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Abstract

The Burton, Cabrera and Frank (BCF) theory plays a key conceptual role in understanding and modeling the crystal growth of vicinal surfaces. In BCF theory the adatom concentration on a vicinal surface obeys to a diffusion equation, generally solved within quasi-static approximation where the adatom concentration at a given distance x from a step has a steady state value $n(x)$. Recently, we show that going beyond this approximation [B. Ranguelov and S. Stoyanov, Phys. Rev.B, 76, 035443 (2007)], for fast surface diffusion and slow attachment/detachment kinetics of adatoms at the steps, a train of fast-moving steps is unstable against the formation of steps density waves. More precisely, the step density waves are generated if the step velocity exceeds a critical value related to the strength of the step-step repulsion. This theoretical treatment corresponds to the case when the time to reach a steady state concentration of adatoms on a given terrace is

comparable to the time for a non-negligible change of the step configuration leading to a terrace adatom concentration $n(x,t)$ that depends not only on the terrace width, but also on its "past width". This formation of step density waves originates from the high velocity of step motion and has nothing to do with usual kinetic instabilities of step bunching induced by Ehrlich-Schwoebel effect, surface electromigration and/or the impact of impurities on the step rate. The so-predicted formation of step density waves is illustrated by numerical integration of the equations for step motion. In order to complete our previous theoretical treatment of the non-stationary BCF problem, we perform an in-situ reflection electron microscopy experiment at specific temperature interval and direction of the heating current, in which, for the first time, the step density waves instability is evidenced on Si(111) surface during high Si adatoms deposition rates.

1. Introduction

The two main assumptions of the original Burton Cabrera and Frank (BCF) theory [1] are (i) that the steps on the vicinal surface move slowly during growth and that (ii) thank to very fast exchange with the vapor - the adatom concentration field on a given terrace with fixed boundaries (the steps) instantly reach its steady state. On this ground, the BCF theory provides reasonable explanation of most of the crystal growth observations since more than sixty years. However, when the step velocities become very high (it can be the case in molecular beam epitaxy) a modification of the BCF

theory is required. There have been several attempts to go beyond the quasi-static approximation in the BCF model: Ghez and Iyer [2] treated the step motion as a Stefan problem, while Ghez et al. [3] and Keller et al. [4] as well as Dufay et al. [5] clarified the stability of a step flow in a presence of an advection effect. In a more recent treatment, Ranguelov and Stoyanov [6, 7] introduced a new approach to study the instability of a vicinal surface with fast-moving steps when furthermore the surface diffusion is very fast, but the attachment and detachment of atoms from the steps are relatively slow processes. In this treatment the adatom concentrations on the terraces is time-dependent and cannot instantly reach their steady state values. Ranguelov and Stoyanov [6] showed that in these conditions, step density waves are generated at the crystal surface when the velocity of the step train exceeds a critical value. Here, we give an additional experimental proof of this new type of instability by studying in-situ the step dynamics of a Si(111) surface, submitted to a high Si deposition rate, by means of low distortion reflection electron microscopy (LODREM) [8]. The experiment is performed in the temperature range and direction of the heating current at which no "classical" step bunching instability is observed, so the electromigration of adatoms is excluded as a possible reason for the observed instability.

2. Equations for adatom concentrations and terrace widths evolution at growth

In a mesoscale approach, the processes at the crystal surface are described by two types of variables – the concentration n_j of adatoms and the width $l_j = x_{j+1} - x_j$ of the jth terrace (as shown in Fig.1, x_j denotes the position of

the jth step). In the limit of fast surface diffusion the concentration n_j has a constant value over the whole terrace, but it can vary with the sublimation time and the size of the terrace. The rate of advance of jth step is determined by the flux that results from the elemental fluxes coming to (or from) the jth step to (or from) the upper and the lower terrace. Introducing the step kinetic coefficient K, which describes the exchange of atoms between the crystal phase and the dilute layer of adatoms, the rate of motion of the jth step is given by

$$\frac{dx_j}{dt} = -K\Omega[n_j - n_s^e(j)] - K\Omega[n_{j-1} - n_s^e(j)] \tag{1}$$

Here Ω is the area of one atomic site at the crystal surface and the sign minus provides for a positive velocity of the steps during sublimation (see Fig.1) when $n_j < n_s^e(j)$. Thus, the velocity of a step is assumed to depend linearly on the local deviation $[n_j - n_s^e(j)]$ of the adatom concentration from its equilibrium value $n_s^e(j)$.

The time derivative of the adatom concentration on the jth terrace is given by

$$\frac{dn_j}{dt} = R - \frac{n_j}{\tau_s} - \frac{2Kn_j}{l_j} + \frac{K}{l_j}\left[n_s^e(j+1) + n_s^e(j)\right] \tag{2}$$

where τ_s is the average life-time of an adatom in a state of mobile adsorption on the crystal surface (i.e. $\frac{n_j}{\tau_s}$ is the desorption flux) and R is the deposition flux.
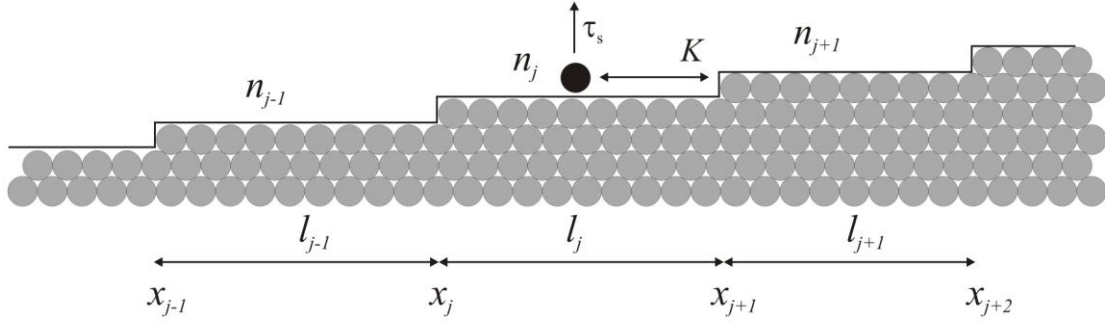
Figure 1. Schematic view of a vicinal surface with straight steps. The position of the jth step is denoted by x_j, the width of the jth terrace is $l_j = x_{j+1} - x_j$ and the concentration of adatoms on the jth terrace is n_j. An adatom is represented as a black disk.

Equation (2) has a very clear physical meaning – the adatom concentration change is due to two processes: a decreasing due to the desorption (the second term on the right hand side) and attachment of adatoms to the steps (the third term), and an increase due to the detachment of atoms from the steps (the last two terms in the right hand side of Eq.(2)) and the deposition flux R. Here, one must have in mind, that the equilibrium value of the adatom concentration $n_s^e(j)$ is not a constant, but because of step-step repulsion, depends on the step configuration, by the expression [9-13]

$$n_s^e(j) = n_s^e \left[1 + \tilde{A} \left(\frac{1}{l_{j-1}^3} - \frac{1}{l_j^3} \right) \right], \qquad (3)$$

where $\tilde{A} = 2\Omega g / kT$. The step repulsion coefficient $g(T)$ is defined [13] through the expression $f(\rho) = f(0) + \kappa\rho + g\rho^3$ for the surface free energy per unit projected area of a vicinal surface with a density of steps ρ.

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Introducing dimensionless variables $\tau = Kt/l$, $\tau_s' = K\tau_s/l$, $\eta_j = l_j/l$, $c_j = n_j/n_s^e$, $c_{st} = R\tau_s/n_s^e$ and $\varepsilon = \tilde{A}/l^3$, where l is the initial equidistant inter-step distance, one obtains an equation about the dimensionless concentrations

$$\frac{dc_j}{d\tau} = \frac{c_{st}}{\tau_s'} - \frac{c_j}{\tau_s'} - \frac{2c_j}{\eta_j} + \frac{2}{\eta_j} + \frac{\varepsilon}{\eta_j}\left(\frac{1}{\eta_{j-1}^3} - \frac{1}{\eta_{j+1}^3}\right) \tag{4}$$

and an equation about the dimensionless terraces widths

$$\frac{d\eta_j}{d\tau} = -n_s^e\Omega\left\{c_{j+1} - c_{j-1} + 2\varepsilon\left(\frac{1}{\eta_{j+1}^3} - \frac{2}{\eta_j^3} + \frac{1}{\eta_{j-1}^3}\right)\right\}. \tag{5}$$

These coupled equations describe the evolution of the vicinal crystal surface during crystal growth [6].

3. Linear stability analysis of the coupled equations for a train of moving steps

The coupled equations (4) and (5) describe the time evolution of the adatom concentrations on the vicinal terraces and the terrace widths respectively. Usually these equations are solved by numerical integration, as done in section 4. Here we will present briefly only the final results obtained from a linear stability analysis (LSA) approach applied to equations (4) and (5). Details about the LSA procedure are given in [6]. The linear stability analysis is a very powerful and efficient analytical tool for evaluating the conditions at which the system of steps will evolve from equidistant distribution of steps towards an instability in the form of bunches or small groups of steps. The classical procedure of the LSA considers small deviations from the equidistant step train and constant adatom concentrations. Using series expansion and elements of Fourier analysis one can find the conditions at which the deviations in the terraces widths from

the equidistant distribution increase with time, and thus the vicinal crystal surface will be unstable. The main result from the LSA [6] is that in the case of crystal growth the crystal surface will be unstable if the velocity V of the steps is

$$V > \frac{V_{cr}}{c_{st}} \tag{6}$$

where

$$V_{cr} = 6K\varepsilon = \frac{12K\Omega g}{kTl^3} \tag{7}$$

This means that even in an absence of destabilizing factors (like Schwoebel effect, electromigration of adatoms, impurities, etc.), the surface could be unstable if the velocity of the steps exceed some critical value.

4. Non-linear dynamics of fast moving steps – late stages of vicinal surface instability

The result of the numerical integration of eqs.(4) and (5) shows a gradual formation of a periodical array of identical step density waves traveling on the vicinal crystal surface at growth conditions and fulfilled condition of equation (6). For the integration of eqs.(4) and (5) we need numerical values of the parameters $\tau_s' = K\tau_s/l$, $\varepsilon = \tilde{A}/l^3$, $c_{st} = R\tau_s/n_s^e$ and $n_s^e\Omega$. The values to be used should be in agreement with the assumptions of our model: for instance, the parameter Ωn_s^e can vary in a wide interval depending on the temperature and the properties of the material. Rather exotic situation exists at the (111) vicinal surface of Si where $\Omega n_s^e \approx 0.1$ in agreement with the experimental findings [14]. Such a high value of the parameter Ωn_s^e introduces a restriction, which is in the form of inequality $c_{st} \leq \tau_s'$, when

$\tau_s^/ >> 1$. The parameter ε characterizes the step-step repulsion and values $\varepsilon \leq 10^{-3}$ will be used in the numerical integration of the equations.

We integrate the equations (4) and (5) and calculate the step trajectories in a frame moving with the average velocity of the step train. The results in Fig.2 clearly show the formation of an array of identical step density waves – the system of equidistant steps (top image) evolves to step density waves at the late stages of vicinal instability (bottom image).
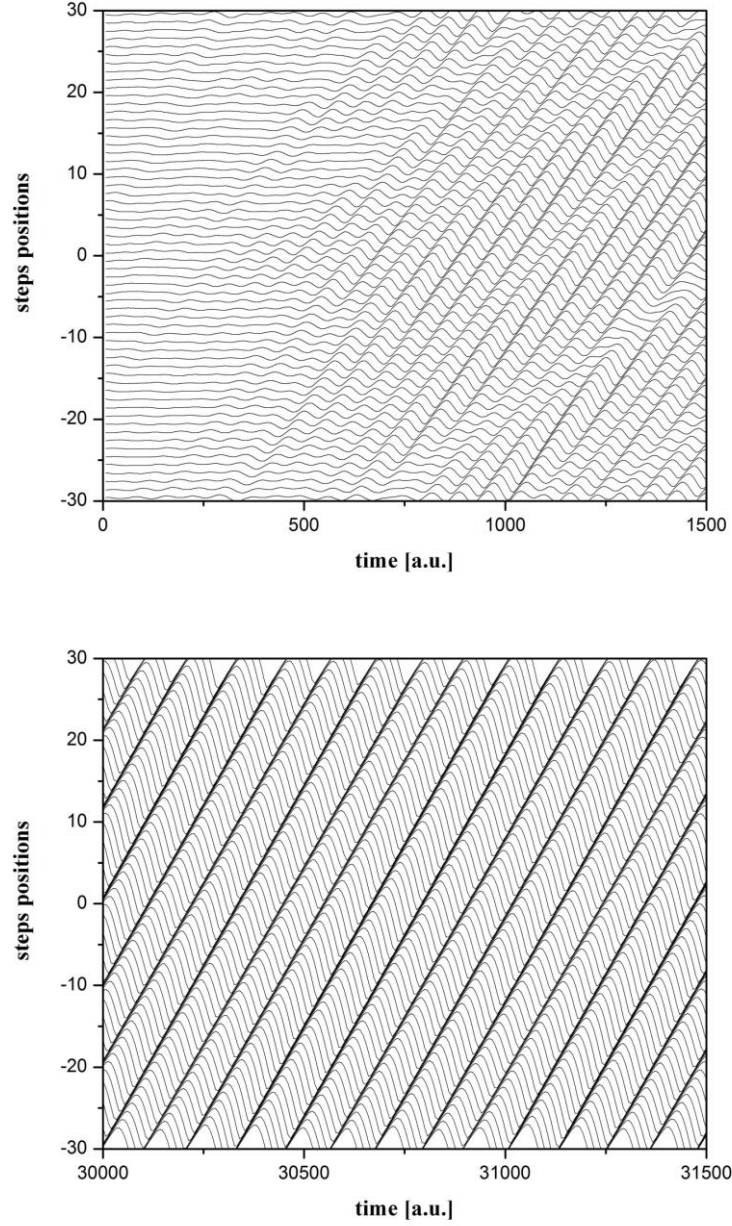
Figure 2. Formation of step density waves at the surface of a growing crystal Step trajectories are calculated for $\tau_s^/ = 100$, $\varepsilon = 10^{-3}$, $c_{st} = 100$ and $n_s^e \Omega = 0.1$. Upper image: starting configuration of nearly equidistant steps; Lower image: regular step density waves in the late stage of crystal growth process.

It is worth to mention once more time, that the kinetic instability manifested in Fig.2 is completely different from the instability of a step flow in a

presence of advection effect [2-5] and from the classical step bunching instability induced by electromigration force acting onto adatoms. The physical ground of this new kinetic instability is the kinetic memory effect which is an essential feature of the step dynamics in crystal growth at high deposition rate [6, 7].

Our results show that the formation of step density waves by fast moving steps is by no means a universal effect, but on the contrary, this phenomenon takes place in a rather limited range of values of the experimental parameters and material constants. These constraints lead to a true challenge to try to find experimental evidence for such step density waves at high deposition growth rates. Our experimental results will be discussed in the following section.

Our non-stationary treatment of the BCF theory of vicinal crystal growth [6] was generalized in the light of the common experimental case, when the adatoms are a subject of the acting electromigration force f during their diffusion onto terraces [7]. The origin of the electromigration force is connected with the applied heating direct current (DC) flowing through the sample [15]. The electromigration force could be directed step-down (from higher to lower terraces) or vice versa - step-up (from lower to higher terraces). Again, by means of LSA we have defined the conditions for unstable growth of the vicinal surface – in this case, when the electromigration force is relatively weak (both in step-down or step-up direction), the step dynamics is dominated by the generation of step density waves. If the electromigration force exceeds a critical value [7], then at step-down direction it leads to classical step bunching with coarsening, while in step-up direction (positive sign of the electromigration force) it could completely eliminate the formation of step density waves. Figure 3 indicates

this case, in which the electromigrating force is acting onto the diffusing atoms (step-up direction), but its amplitude is still not enough to eliminate the step density waves.
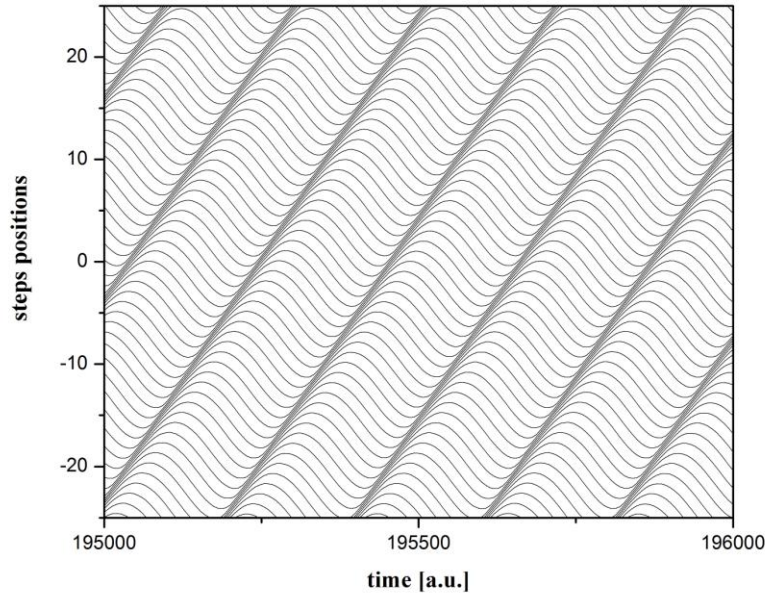

Figure 3. Weak step density waves at growth and step-up electromigration force. Step trajectories are calculated for $\tau_s^I = 100$, $\varepsilon = 10^{-3}$, $c_{st} = 100$, $n_s^e \Omega = 0.1$ and $f = 0.0210$.

5. Experimental results – step density waves at growth of Si(111) vicinal surface and high deposition rates

In order to observe in-situ the theoretically predicted step density waves dynamics, we use REM and LODREM microscopy techniques on a vicinal of a Si(111) surface annealed by Joule heating. These conditions allow us to get a clean surface during the whole experiment and to activate surface diffusion in order to ensure adatom motion and thus step flow by adatom

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incorporation. In these annealing conditions the electromigration force cannot be hindered in the in-situ growth experiments. But, as the LSA shows, there is a way to eliminate the influence of the electromigration force onto the surface instability: the step density waves type of instability will be observed at high enough deposition rates and step-up direction current at which no step bunching occurs. For this purpose the experiments are done at a temperature below 1250 °C and step-up direction of the electromigration force. These are high temperature conditions in which a Si(111) vicinal surface is known to be stable in classical growth conditions, that means when exposed to "reasonable " incident flux of silicon atoms [16][i]. We applied the maximum incoming flux of adatoms compatible with our experimental conditions by using a Si external source heated just below the Si melting point and located in the very close vicinity of the Si surface under study. Details about the sample holder, sample preparation and the control of thermodynamic conditions in vicinity of the sample, as well as the ultra high vacuum conditions are given elsewhere [17, 18]. In these conditions the step velocity reaches approximate value of one micrometer per second, so that we expected to be able to catch the initial stages of formation of a step density wave.

Our new and essential experimental result is illustrated in the image sequence in Figure 4. Freshly cleaned sample of n-doped Si(111) wafer with miscut angle smaller than 0.1 degrees is introduced inside the microscope chamber, where under typical ultra high vacuum conditions it is flashed at 1250 °C and subsequently annealed at 800 °C for 20 minutes. After this cleaning procedure the surface consists of monatomic steps separated by

approximate equidistance of 1 micrometer [19], thus representing the local vicinity angle – Figure 4a.

The initial equidistant step distribution, shown in Figure 4a – monatomic steps at a distance around 1 micrometer is kept in a quasi-thermodynamic equilibrium with the ambient phase at a constant temperature of 1220 °C by step-up direction of the heating DC.
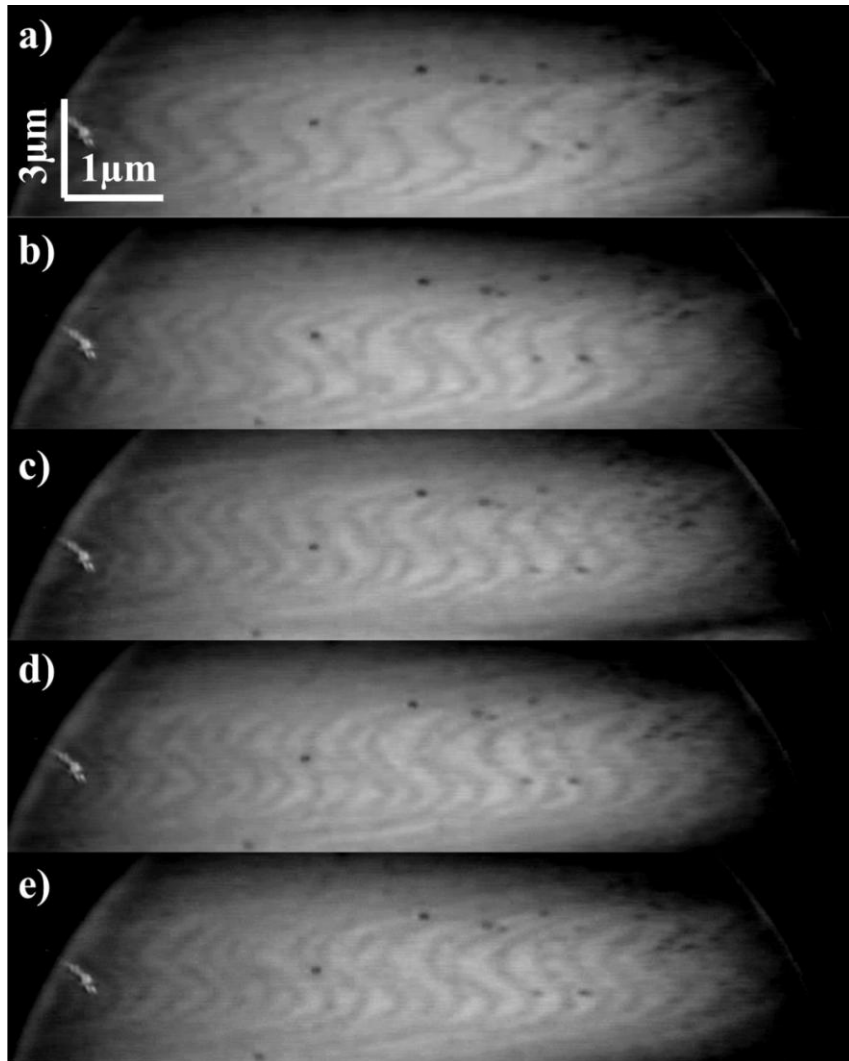

Figure 4. Image sequence taken by LODREM technique at 1220 °C – growth of Si(111) vicinal surface at step-up current direction and deposition

flux of 5 bi-layers per second. a) initial vicinal surface with almost equidistant monatomic steps, b) c) d) e) sequence of images taken in 3s. time interval - step density waves consisting of two steps. Width of the screen is 10 micrometers.

Having in mind the complex behavior of the Si(111) surface towards step bunching, we use a temperature that is slightly below 1250 °C and step-up direction of the heating DC, because at such conditions the classical step bunching process caused by electromigration is not realized. Under such conditions and moderate values of the deposition flux the surface is stable and the crystal growth process proceeds via step flow growth mode at which the initial step distances are preserved during growth. Our numerical experiments never show in-situ step bunching at 1220 °C and step-up direction of the DC current. Increasing the deposition flux up to 5 bilayers per second (this is the maximum possible realized value for the deposition flux) we observe the movement of the steps and after certain time (approx. 10 s) the initial equidistant distribution is gradually "switched" to persistence of two steps density waves formation. These density waves are stable (b, c, d, e, images on Figure 4) and exist until the incoming flux is kept to such high deposition rates.

As far as we know this is the first time of in-situ experimental observation of the theoretically predicted new type of surface instability, caused by high velocity of moving steps on growing vicinal crystal surface.

This experiment thus is the first experimental proof of a new type of instability mainly due to non-steady state effects that occur in the limit of high flux and in large surface diffusion limit.

6. Conclusions

We have shown both by theoretical analysis and experimental setup the existence of a newly type of vicinal surface instability during growth. There exists a critical velocity V_{cr} of a step train (given by Eq.(7)) which plays an essential role in the criterions for a stability of vicinal surface during crystal growth by step flow. This instability is theoretically predicted in the regime of slow kinetics at the steps and fast diffusion of adatoms on the terrace surface. During vicinal crystal growth instability occurs when the step velocity is larger than V_{cr}/c_{st}. The physics of this effect is substantially different from the physics of the instabilities, induced by Ehrlich-Schwoebel effect, electromigration of adatoms, impurities, etc. By careful experiment on Si(111) vicinal surface at 1220 °C and applying large possible values of the incoming flux of adatoms, we have achieved the maximal possible growth rate at such temperature of the sample surface. By means of reflection electron microscopy we have observed formation of small step density waves – manifestation of a new kinetic surface instability during growth, which is completely different from the classical step bunching. Thus we have demonstrated that when the step motion is very fast, the quasi-static approximation in the BCF theory of crystal growth is no more valid and the non-steady state effects in the crystallization kinetics become important.

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[i] The lower and higher limits of the temperature domain for which there is no step bunching with step-up current but bunching with step-down current (in classical conditions of flux) vary slightly according to the authors. In our case this domain roughly corresponds to 1100-1250°C (temperatures have been measured by optical pyrometry calibrated on the 7x7 ←→1x1 surface transition that occurs close to 830°C).