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Two-Dimensional Motion of Unstable Steps Induced by Flow in Solution

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By carrying out Monte Carlo simulation, we study step instabilities during crystal growth from solution. In previous studies [M. Sato: J. Phys. Soc. Jpn. **79** (2010) 064606; M. Sato: J. Cryst. Growth **381** (2011) 5; M. Sato: J. Phys. Soc. Jpn. **80** (2011) 024604], we used a one-dimensional model, so that we were unable to study another type of instability, step wandering. In this research, we use a two-dimensional model to study both step wandering and step bunching. When the flow of solutes is in the step-down direction, a regular array of steps is unstable and bunches of steps are formed. Owing to the step bunching, fluctuations along the steps are enlarged and step wandering is induced. If the direction of flow is opposite, a regular array of steps is stable and step bunching does not occur. Although a single straight step is unstable in the case of long-wavelength fluctuations, step wandering does not occur on a vicinal face. Thus, with a step-up flow, the vicinal face is stable against both step bunching and step wandering.

KEYWORDS: vicinal face, step bunching, flow in solution

1. Introduction

When a vicinal face grows from a solution, instabilities of steps are caused by a flow of solutes. Assuming that the kinetic coefficient of the vicinal face is proportional to the density of steps, Chernov and coworkers¹⁻³⁾ studied the formation of step bunches. They neglected fluctuations along the steps and used a one-dimensional model. They considered a high-density vicinal face, so that the vicinal face was treated as a linear sink of solutes. When the flow in a solution and the motion of steps are in the same direction, the vicinal face is unstable in the case of fluctuations of long wavelength. The time evolution of an unstable vicinal face was studied in ref. 4. A nonlinear evolution equation was derived, and from numerical simulations, the formation of a quasi-regular array of high step density, which corresponds to the formation of step bunches, was observed.

In the above studies, the steps were assumed to be straight. Step bunching on a one-dimensional vicinal face under a two-dimensional diffusion field in a solution was investigated. However, if we consider a two-dimensional vicinal face and take account of fluctuations along

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steps, another type of instability, step wandering, is possible. Potapenko⁵⁾ studied step wandering and showed that the wandering of a growing step is induced by a flow in the step-up direction, namely, by a flow whose direction is opposite to the step motion. In the study, linear stability analyses were carried out, but detailed motions of steps were not investigated. Thus, in this research, by carrying out Monte Carlo simulations, we study the behaviors of steps on a destabilized two-dimensional vicinal face. In §2, we introduce the model. In §3, we show the results of our simulation. In §4, we summarize the results and give brief discussions.

2. Model

Our model is a two-dimensional version of the step flow model that we used in our previous papers.⁶⁻⁸⁾ As shown in Fig. 1, we consider a cubic lattice to express the diffusion field of solutes in a solution and a square lattice to express a vicinal face facing the solution. On the vicinal face, the x -direction is parallel to straight steps and the y -direction is the downhill direction. The height of atomic steps is sufficiently small that we neglect the effect of step height on the diffusion of solutes: the position of vicinal face is given by $z = 0$ (Fig. 1(b)) and use the periodic boundary condition in both directions.

Fig. 1. Schematic figures of (a) vicinal face and (b) our model. Squares and circles represent solid atoms and atoms in solution, respectively. Dark squares are solid atoms that form steps.

In our model, active atoms are solid atoms forming steps and atoms in a solution. In each Monte Carlo trial, we randomly choose one active atom. When an atom in the solution is chosen, we try to move the atom to one of the nearest-neighboring sites in a diffusion trial. A flow of solutes in the solution is expressed as the asymmetry of hopping probabilities.^{9,10)} When the flow is in the y -direction, an atom at site (x_i, y_i, z_i) moves to sites $(x_i \pm 1, y_i, z_i)$

or $(x_i, y_i, z_i \pm 1)$ with probability $1/6$, and the probability for the atom to move to sites $(x_i, y_i \pm 1, z_i)$ is given by

$$p_{\pm} = \frac{(1 \pm p_{\text{flow}})}{6}. \quad (1)$$

For the diffusion coefficient to be equal to 1, we set the increment of time after each diffusion trial to $\Delta t = 1/6N_a$, where N_a is the number of atoms in the solution.

The parameter p_{flow} represents the effect of the flow of solutes. With increasing p_{flow} , the effect of the flow becomes stronger. Owing to the viscosity of the solution, p_{flow} should become 0 near the vicinal face. Thus, for simplicity, we assume that p_{flow} is proportional to the altitude from the vicinal face: p_{flow} at $z = z_i$ is given by $p_{\text{flow}} = p_{\text{flow}}^0(z_i - 1)$. The flow is in the step-up direction with a negative p_{flow}^0 and in the step-down direction with a positive p_{flow}^0 . When the altitude is sufficiently high so that $|p_{\text{flow}}| > 1$, p_+ and p_- become negative or larger than 1 if we use eq. (1). In such a case, we set the hopping probabilities p_+ and p_- to 1(0) and 0(1), respectively.

Fig. 2. Schematic figures of solidification process in (a) vicinal face and (b) our model.

If an atom comes to $(x_i, y_i + 1, 1)$ after a diffusion trial and attaches to an atom forming a step at $(x_i, y_i, 0)$, a solidification trial is successively performed. If the solidification trial succeeds, the position of the atom forming the step advances to $(x_i, y_i + 1, 0)$ and the atom in the solution at $(x_i, y_i + 1, 1)$ vanishes (Fig. 2(b)).

If we choose an atom forming a step as an active atom, a melting trial of the atom is performed with a probability p_- . If the atom forming a step at $(x_i, y_i, 0)$ is melted, the position of the step recedes to $(x_i, y_i - 1, 0)$ and an atom is expelled to site $(x_i, y_i, 1)$ (Fig. 3).

Fig. 3. Schematic figures of melting process in (a) vicinal face and (b) in our model.

In our algorithm, one site can be occupied by only one atom. Thus, if site $(x_i, y_i, 1)$ is already occupied by another atom, the melting trial is not carried out (Fig. 4).

Fig. 4. Forbidden melting process in our algorithm. More than one atom cannot occupy one site.

The solidification probability p_+ and the melting probability p_- are given by¹¹⁾

$$p_{\pm} = \frac{1}{e^{(\Delta E \mp \phi)/k_B T} + 1}, \quad (2)$$

where ϕ is the chemical potential gain upon solidification, and ΔE is the change in the step energy defined as $\Delta E = \epsilon \times$ (the change in step perimeter). We use solid-on-solid type steps: the positions of steps are expressed as a single-valued function of x . Half of the bonding energy, ϵ , is related to the step stiffness $\tilde{\beta}$ as¹¹⁾

$$\frac{\tilde{\beta}}{k_B T} = 2 \sinh^2 \frac{\epsilon}{2k_B T}. \quad (3)$$

We assume that the kinetic coefficient of steps is sufficiently large so that the density of atoms at kinks of steps is equal to the equilibrium atom density, c_{eq} . Thus, c_{eq} satisfies $c_{\text{eq}} p_+ = (1 - c_{\text{eq}}) p_-$. Since the perimeter of a step does not change with solidification or melting at a kink, c_{eq} is given by¹¹⁾

$$c_{\text{eq}} = \frac{1}{e^{\phi/k_B T} + 1}. \quad (4)$$

In our model, we keep the concentration of atoms a constant, *i.e.*, c_{∞} , in the region in which

the altitude is larger than the critical value $z_{\max}$. If c_{∞} is higher than c_{eq}^0 , solidification frequently occurs and the steps advance. In the opposite case, melting occurs more frequently than solidification and the steps recede.

3. Results of Simulation

First, we neglect a flow in a solution and investigate how the growth rate of a vicinal face depends on the density of steps. The system size is $L_x \times L_y \times L_z = 256 \times 256 \times 15$ and $z_{\max} = 10$. The parameters ϵ and ϕ are 1.0 and 3.0, respectively, so that $\tilde{\beta}/k_B T = 0.54$ and $c_{\text{eq}} = 0.047$. The density of atoms in the region where $z_{\max} < z < L_z$ is kept $c_{\infty} = 0.1$. Since c_{∞} is larger than c_{eq} , solidification occurs more frequently than melting. The steps advance and the vicinal face grows. Figure 5 shows the dependence of the growth rate of a vicinal face,

Fig. 5. Dependence of growth rate of vicinal face on number of steps.

V , on the distance between steps, l . When the step density is low, the growth rate increases proportionally to the number of steps. With increasing the number of steps, the increment in the growth rate becomes gradual. The step velocity growing from a solution is expressed as¹²⁾

$$v_s = \Omega(c_{\infty} - c_0) \left[\frac{1}{K_s} + \frac{a}{\pi D} \ln \left\{ \frac{l}{a} \sinh \left(\frac{\pi l_D}{l} \right) \right\} \right]^{-1}, \quad (5)$$

where Ω is the atomic volume in solid phase, D is the diffusion coefficient, K_s is the kinetic coefficient of a step, l is the terrace width on a vicinal face, a is the height of a step, and l_D is the width of the boundary layer. From eq. (5), if l is sufficiently large so that $\pi l_D/l \ll 1$, v_s is independent of l . The growth rate of a vicinal face, $v_s a/l$, is proportional to the step density. In contrast, if l is sufficiently small so that $a l_D K_s / D l \ll 1$, the growth rate of a vicinal face is independent of l . In our simulations, since the terrace width is too small, the dependence

of the growth rate is not investigated when the step number is more than 64. However, the growth rate probably saturates with sufficiently high step density if we carry out simulation with a larger system and a larger number of steps. Thus, the dependence of the growth rate of a vicinal face on the step number qualitatively agrees with the assumption made in a previous study.¹⁾

To see the effect of a flow on the two-dimensional behaviors of steps, we add a flow in a solution and carry out simulations. Figure 6 show typical snapshots of a vicinal face under a flow in a solution. The number of steps is 16, and other parameters are the same as those in Fig. 5. To show the positions of steps clearly, we alternately change the color of terraces. Initially, we set the positions of steps equidistant. When the flow in the solution is absent (Fig. 6(a)) or present (Fig. 6(b)) in the step-up direction, thermal fluctuations of step positions occur, but the vicinal face is stable and the distance between steps is kept regular. In contrast, with a step-down flow (Fig. 6(c)), the vicinal face is unstable and step bunching occurs. The relation between the stability of a vicinal face and the direction of a flow agrees with the stability analyses.¹⁻³⁾

Fig. 6. Snapshots of vicinal face with (a) $p_{\text{flow}}^0 = 0.0$, (b) $p_{\text{flow}}^0 = -0.1$, and (c) $p_{\text{flow}}^0 = 0.1$. The time is about $t = 1.8 \times 10^3$.

Figure 7 shows the time evolution of the vicinal face with a step-down flow. The parameters and initial conditions are the same as those in Fig. 6(c). In the initial stage, the steps fluctuate, but are straight and equidistant on average (Fig. 7(a)). Then, the amplitude of the fluctuations increases (Fig. 7(b)) and the pairing of steps occurs in many places (Fig. 7(c)). Some parts of a step form a pair with the lower side step and other parts of the step form a pair with the upper side step, which increases the amplitude of fluctuations (Fig. 7(d)). In a later stage, short bunches are formed (Fig. 7(f)). With increasing time, the bunches become longer and

larger (Fig. 7(g)). In the late stage (Figs. 7(h) and (i)), similarly to our previous studies,^{6–8)} members in bunches change with time through the frequent separation and collision of steps, but the size of bunches seems not to change.

Fig. 7. Time evolution of vicinal face. Figures shows the vicinal face at (a) $t = 1.9 \times 10$, (b) $t = 1.0 \times 10^3$, (c) $t = 2.8 \times 10^3$, (d) $t = 4.6 \times 10^3$, (e) $t = 6.4 \times 10^3$, (f) $t = 9.1 \times 10^3$, (g) $t = 1.2 \times 10^4$, (h) $t = 1.4 \times 10^4$, and (i) $t = 1.8 \times 10^4$.

Figure 8 shows a typical vicinal face in the late stage. We observe the vicinal face from the z -direction to show the distance of steps exactly. The length of a line segment, a , at the upper side position in Fig. 8 is 20, which is two times of the $z_{\max}$. Only a few steps are present in the length. The step distance in a bunch is sufficiently large for us to neglect the effect of

the step height on the diffusion field in a solution. Thus, our assumption to neglect the step height is valid.

Fig. 8. Typical snapshot in a late stage, which is seen from the z -direction. The length of a segment at the upper right is 20.

To see how the amplitude of fluctuation changes, we investigate the time evolution of the width of fluctuation of steps, w_s , and that of the terrace width, w_t , which are defined as

$$w_s = \sum_{j=1}^N \sum_{i=1}^{n_s} \sqrt{\frac{1}{L_x} \sum_{m=1}^{L_x} \left[y_j^{(i)}(x_m) - \bar{y}_j^{(i)} \right]^2}, \quad (6)$$

$$w_t = \sum_{j=1}^N \sum_{i=1}^{n_s} \sqrt{\frac{1}{L_x} \sum_{m=1}^{L_x} \left[l_j^{(i)}(x_m) - \bar{l} \right]^2}. \quad (7)$$

N is the number of samples, n_s is the number of steps in one sample, $y_j^{(i)}(x_m)$ is the position of the i th step in the j th sample at $x = x_m$, and $\bar{y}_j^{(i)}$ is the step position averaged with regard to x_m . Since the lattice constant is equal to 1 in our simulation, the x -coordinate x_m is expressed as $x_m = m$, ($m = 1, 2, \dots, L_x$). The width of the i th terrace in the j th sample is $l_j^{(i)}$, and the average terrace width is $\bar{l}$. Figure 9 shows the time evolutions of w_s and w_t , which are averaged using 20 samples in Fig. 9(a) and using 30 samples in Fig. 9(b). With a step-up flow, both w_s and w_t increase in the initial stage by thermal fluctuations, but seem to saturate immediately with small amplitudes. With a step-down flow, both widths are much larger than those with a step-up flow, which is consistent with the snapshots in Fig. 6. In the initial stage, w_t is larger than w_s , but eventually, both widths become the same, which means that the steps are kept straight and the distances between steps fluctuates in the initial stage; the fluctuation of the step distances is mainly caused by step wandering in the late stage. In

Fig. 9. Time dependences of widths w_s and w_t in (a) initial stage and (b) long-time range. Marks represent ($\triangle$) w_t with a step-down flow, ($\blacktriangle$) w_t with a step-up flow, ($\circ$) w_s with a step-down flow, and ($\bullet$) w_s with a step-up flow.

the initial stage (Fig. 9(a)), the widths increase as $w_s \sim t^\alpha$ and $w_t \sim t^\beta$. The exponents seem to be $\alpha = \beta = 1/3$. β is the same as that obtained in a one-dimensional model.^{6–8)}

Fig. 10. Time dependences of widths of isolated step with step-up flow ($\square$), and step-down flow ($\circ$), and without flow ($\bullet$) in (a) initial stage and (b) long time-range. The parameters are the same as those in Fig. 9

In the above results, a step-down flow causes both step wandering and step bunching. The direction of the flow that causes step wandering is opposite to that in the stability analysis.⁵⁾ The difference is probably caused by the effect of step bunching. If a step is isolated in the system, the formation of step bunches is impossible. Step wandering expected from the linear

stability analysis probably occurs. To address the conditions that cause step wandering, we carry out simulation with an isolated step. Figure 10 shows the time evolution of w_s with an isolated step. The data are averaged using 40 samples in Fig. 10(a) and using 60 samples in Fig. 10 (b). As expected from the linear stability analysis, the direction that causes the step wandering is opposite to that in Fig. 6. The step wandering does not occur and w_s is small with a step-down flow; owing to the step wandering, w_s becomes larger with a step-up flow. With the parameters we used in in Fig. 10, the supersaturation of solutes is sufficiently high so that the step advances fast. When a flow is absent, solutes move to the step-up direction with regard to the advancing steps. Thus, w_s without a flow is as large as that with a step-up flow. In the initial stage with a step-up flow (Fig. 10(a)), w_s increases with time as t^β with $\beta = 1/2$. Then, the exponent β becomes $1/3$, and w_s saturates in the late stage.

Fig. 11. Time evolution of absolute position of a single step. The initial step position is $y = 0$.

Figure 11 shows the time evolution of the absolute position of the step. To see the pattern of a fluctuated step clearly, we use $c_\infty = 0.2$, which is larger than that we used in other simulations. The wandering step shows a chaotic pattern: the positions of projecting parts change with time. The value of the exponent, $\beta = 1/3$, and the chaotic pattern are similar to the wandering pattern in the surface diffusion field.

4. Discussion and Conclusion

In this study, we carried out Monte Carlo simulations and studied step instabilities induced by a flow in a solution. On a vicinal face, step bunching occurs with a step-down flow. Small bunches are formed in an early stage. Then, by repeating the collision and separation of steps, the size of bunches increases. The direction of a flow that causes step bunching agrees with that found in the previous studies.

According to the boundary layer theory, the flow rate is proportional to the altitude near

the vicinal face. With increasing altitude, the flow rate gradually increases and saturates. Since the exact form of the flow rate is complicated, we assumed that p_{flow} is proportional to the altitude of atoms near the vicinal face and equal to 1 sufficiently far from the vicinal face. Our model is very simple but roughly satisfies the fundamental feature of the flow rate given by the boundary layer theory.

In our simulation, the system size in the z -direction is small because of our poor computing environment. Since the density of solute at $z > z_{\text{max}}$ is kept constant, the gradient of the density of solute is higher and the step motion is faster than those in a deep system. In addition, the long-range interaction between steps though the surface diffusion is interrupted. Thus, if we carried out simulation with a deeper system, the time scale and length scale may change, but the qualitative behaviors of the steps we studied in this paper, *e.g.* the exponents α and β and the direction that causes step wandering and bunching, may not probably change.

In our model, the steps on a vicinal face fluctuate widely when the flow is in the step-down direction. The wide fluctuation is caused by the step bunching. During step bunching, the separation and collision of steps repeatedly occur. Some steps are often included in two bunches. Namely, the steps across a large terrace; some parts of them are in the upper-side bunch and other parts are in the lower-side bunch. Step wandering is induced by the interaction of steps through the diffusion field. Thus, the cause of the wide fluctuation is different from that of the step wandering expected from the linear stability analysis.⁵⁾

If one step is isolated, the step wandering expected from the linear stability analysis occurs with a step-up flow. In an early stage, the width of fluctuation increases with time as t^β . The exponent β changes from $1/2$ to $1/3$. The motion of the step is chaotic: the annihilation and creation of projected parts repeatedly occur. The behavior is similar to the wandering pattern in the surface diffusion field,^{11,13–15)} which is expressed as a solution of the Kuramoto-Sivashinsky (KS) equation.^{16,17)} Since the universality class of the KS equation is the same as that of the Kardar-Parisi-Zang (KPZ) equation,^{18,19)} the exponent $\beta = 1/3$ and the chaotic motion show that the wandering pattern of the isolated step is also expressed as the KS equation. In our simulation, the step wandering expected from the linear stability analysis⁵⁾ is suppressed and does not occur on a vicinal face. Experimentally, forming an isolated step may be difficult. Thus, the step wandering caused by step bunching is probably observed in experiment.

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