentials between the film atoms and between the film and the substrate atoms are both given by Morse potentials with the elliptic screening function proposed by Baskes [11]. We change the ratio of the atomic interactions between the film atoms and between the film and the substrate atoms by changing one of the Morse parameters, D that is connected to the cohesive energy of the element. We have performed the simulations with fixed D_{ff} = 0.250 eV changing D_{fs} = 0.375, 0.250, 0.125 eV, where D_{ff} is the D parameter for the film-film interaction and D_{fs} is that for the film-substrate interaction. We fix the Morse parameter corresponding to the first nearest neighbor distance equal to that of the substrate, which means we limit the simulations to the cases that no lattice mismatch between the film and the substrate exists except at the valley and at the ridge. The MC simulations performed by S. Ozawa, et al. suggest that the film grows on a flat substrate in the Volmer-Weber (VW) mode for D_{ff}/D_{fs}=2 and in the Frank-Van der Merwe (FM) mode for $D_{ff}/D_{fs}\leq 1$ [13]. The deposition rate is assumed to be 1 ML/s. The simulations have been performed for the substrate temperatures of 200 K and 300 K.

3. RESULTS AND DISCUSSIONS

3.1 The growth at 300 K

Figures 1-3 show the plan and side views of the film structures at 0.3, 1, 3 ML grown at 300 K for D_{fs}=0.375, 0.250, 0.125. The first nucleation starts at the valley site for any cases. As for D_{fs}=0.375 and 0.250 nucleation also takes place on the terrace shown in the figures 1(a) and 2(a), while all the deposition atoms are incorporated into the island nucleated at the valley for D_{fs}=0.125. This is understood in terms of the hopping frequency of an adatom.

The numbers of hops on a free terrace during the deposition period assumed in the simulations are 0.4, 1000, $2x10^6$ for D_{fs}=0.375, 0.250, 0.125, respectively. An adatom can easily jump over the ridge for D_{fs}=0.125, but is blocked by the ridge for D_{fs}=0.375 and 0.250. The number of each event that occurred in the actual simulations up to 0.3 ML is as follows. The numbers of hops on the substrate terraces are 126, 1257, 1018 and the numbers of hops over the ridge are 0, 2, 8 for D_{fs}=0.375, 0.250, 0.125, respectively. It should be noticed that the atoms in the second row from the valley displace from the hollow sites to form the triangle lattice to relieve the stress caused by the valley. The interaction between the film and the substrate is so weak that the adatoms form the triangle lattice even far from the valley in spite of the growth on the square lattice of the substrate for D_{fs}=0.125. Since we assumed to fix the value of D_{ff} the growth kinetics on top of the islands is the same for all the cases. At 1 ML the film structures for D_{fs}=0.375 and 0.250 are almost the same. The down-step diffusion that is possible at 300 K is considered to cover the initial difference of the island shape. Some unoccupied sites remain in the first layer, while new nucleation has started in the second layer rather near the ridge. As for D_{fs}=0.125 the atoms aggregate to form a three-dimensional (3D) island which propagates from the valley toward the ridge. Amorphous growth has occurred on the strained triangle lattice of the first layer probably because the number of the MD steps is too small to relax the structure completely. The film height near the ridge is apparently higher than that near the valley at 3 ML for the cases of D_{fs}=0.375 and 0.250. On the other hand for D_{fs}=0.125 more atoms stay near the valley than near the ridge and the ridge-and-valley structure is smoothened consequently as the film grows.

3.2 The growth at 200 K

Figures 4-6 show the plan and side views of the film structures at 0.3, 1, 3 ML grown at 200 K for D_{fs}=0.375, 0.250, 0.125, respectively. The dependence of the structural character of the film on D_{fs} at 200 K is similar to that at 300 K. The feature of the growth mode is even pronounced at 200 K. The difference in the nucleation densities in Fig. 4(a) and in Fig. 5(a) is considered to reflect the difference in the diffusion lengths of free adatoms on the terrace. The preferential island growth near the ridge is more clearly seen at 200 K than at 300 K, which is considered to be due to that the migration on top of the film is limited and the down-step diffusion is very hard at 200 K. The distribution of the unoccupied sites in the first layer seems to be more affected by the initial nucleation process at 200 K than at 300 K also as a consequence of the limited interlayer atomic transport. The tendency that the film height near the ridge becomes higher than that near the valley at 3 ML for the cases of D_{fs}=0.375 and 0.250 is also pronounced at 200 K. The bare substrate surface is still seen at a few sites near the valley. There seems to be a self -shadowing effect of the film, that is, the probably for a deposition atom to reach the valley decreases when the growth at the terraces advances that near the valley forming the (111) facets parallel to the valley and the gate of the facets to the valley becomes narrower as the film grows. As for the case of D_{fs}=0.125 the film grows faster near the valley than near the ridge like as the growth at 300 K. No particular difference between the growth at 300 K and 200 K is recognized within the limit of the present simulations.

4. CONCLUSIONS

The thin film growth on the nano-faceted substrate up to 3 ML is simulated with changing the substrate temperature and the interaction between the film and substrate atoms. We have developed the MD Aided Stochastic MC method in order to perform realistic growth simulations where non-equilibrium structural relaxation of the surface clusters are dealt by MD and thermally activated adatom migrations are dealt by MC method.

The film height near the ridge is higher than that near the valley at 3 ML for the cases of D_{fs}=0.375 and 0.250. On the other hand more atoms stay near the valley than near the ridge and the ridge-and-valley structure is smoothened as a consequence for D_{fs}=0.125. The features of the growth mode are more pronounced at 200 K than at 300 K.

Revealing the complete growth modes on the faceted substrate including the cases with the lattice mismatches between the film and the substrate and for a wider range of the substrate temperature remains as a subject in the future.

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