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Effect of Flow in Solution on Motion of Steps during Solution Growth

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We study step bunching on a vicinal face in solution growth. Assuming that steps are straight, we consider a two-dimensional diffusion field to represent a solution and a one-dimensional vicinal face. The steps are expressed as dots in the vicinal face. Taking account of a flow in a solution, we numerically solve the diffusion equation and the Navier-Stokes equation in the solution, and determine step velocities. If a flow in a solution is absent or is in the step-up direction, a vicinal face is stable. When the flow is in the step-down direction, the vicinal face is unstable and step bunching occurs. In the initial stage, small bunches are formed. Then, owing to the coalescence of small bunches, large bunches are formed.

KEYWORDS: vicinal face, step bunching, flow in solution

1. Introduction

On a vicinal face, which consists of an equidistant array of straight steps, two types of step instabilities occur. One is step wandering, which is the instability along the steps: straight steps are unstable and fluctuate with large amplitudes. The other is step bunching, which is the instability in the step distance. An equidistant array of steps is destabilized and bunches of steps are formed.

During solution growth, step bunching is caused by a flow in a solution.¹⁻⁴⁾ Chernov and coworkers theoretically studied the stability of a vicinal face.⁵⁻⁷⁾ When a flow in a solution is in the step-down direction, the vicinal face growing from a solution is unstable. Bredikhin and co-workers studied the time evolution of the vicinal face, and numerically showed the formation of an equidistant train of bunches.^{3,4)} In previous studies,^{3,5-7)} the step distance was assumed to be so high that the vicinal face was treated as the linear sink of atoms. The motion of each steps during step bunching was not investigated.

Recently, we have studied the motion of discrete steps by carrying out Monte Carlo simulations.⁸⁻¹⁰⁾ We used a lattice in a solution and expressed the diffusion of solutes as the hopping of atoms to the nearest-neighboring sites. The flow in a solution is taken into account

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in an anisotropy of hopping probabilities.^{11,12)} During growth, step bunching occurs with a step-down flow, which agrees with previous studies.⁵⁻⁷⁾ When the bunches are large, the separation and collision between steps and bunches repeatedly occur. In previous studies,⁵⁻⁷⁾ the effect of the flow on the diffusion of solutes is simplified, but the flow should be treated more precisely.

In this study, to take account of a flow in a solution in detail, we numerically solve the Navier-Stokes equation and diffusion equation, and study the motion of steps. We introduce our model in §2 and show our results in §3. We summarize and give a brief discussion in §4.

2. Model

When a solution is incompressible, the velocity of the solution, $\mathbf{v}$, is determined by the Navier-Stokes equation,

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{v}, \quad (1)$$

where ρ is the density of the solution, ν is the kinematic viscosity, and p is the pressure. We keep dp/dx constant in our simulation. The equation of continuity is given by

$$\nabla \cdot \mathbf{v} = 0. \quad (2)$$

The velocity of a flow vanishes in terraces, so that $\mathbf{v} \cdot \mathbf{n} = 0$, and $\mathbf{v} \cdot \mathbf{l} = 0$, where $\mathbf{n}$ and $\mathbf{l}$ are the unit vectors normal to the vicinal face and parallel to the vicinal face, respectively. The diffusion equation of the solute is given by

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} + (\mathbf{v} \cdot \nabla) c = D \nabla^2 c(\mathbf{r}, t), \quad (3)$$

where $\mathbf{v}$ is the velocity of the solution, $c(\mathbf{r}, t)$ is the concentration of the solute and D is the diffusion coefficient. We consider the vicinal face with a low step density, and the height of each atomic step is sufficiently small. For simplicity, we assume that the steps are straight. The vicinal face is expressed as a line and the steps are expressed as points on the line. The x -axis is parallel to the vicinal face and the y -axis is normal to the vicinal face. The vicinal face is given by $y = 0$. The region where $y \leq 0$ is solid and the region where $0 < y$ is liquid.

The current of the solute transported to the step positions, $\mathbf{j}$, is proportional to the gradient of the density of solute:

$$\mathbf{j} = D \nabla c|_{x_s}, \quad (4)$$

where x_s is the step position. The current of the solute solidified at the steps is proportional to the difference between the solute density and the equilibrium one. Thus, at each step position,

the solute density satisfies

$$D \nabla c|_{x_s} \cdot \mathbf{n} = K(c|_{x_s} - c_{\text{eq}}), \quad (5)$$

where c_{eq} is the equilibrium solute density at a step position and K is the kinetic coefficient. Far from the vicinal face, we assume that the solute density is kept constant as

$$c|_{y=y_{\text{max}}} = c_{\text{max}}. \quad (6)$$

By solving the diffusion equation, eq. (3), and the Navier-Stokes equation, eq. (1), with the boundary conditions eqs. (5) and (6), we obtain the distribution of solutes in a solution. The step velocity is given by

$$V_s = \Omega K(c|_{x_s} - c_{\text{eq}}), \quad (7)$$

where Ω is the atomic area in solid.

In numerical simulation, we use dimensionless variables. When we use a typical length L and a typical velocity v_0 , the Navier-Stokes equation is expressed as

$$\frac{\partial \tilde{\mathbf{v}}}{\partial \tilde{t}} + (\tilde{\mathbf{v}} \cdot \tilde{\nabla}) \tilde{\mathbf{v}} = -\tilde{\nabla} \tilde{p} + \frac{1}{Re} \tilde{\nabla}^2 \tilde{\mathbf{v}}, \quad (8)$$

where $\tilde{v} = v/v_0$, $\tilde{\nabla} = L\nabla$, $\tilde{p} = p/\rho v_0^2$, and the Reynolds' number $Re = Lv_0/\nu$. When the density of solution is scaled by c_{eq} , the diffusion equation is given by

$$\frac{\partial \tilde{c}(\tilde{\mathbf{r}}, \tilde{t})}{\partial \tilde{t}} + (\tilde{\mathbf{v}} \cdot \tilde{\nabla}) \tilde{c} = \tilde{D} \nabla^2 \tilde{c}(\tilde{\mathbf{r}}, \tilde{t}), \quad (9)$$

where $\tilde{D} = D/Lv_0$. The boundary conditions are given by

$$\tilde{c}|_{\tilde{y}=\tilde{y}_{\text{max}}} = \tilde{c}_{\text{max}}, \quad (10)$$

$$\tilde{D} \nabla \tilde{c}|_{\tilde{x}_s} \cdot \mathbf{n} = \tilde{K}(\tilde{c}|_{\tilde{x}_s} - 1), \quad (11)$$

where $\tilde{K} = K/v_0$. The scaled step velocity $\tilde{V}_s$ is V_s/v_0 , which satisfies

$$\tilde{V}_s = \Omega c_{\text{eq}} \tilde{K}(\tilde{c}|_{\tilde{x}_s} - 1). \quad (12)$$

3. Results

In our simulation, we generate a square mesh in a solution and solve the diffusion equation and Navier-Stokes equation by the upwind difference method. First, we investigate the dependence of the stability of a vicinal face in the direction of flow in a solution. We use the depth of solution, y_{max} , as a typical length to scale variables: $L = y_{\text{max}}$. In our simulation, the deformation of the vicinal face caused by the modulation of step density is neglected and a periodic boundary condition is used in the x -direction.

Figure 1 shows the time evolution of step positions. The parameters we used are $\tilde{c}_{\text{max}} = 1.0$,

Fig. 1. Time evolutions of positions of steps (a) with step-up flow, (b) without flow, and (c) with step-down flow.

$\Omega c_{\text{eq}} = 8.0 \times 10^{-7}$, and $Re = 50$, and the scaled gradient of the pressure p in the x -direction satisfies $\tilde{G} = (dp/dx)L/\rho v_0^2 = 0.1$. The scaled system size in the x -direction is 2, which is divided by 400 meshes. The number of the steps N is 16. The steps are placed on a vicinal face at regular intervals with a small random fluctuation. Initially, the density of the solute is uniform with $\tilde{c}_{\text{max}}$. The density of the solution is so high that the steps advance.

When the flow is in the step-up direction (Fig. 1(a)) or absent (Fig. 1(b)), step bunching does not occur and the vicinal face is stable. In contrast, when the flow is in the step-down direction (Fig. 1(c)), namely, the direction of the flow is opposite to the step motion, the vicinal face is unstable and some pairs of steps and small bunches appear in the initial stage. Figure 2 shows the time evolution of the destabilized vicinal face in later stages. The step distances in bunches become short. Namely, the bunches become tight (Fig. 2(a)). Some of the bunches are once broken to a few tight step pairs. Then, the pairs again gather and start to form bunches. The bunches grow by the coalescence of step pairs. In the stage, separation and collision occur repeatedly. When we use a faster flow, the frequency of separation and collision increases. These results are in agreement with those of previous studies.^{8–10)}

The formation of bunches is explained by the asymmetry of the diffusion field due to a flow in a solution.^{13,14)} For the step-down flow, the gradient of the diffusion field in front of an advancing step is steeper than that at the rear. The number of solutes reaching the step is greater than from the rear side than from the front side. If the width of the upper terrace is

Fig. 2. Time evolutions of positions of steps with step-down flow for (a) $2000 < \tilde{t} < 2500$, (b) $3000 < \tilde{t} < 3500$, and (c) $4000 < \tilde{t} < 4500$.

smaller than the average width, owing to overlap of the diffusion fields, the number of solutes solidified at the step decreases. Thus, the step velocity slows and paring of steps occurs. With the step-up flow, the asymmetry of the diffusion field is opposite. The velocity of steps whose lower terrace is narrow is slow, so that the vicinal face becomes stable.

Fig. 3. (Color online) Asymmetric distributions of solutes around a bunch (a) without flow and (b) with step-down flow.

Figure 3 shows the density of the solute around a bunch, in which the asymmetry of the diffusion field caused by the flow is showed. We place 3 steps at $x = 1.0$ and observe the distribution of the solutes around the steps. When the flow is absent (Fig. 3(a)), the equidistant train of steps is stable. Thus, we show the distribution of the solutes before the

bunch is broken. In the case without flow, the distribution of solutes around the steps is symmetric. The countour lines of solutes form a semicircle whose center is at the bunch position. When we add a flow in the step-down direction (Fig. 3(b)), the distribution of solutes becomes asymmetric. At the upper side of the steps, the density of solutes increases rapidly, but changes gradually at the lower side of steps.

Fig. 4. Time evolutions of step position with ($\circ$) $\tilde{v} = 0$, ($\triangle$) $\tilde{G} = -0.1$, and ($\square$) $\tilde{G} = 0.1$.

Fig. 5. Dependence of average step velocity on flow rate.

Figure 4 shows the time dependence of average step velocity, which is defined as

$$\tilde{V}_s(\tilde{t}) = \frac{1}{T} \int_{\tilde{t}-T/2}^{\tilde{t}+T/2} dt' \tilde{V}_s(t'). \quad (13)$$

The time interval to average the data, T , is 8. In our simulation, the initial density of solutes

is much higher than that in equilibrium, so that the steps move faster in the initial stage. Then, owing to the solidification of the solute at steps, the density decreases and the average velocity gradually becomes slower. Since the difference between the profile of $\tilde{V}_s$ with a step-up flow and without a flow is small, we cannot see such a difference in Fig. 4. In contrast, with step-down drift, the difference of the time evolution from that in the case without flow is large.

Figure 5 shows the dependence of step velocity averaged at the time interval $0 < \tilde{t} < 1500$. When the flow is in the step-up direction ($\tilde{G} < 0$), the average step velocity is slightly larger than that in the case without a flow. When the flow is in the step-down direction ($\tilde{G} > 0$), the step velocity is smaller than that without a flow. When the flow rate is low, the step velocity decreases with increasing flow rate. However, when the flow rate is larger than 0.1, the flow rate increases again.

4. Summary and Brief Discussion

In this paper, we studied the step bunching induced by a flow in a solution. In previous studies,^{8–10)} the effect of a flow in a solution is simplified. Thus, to take account of the effect of a flow more precisely, we numerically solved both the Navier-Stokes equation and the diffusion equation at the same time, and studied the motion of steps. Without a flow in a solution or with a step-up flow, the vicinal face is stable. In contrast, with a step-down direction, the vicinal face is unstable and step bunching occurs. The results agree with those of previous studies.^{5–10)}

With a step-down flow, the average step velocity is smaller than that in the case without a flow. When the flow rate is low, the velocity decreases with increasing flow rate. When the flow rate is larger than the critical value, the average velocity starts to increase. The change in the growth rate is related to the motion of steps. In our simulation, the separation of single steps from bunches hardly occurs with a slow flow. In such a case, since a bunch moves slower than a single step, the growth rate of a vicinal face is lower than that in the case without a flow. The frequency of the separation of single steps increases with increasing flow rate if the flow rate is larger than its critical value. Single steps on terraces move faster than bunches so that the average step velocity increases.

In this study, we solved the Navier-Stokes equation to determine the motion of a solution and showed that the shear flow in the step-down direction is caused by step bunching. To compare the numerical results with experimental results, we need to solve the boundary layer

equation instead of the Navier-Stokes equation to determine the flow in a solution. Since the important effect to cause the step bunching is the presence of shear flow near the vicinal face, the qualitative results, *i.e.*, the direction that induces bunching, may be unchanged even if we solve the boundary layer equation. however, now we plan to study the motion of steps under a boundary layer flow.

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