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Formation of Step Bunches Induced by Flow in Solution

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We study the formation of step bunches induced by flow in solution during growth. In our previous study [M. Inaba and M. Sato: J. Phys. Soc. Jpn. **80** (2011) 074606], we showed that the step-down flow in solution causes bunching. In this research, we study the dependence of step behavior on some parameters. With a slow flow, the separation and coalescence between steps and bunches occur frequently during step bunching. With increasing flow rate, the frequency decreases and tight bunches are formed. The decrease in the frequency also occurs with increasing strength of the repulsion between steps.

KEYWORDS: vicinal face, step bunching, flow in solution

1. Introduction

On a vicinal face, which is formed with an equidistant array of straight steps, the steps show two types of instabilities, i.e., step bunching and step wandering. Step bunching is the instability with regard to the step distance: an equidistant array is unstable and bunches of steps are formed. Step wandering is the instability in fluctuations along steps, which is the instability perpendicular to the steps.

One of the causes of the instabilities is the flow added in the diffusion field. On a Si(111) vicinal face heated by direct electric current, the flow of adatoms is induced by the current.^{1,2)} The direction of the flow in the surface diffusion field is parallel or antiparallel to the current direction. If the steps are permeable,^{3,4)} the flow in the step-up direction causes step bunching during sublimation: the direction of step motion and the direction of the flow are the same. When the step is impermeable,⁵⁻¹⁴⁾ i.e., the diffusion of adatoms between neighboring terraces is neglected, step bunching occurs

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with the step-down flow. Without the evaporation of adatoms, the form of a bunch is symmetric, and the separation of steps from bunches does not occur. With evaporation, the separation of steps frequently occurs. The step distance gradually increases at the upper side edge of a receding bunch, so that the form of a bunch becomes asymmetric.

Step bunching also occurs during solution growth if the flow is added in solution. Chernov and coworkers carried out a stability analysis.^{15–17)} Since they assumed that the steps are straight, the vicinal face was expressed as a line in a two-dimensional diffusion field. They showed that an equidistant array of steps is unstable with step-down flow. Bredikihin et al. studied the time evolution of the one-dimensional vicinal face, and numerically showed that bunches appear periodically.^{18,19)} In their studies, it was assumed that the step distance is short. The step density was so high that the vicinal face was treated as a linear sink of atoms.

Recently, one of us has carried out Monte Carlo simulations with lattice models and studied the motion of discrete steps during step bunching.^{20–23)} In the model, the flow in solution was taken into account as the anisotropy of the probability of a diffusion trial. In the studies, the separation of single steps repeatedly occurs during step bunching. We also studied step bunching by another approach. In ref. 24, we numerically solved the diffusion equation of the solute and studied the motion of steps in a one-dimensional model. In the study, we investigated the dependence of the average velocity of steps on the flow rate during step bunching. With a slow step-down flow, the average velocity of steps is smaller than that without a flow. With increasing the flow rate, the velocity takes a minimal value and then increases.

In this research, we study the dependence of the process of bunching on some parameters. Similarly to our previous study,²⁴⁾ we numerically solve the diffusion equation and study the time evolution of motion of steps. In § 2, we introduce our model. In § 3, we show results of our simulation. In § 4, we summarize our results and give brief discussion.

2. Model

The model we use is the same as that in ref. 24. We consider an incompressible solution. The velocity of the solution, $\mathbf{v}$, is given 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. Since the solution is assumed to be incompressible, the continuity equation is given by

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

Owing to the viscosity, the velocity of a flow vanishes on terraces, so that $\mathbf{v} \cdot \mathbf{n} = 0$,²⁵⁾ and $\mathbf{v} \cdot \mathbf{l} = 0$, where $\mathbf{n}$ and $\mathbf{l}$ are the unit vectors normal and parallel to the vicinal face, respectively. When we take account of a flow in the solution, the diffusion equation of solutes 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.

Since we assume that the steps are straight, the vicinal face is expressed as a line coming in contact with a two-dimensional diffusion field of the solute (Fig. 1). We consider a vicinal face with a low step density, and neglect the height of each atomic step, so that the steps are expressed as points on a straight 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.

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

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

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

where x_n is the position of the n th step. The number of solute atoms solidified at the steps is proportional to the difference in the solute density from the equilibrium value. Thus, at each step position, the solute density satisfies

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

where $c_{\text{eq}}^{(n)}$ is the equilibrium solute density at the n th step position and K is the kinetic coefficient. We assume that the solute density far from the vicinal face 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 the solution. Then, we obtain the step velocity of the n th step, V_n , as

$$V_n = \Omega K (c|_{x_n} - c_{\text{eq}}^{(n)}), \quad (7)$$

where Ω is the atomic area in the solid. When the density of the step interaction energy is given by ζ_n , the equilibrium solute density, $c_{\text{eq}}^{(n)}$, is expressed as

$$c_{\text{eq}}^{(n)} = c_{\text{eq}}^0 + \frac{\Omega c_{\text{eq}}^0}{k_B T} \frac{\partial \zeta_n}{\partial x_n}, \quad (8)$$

where c_{eq}^0 is the equilibrium solute density of an isolated step, k_B is the Boltzmann constant, and T is the temperature. If the repulsive potential between steps is a power law potential, the interaction energy of the n th step is given by

$$\zeta_n = A \sum_{m \neq n} |x_m - x_n|^{-\nu}, \quad (9)$$

where $A > 0$ for repulsive interaction. For simplicity, only the interaction between the neighboring steps is taken into account in our simulation.

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

$$\frac{\partial \tilde{\mathbf{v}}}{\partial \tilde{t}} + (\tilde{\mathbf{v}} \cdot \tilde{\nabla}) \tilde{\mathbf{v}} = -\tilde{\nabla} \tilde{p} + \frac{1}{Re} \tilde{\nabla}^2 \tilde{\mathbf{v}}, \quad (10)$$

where $\tilde{v} = v/v_0$, $\tilde{\nabla} = L \nabla$, $\tilde{p} = p/\rho v_0^2$, and Reynolds' number $Re = L v_0/\nu$. When the density of the solution is scaled by c_{eq}^0 , the diffusion equation is given by

$$\frac{\partial \tilde{c}(\tilde{\mathbf{r}}, \tilde{t})}{\partial \tilde{t}} + (\tilde{\mathbf{v}} \cdot \tilde{\nabla}) \tilde{c} = \tilde{D} \tilde{\nabla}^2 \tilde{c}(\tilde{\mathbf{r}}, \tilde{t}), \quad (11)$$

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

$$\tilde{c}|_{\tilde{y}=\tilde{y}_{\max}} = \tilde{c}_{\max}, \quad (12)$$

$$\tilde{D} \nabla \tilde{c}|_{\tilde{x}_n} \cdot \mathbf{n} = \tilde{K}(\tilde{c}|_{\tilde{x}_n} - \tilde{c}_{\text{eq}}^{(n)}), \quad (13)$$

where $\tilde{K} = K/v_0$. The scaled equilibrium solute density is expressed as

$$\tilde{c}_{\text{eq}}^{(n)} = 1 - \tilde{A} \sum_{m=n\pm 1} |\tilde{x}_m - \tilde{x}_n|^{-(\nu+1)}, \quad (14)$$

where $\tilde{A} = \nu A/l^{(\nu+1)} K_B T$. The scaled step velocity $\tilde{V}_n$ is V_n/v_0 , which satisfies

$$\tilde{V}_n = \Omega c_{\text{eq}} \tilde{K}(\tilde{c}|_{\tilde{x}_n} - \tilde{c}_{\text{eq}}^{(n)}). \quad (15)$$

In our simulation, the gradient of the pressure is kept constant and the boundary condition in the x -direction is the periodic boundary condition.

3. Results of Simulations

Fig. 2. Initial stage of time evolution of step positions with (a) $\tilde{G} = (dp/dx)L/\rho_0 v_0^2 = 0.025$, (b) $\tilde{G} = 0.0375$, and (c) $\tilde{G} = 0.0625$.

First, we investigate how the motion of steps during step bunching changes with the flow rate. In our previous study,²⁴⁾ we already showed that step bunching does not occur with a step-up flow or without a flow, so that we hereafter study step bunching with a step-down flow. The parameters are $\tilde{c}_{\max} = 1.1$, $Re = 50$, $\tilde{D} = 10^{-4}$, and $\tilde{A} = 1.25 \times 10^{-8}$. The scaled system size in the x -direction is 2 and that in the y -direction, $\tilde{y}_{\max}$, is 1. The number of steps is 50. The exponent of the power-law potential

is $\nu = 2$, which is equal to the exponent for an elastic repulsion.^{26,27)}

Initially, steps are equidistant with a small random fluctuation and the concentration of solute is uniform at $\tilde{c}_{\max}$ in the solution. Since the concentration of solute is higher than c_{eq}^0 , the steps advance. Figure 2 shows the initial stage of the time evolution of step positions during step bunching with various flow rates. Although the array of advancing steps is unstable and step bunching occurs, we cannot clearly see the modulation of the step distance in the stage. The motion of steps seems to be independent of the flow rate.

Fig. 3. Late stage of time evolution of step positions. The values of $\tilde{G}$ are the same as those in Fig. 2.

The difference in the time evolution of step bunching becomes noticeable in a later stage (Fig. 3). When the flow rate is low [Fig. 3(a)], the separation and collision of steps repeatedly occur during bunching, which is similar to the step bunching in a previous study.²⁴⁾ With increasing flow rate, the frequency of the separation decreases [Fig. 3(b)] and the bunches become tight. With a sufficiently high flow rate [Fig. 3(c)], the separation of steps is hardly seen.

The suppression of the separation of single steps is also caused by decreasing the strength of the repulsion between steps. Figure 4 shows the initial stage of the time evolution with various strengths of repulsion. Small bunches are formed with a weak repulsion [Fig. 4(a)]. With increasing strength of the repulsion, the form of the bunches

Fig. 4. Initial stage of time evolution of step positions with various strengths of repulsion. The parameters used in (a) are the same as those in Fig. 2(a). In (b) and (c), $\tilde{A} = 0.15$ and 0.25 , respectively.

becomes clearer [Fig. 4(b)]. The modulation of the step distance with a small amplitude is observed for a sufficiently strong repulsion [Fig. 4(c)].

Fig. 5. Late stage of time evolution of step positions with various strengths of repulsion. The parameters are the same as those in Fig. 4.

The difference in the process of bunching is observed more clearly in a later stage. Figure 5 shows the late stage of step bunching. When the repulsion is weak, the separation of steps does not occur and a tight bunch is formed [Fig. 5(a)]. For a strong

repulsion [Fig. 5(b)], the separation of steps starts. For a sufficiently strong repulsion [Fig. 5(c)], the frequency of the separation increases. Thus, in the process of forming step bunches, the effect of the decrease in the strength of the repulsion is similar to that of the increase in the flow rate.

Fig. 6. Profile of step bunches at (a) $\tilde{t} = 1000$, (b) $\tilde{t} = 2000$, (c) $\tilde{t} = 2500$, and (d) $\tilde{t} = 5000$.

During step bunching, the step density in bunches seems to change with the bunch size, so that we see a dependence of the inclination of bunches on the bunch size. Figure 6 shows the profiles of the vicinal face during step bunching. In our simulation, we neglect the height of the atomic step when we solve the diffusion equation in a solution. However, to see how the inclination in step bunches changes during step bunching, we consider the height of atomic steps in drawing Fig. 6. The parameters are the same as those in Fig. 2(a). In the initial stage ($\tilde{t} = 1000$), the form of the step bunches is not clear. We cannot distinguish individual bunches. With increasing time ($\tilde{t} = 2000$ and 2500), we can see the modulation of the inclination of the vicinal face with a small amplitude. Both the bunch size and the inclination in bunches are small, and the form of a bunch seems to be symmetric: the difference between the inclination in bunches at the upper side

edge and that in bunches at the lower side edge is small. In a later stage ($\tilde{t} = 5000$), the bunch size increases. The form of a bunch becomes asymmetric because the separation of single steps from the lower side edge occurs frequently.

Figures 7 and 8 show the change in the step density and the concentration of solute around bunches during the collision of two bunches, respectively. We form two bunches with different sizes [Fig. 7(a)]. In both bunches, the density of steps is highest at the center part. The step density of the large bunch is higher than that of the small bunch, and the large bunch is more asymmetric than the small bunch. The concentration of solute around the large bunch is lower than that around the small bunch [Fig. 8(a)]. We can see that the small bunch affects the concentration of solute around the large bunch. Since the small bunch advances faster than the large bunch, the collision of the two bunches occurs. During the collision, the step density in the large bunch temporally changes in shape [Fig. 7(b)]. However, the shape of the step density is recovers after the collision [Fig. 7(c)]. The concentration of solute after the coalescence of bunches [Fig. 8(c)] is more asymmetric than that before the coalescence.

Fig. 7. Change in density of steps during collision of two bunches. (a) two bunches with different sizes are present at $\tilde{t} = 4986$, (b) two bunches collide at $\tilde{t} = 5950$, and (c) a single bunch is formed by coalescence at $\tilde{t} = 9992$.

4. Summary and Brief Discussion

In this report, using the model in ref. 24, we studied how the process of step bunching changes with changes in the values of some parameters. A transition from step bunching with the separation of steps to that without the separation was observed when we changed the flow rate or the strength of repulsion. When the step repulsion is strong or the flow rate is low, the separation of steps frequently occurs. The frequency of separation decreases with increasing flow rate or decreasing strength of step repulsion,

Fig. 8. (Colored on line) Change in concentration of solute during collision of two bunches. (a) Two bunches with different sizes are present at $\tilde{t} = 4986$, (b) two bunches collide at $\tilde{t} = 5950$, and (c) a single bunch is formed by coalescence at $\tilde{t} = 9992$.

and finally the separation of steps hardly occurs and tight step bunches are formed.

In our simulation, the step density in a bunch is highest at the center part, but the form of bunch is asymmetric: the bunch is looser at the lower side edge (at the edge in the moving front) than at the upper side edge (at the edge in the rear side), which is the same as that in the step bunching induced by the flow in the surface diffusion field. The formation of asymmetric bunches is different from the result in ref. 28. In the study,²⁸⁾ the authors neglect the effect of the motion of individual steps and consider the time evolution of step density, but in our study, we took account of the motion of each step. This difference causes the difference in the form of bunches.

In previous studies,^{18,19,23)} an upper limit of the bunch size exists, and an equidistant array of bunches is formed. In our simulation, however, the limit of the bunch size was not seen and a large single bunch was finally formed. The cause of this difference is uncertain, but we surmise that there are two possible causes. One is the system size of our simulation in the x -direction. In our simulation, the number of steps was not more than 50, and the system is not large. Since our computational resources are limited, we cannot carry out simulations with a large system to confirm the formation of an array of bunches. However, if we carry out simulations with a large system and more steps, a periodic array of large bunches may be observed. The other possibility is the difference in the depth of the diffusion field in the solution. In previous studies,^{18,19,23)} compared with the width of the system size in the x -direction, the depth of the diffusion field is very small, so that the interaction between bunches through the diffusion field is limited. Thus, if the bunches are large and the distance between them is sufficiently large, each bunch moves independently and bunches with the same size periodically appear.

According to the results of a previous experiment,²⁸⁾ the step bunches is not formed with an extreme fast flow. The similar phenomenon, which was not reported in previous studies, occurs in our simulation. However, as we mentioned in the above paragraph, we use a small system and a periodic boundary condition in the x -direction. so that, if the flow is extremely fast, the modified diffusion field in the downstream affects bunches upstream. Thus, we have to carefully consider the agreement of our results with experimental results.

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