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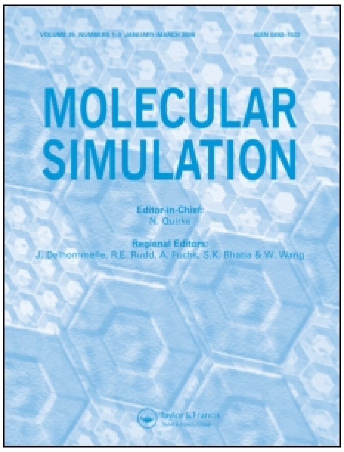

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MONTE-CARLO SIMULATIONS OF THE GROWTH OF THIN METAL FILMS AND OSCILLATION OF SURFACE STEP DENSITY

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The growth of metal films was simulated with two models of surface diffusion and the relationships between the evolution of surface step densites and growth condition were investigated. In one case, we modeled thermally activated surface migration by the Arrhenius relation. When nickel grew above 430 K at substrate temperature, clear periodic oscillations of the number of steps on the surface were observed. In the other case, epitaxial growth at 0K was simulated in which we modeled that deposited atoms can move by the hopping employed by the kinetic energy of the evaporated atom. The step density can oscillate with one monolayer growth period when an impinged atom could hop more than 10 times in one direction even at 0K. In the random-hopping-migration model, when the deposited atom can hop more than 28 times, the step density oscillation can be obtained.

KEY WORDS: Crystal growth, RHEED intensity oscillation, surface step density

INTRODUCTION

The observation of temporal oscillations of RHEED (reflection high energy electron diffraction) beam intensity with a period equal to the one monolayer growth time has provided the most direct evidence for the layer-by-layer growth mode. The RHEED beam intensity oscillations were observed at a number of epitaxial metal films and the interpretation caused by a periodically varying surface step denisty in unit area has been accepted.

To date, a variety of computer simulations have been made to understand and control the crystal growth of films, in particular for semiconductor films. We modeled surface migration by the Arrhenius relation and we have shown that the substrate temperature above 430 K is needed for observation of the oscillation of surface step density. This substrate temperature can afford such a sufficient surface diffusion that an adatom is able to jump to one of the nearest-neighbor sites 400 times during the growth of one monolayer. However, in the RHEED experiments of epitaxial metal growth, RHEED intensity oscillations occur at very low temperature in the cases of Ni growing on W [1], Au and Ag on Si [2], Cu and Fe on Ag [3], whereas the surface diffusion length in these cases is almost zero. The temperatures at which RHEED intensity oscillations were observed experimentally are listed in Table 1. The cause of the difference between the experimental and simulated temperature at which RHEED intensity oscillation can be observed has not been well understood. In the present

Table 1 Some examples of metal systems where RHEED intensity oscillations were experimentally observed at low substrate temperature.

	Substrate	*Rate (ML/s)*	T_{sub} *(K)*	*Ref.*
Ni	W(110)	0.05	100	[1]
Au	Si(111)	0.25	95	[2]
Ag	Si(111)	0.25	95	[2]
Pb	Si(111)	0.38	95	[4]
Cu	Ag(100)	0.007	77	[3]
Fe	Ag(100)	0.005	77	[3]

paper, we have investigated the possibility that deposited atoms can move across a surface not only by thermally activated surface diffusion process but also by hopping due to the kinetic energy of the deposited atom and RHEED intensity oscillation at low temperatures.

THE ESTIMATION OF MINIMUM TEMPERATURE FOR RHEED INTENSITY OSCILLATION

In the beginning we evaluated the activation energy for thermal-activated surface diffusion of some metals and estimated the minimum temperature for the observation of the RHEED intensity oscillation by the use of simple model [5] which depends upon a preliminary assumption. The assumption is that the rate at which a adsorbed atoms move away must exceed the rate of arrival of incident atoms for the periodic oscillations of surface step density.

The activation energy for surface diffusion was evaluated by an extremely simple model of surface diffusion of an atom moving from on a normal lattice site to the nearest-neighbor site on an ideal surface. In a normal lattice site the adsorbed atom is normally bonded to its nearest surface neighbors but during a surface diffusion step it will be temporarily bonded to only two. The activation energy E_{sd} is the subtraction between the interaction energy of an atom bonded to its neighbors of the surface E_s and twice of the single bond energy E_l:

$$E_{sd} = E_s - 2E_l \qquad (1)$$

or

$$E_{sd} = E_l\,(C_s - 2)\,, \qquad (2)$$

where C_s is the number of nearest surface neighbors. For example, in the case of diffusion on a Fcc(111) surface the number of surface nearest-neighbors C_s is 3 and the interation energy $E_s = 3E_l$. The activation energy E_{sd} is $E_s - 2E_l = E_l$. The value of the notional single-bond energy E_l is simply calculated by the use of heat of atomization and the number of bond per atom.

If the growth rate is G, which is in monolayer/sec, the number of hopping H from one site to another during the mean-interval that another atom absorbs on the preceding atom is

$$H = G^{-1}\,\nu_0 \exp(-E_{sd}/kT)\,, \qquad (3)$$

where $\nu_0 = 2kT/3h$, T denotes the growth temperature, k is Boltzmann's constant and h is Planck's constant. When $H > 1$, there is the possibility of the growth of layer-by-layer mode. Hence, the minimum temperature for RHEED intensity oscillation $T_{\min}$ is given by

$$\frac{2k}{3Gh} T_{\min} \exp\left(-\frac{E_{sd}}{kT_{\min}}\right) = 1 . \tag{4}$$

The minimum temperature has been calculated for each of a number of metals. The results for the growth rate $G = 0.1$ are listed in Table 2. Except for a few metals the minimum temperature $T_{\min}$ is below room temperature. The calculated value of $T_{\min}$ for Ag was 94 K and is very close to the observed temperature of the growth of Ag on Si(111) substrate. But, for the other metals the estimated minimum temperature is higher than the temperature at which RHEED intensity oscillations could observed experimentally.

GROWTH BY THERMAL ACTIVATED SURFACE DIFFUSION

In the previous section the minimum temperature for RHEED intensity oscillation was estimated roughly. In this section the minimum temperature for Ni was evaluated by a Monte-Carlo simulation of the growth under more realistic assumptions.

The basic assumptions used in our model are as follows. Only single atoms are mobile and impinge at the sites selected at random on the substrate surface. Mobile atoms migrate on the surface through jumping to one of the nearest-neighboring sites: Only the nearest-neighbor interactions are taken into account in computing the potential energy. The surface of the substrate is free from the sites of preferred nucleation, e.g., defects or impurities. The periodic boundary conditions are employed. An atom that has jumped up from the up-side border of the lattice appears again at the bottom of the lattice. No decomposition of clusters occur. Reevaporations of atoms from the surface are not considered in the simulations. We assumed the temperature of the surface to be low enough for neglecting reevaporation.

Table 2 Estimated activation energies Esd and the minimum temperatures for RHEED intensity oscillation for fcc and bcc metals.

	Est (eV)	*Tmin (K)*
Al	0.283	108
V	0.664	247
Cr	0.513	192
Fe	0.535	201
Ni	0.370	140
Cu	0.291	111
Nb	0.946	349
Mo	0.853	315
Pd	0.324	123
Ag	0.246	94
Ta	1.01	372
W	1.11	408
Ir	0.578	216
Pt	0.487	183
Au	0.318	121
Pb	0.169	66

An fcc lattice in which the [111] direction is perpendicular to the film surface was used in this study. The sample lattice with 400 (20 × 20) sites was employed. We modeled surface migration by the Arrhenius relation.

According to Gjostein [6], surface diffusion coefficient D_{sd} for fcc metals is given by the following expression in the substrate temperature range, T, $T/T_m < 0.75$ where T_m is the melting point,

$$D_{sd} = D_0 \exp(-E_{sd}/kT), \tag{5}$$

where

$$D_0 = 0.014\,\mathrm{cm}^2/\mathrm{s} \tag{6}$$

and

$$E_{sd} = 13T_m\ \mathrm{cal/mol}. \tag{7}$$

So, E_{sd} for Ni was set as 0.975 eV. A free atom can jump in one of six possible directions on a trigonal lattice. In the present calculations, the actual direction of each jump was selected by means of a random number generator.

Five simulation runs were carried out for each substrate temperature. We monitored the growth by summing the number of uncombined bonds parallel to the surface. This averaged values of the number of steps on the surface were calculated for five runs.

Time dependence of the number of atomic steps on the surface of 20 × 20 sites is shown in Figure 1 in the range of substrate temperature from 160 K to 470 K. We used 'layers' here as a unit of time in the horizontal axis in Figure 1. One layer denotes the time required for the impingement of sufficient atoms for one monolayer growth. Since the deposition rate in the present simulation was set at 0.5 monolayer/s, one layer corresponds to 2 seconds. Below 400 K, periodic oscillations of the number of

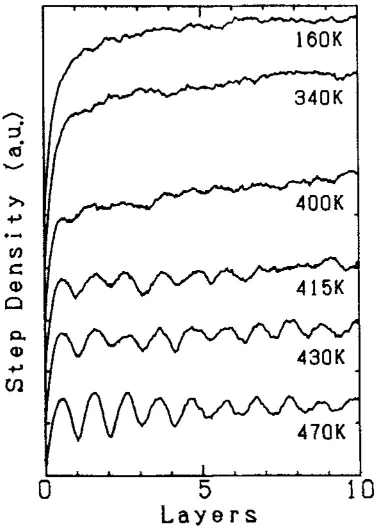

Figure 1 The time dependence of the number of steps on growing surface in thermal activated surface diffusion model.

steps were not observed, and the number of steps increases rapidly until 0.5 monolayer growth and then increases slowly. At 400 K, the number of steps increases until 0.5 layer but then decreases a little until one monolayer growth. Above 430 K, the oscillation continued over 10 times. The maximum number of steps of each oscillation shows no change at 470 K, but the minimum number of steps increased gradually.

The growth mode was clearly three dimensional at 160 K. Even at 470 K, the growth was not completely layer-by-layer mode, whereas the number of steps showed the oscillatory behavior. A large difference in the configurations of deposited atoms between the growth at 160 K and that at 470 K was the number of clusters. The effect of enhanced surface diffusion is apparent by the smaller number of growing cluster at higher temperatures.

The measured RHEED intensity oscillations always show a damping of their amplitude of oscillations. Van Hove and Cohen [7] have found that the damping envelope of measured intensity oscillations is qualitatively different between low-index and vicinal surfaces. They found that on a low-index surface, there was an initial transient, after which the intensity oscillation maxima damped slowly to a nearly constant, non-zero value. In contrast, on vicinal surfaces the intensity oscillations damped rapidly, and the maximum and minima decayed to an intermediate steady state value. The oscillatory behaviors of calculated surface step density at 470 K resemble a typical damped oscillation on a low-index surface. The minima number of steps of each oscillation increases gradually. It corresponds to the damping of the maxima of RHEED intensity oscillation because the increase of the surface step density decreases the RHEED intensity. The maxima of step density (the minima of RHEED intensity) show smaller change than that of the minima of step density (the maxima of RHEED intensity).

In computer simulations we needed a substrate temperture above 430 K for observation of the oscillation of the number of steps. At this substrate temperature a sufficient surface diffusion length is given so that an adatom is able to jump to one of the nearest-neighbor site 400 times during the growth of one monolayer.

DIFFUSION BY KINETIC ENERGY OF EVAPORATED ATOM

A growing surface was simulated by 64 × 64 point square grid resembling a (001) substrate of a simple cubic lattice for a convenience of calculations. Some test runs were also made both on the 32 × 32 point and 16 × 16 point lattices.

We have set the substrate temperature to be 0K. Since at 0K re-evaporation and thermally activated surface diffusion can be neglected. The migration of an atom was assumed to take place by using its kinetic energy in the vapor phase.

The arrival behavior of an atom to the growing surface was simulated by generating atoms at random points on the grid. Here, it was assumed that only single atoms impinge upon the surface. Any atom can only migrate once just after its arrival on the surface. One migration-process consists of several hoppings to the nearest-neighbor site. The migrated atom can hop H times which is only one adjustable parameter in one migration process. Since we assumed that only single atoms are mobile on the surface, the migrations were terminated when other atoms existed at the nearest-neighbor sites of the migrating atom. Two different types of migration were considered. One type is the one-directional- hopping-migration, in which the hopping direction of an impinged atom is randomly selected from four possible directions once at its arrival. Then the atom hops to the nearest-neighboring site in this direction. The other type is the random-hopping-migration. In this model of migration, the direction of hopping is selected at random each time before hopping. So, atoms migrate by the random walk.

Very slow deposition rate was assumed. After the preceding atom impinged and already migrated the next atom was allowed to impinge. The crystal growth was simulated in the presented model by the repetition of the impingement of an atom and its successive migration.

In the one-directional-hopping-migration model the time dependences of the step density on the surface of 64 × 64 sites are shown in Figure 2 in the range of $H = 0$ to 64. When no migration of deposited atoms takes place ($H = 0$), periodic oscillation of the step density was not observed and the step density increased rapidly. For the case in which the number of hopping is 8 times the oscillation with small amplitude disappeared after the growth of five layers and then the step density slowly increased. When we set H more than 16, the oscillation with a regular amplitude continued up to 10 layers. In Figure 3, the evolution of the step density with time is shown for the range of the number of hopping from 5 to 11 in detail. At $H = 5$ no oscillation occurred. In the range of $H = 6$ to 9 small oscillations can be observed. But the period of the oscillations fluctuated with time and did not exactly correspond to the time required for one monolayer growth and the oscillations disappeared after the growth of about five layers. When H was larger than 10, the period of the oscillation became stable and was exactly equal to the one monolayer growth time.

In the case of the random-hopping-migration the time dependences of the step density on the surface of 64 × 64 sites are shown in Figure 4 in the range of $H = 4$ to 64. When H is below 12, no oscillation occurred. Stable oscillation with a period equal to the one monolayer growth time could be observed, when H was greater than 28. If the activation energy of one hopping is supposed to be about 0.4 eV, 28 times

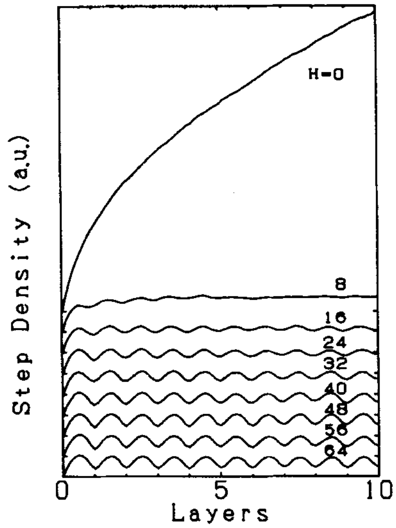

Figure 2 The time dependence of the step density in one = directional-migration-model.

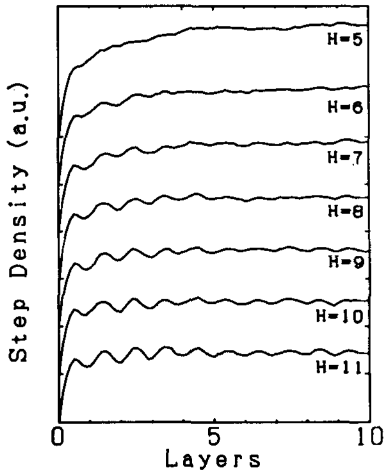

Figure 3 The step density evolution in one-directional-migration-model.

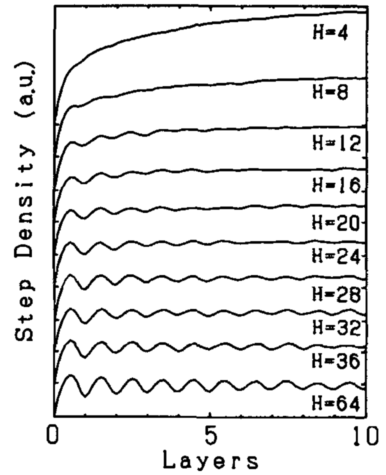

Figure 4 The time dependences of the step density in the random-hopping-migration-model.

hopping means that the impinging atom keeps about 0.01 eV of the kinetic energy. In the random walk theory effective migration length is given by $H^{-1/2} a$, where a is the distance between the nearest-neighboring sites. When H is 28, effective migration length becomes about $5a$. It is surprising that the step density of growing surface could oscillate even when the deposited atoms are able to migrate such a short effective migration distance.

Compared the one-directional-migration model with the random-hopping-migration model with the random-hopping-migration one at $H = 64$, the damping envelope of oscillations was qualtitatively different. It was found that in the one-directional-migration model the ampltude to step density oscillation is nearly constant and the minima and the maxima did not change. In contrast, in the random-hopping model the oscillations of the step density damped gradually and the maxima and minima of the step density decay to an intermediate steady state value. It may be caused by the difference of the probability of the nucleation between the two models. Namely, the diffusion area in which adatoms can move is smaller in the one-dimensional-migration model than that in the random-hopping model. The probability that an adatom comes across a step is lower in the one-dimensional-migration. Therefore the probability of the nucleation is higher and the growth in the one-dimensional-migration model is carried out by the repetition of the nucleation and the two-dimensional spread of nuclei. In this case the amplitude of step density oscillation does not damp. In the random-hopping model the probability of the nucleation is lower than that of the one-dimensional-migration model. At the first stage of the growth some nucleations occur and surface step density shows oscillatory behavior. But adatoms can move in a large area and many adatoms are taken into surface steps. So the growth gradually comes to be carried out by the movement of steps upon the surface. Therefore the oscillation of the step density damps gradually.

CONCLUSIONS

The minimum temperature was calculated for various metals. The estimated minimum temperature is higher than that by experimental RHEED intensity oscillations. Subsequently, we simulated a growth of metal films by using two models related with surface diffusion. One of them was modeled for thermally activated surface migration by Arrhenius relation. When the substrate temperature was above 430 K, clear periodic oscillations of the number of steps on the surface could be observed. In the other case, epitaxial growth at 0K was simulated and we modeled in such a way that deposited atoms can move by hopping by using the kinetic energy of the atom. The step density could oscillate with one monolayer growth period when an impinged atom could hop more than 10 times in one direction even at 0K. In the random-hopping-migration model, when the deposited atom could hop more than 28 times, the step density oscillation could be shown. In an actual deposition process the migration of the impinged atoms should be affected by both substrate temperature and the kinetic energy, especially in the low substrate temperature region. In this case the migration length would be longer than that expected from the surface diffusion constant.

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