Instability of vicinal crystal surfaces with transparent steps: Transient kinetics and non-local electromigration

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Abstract

The steps at the crystal surfaces could be partially transparent in the sense that the migrating adatoms can cross the steps without visiting a kink position. In the case of significant transparency the velocity of a given step in a given moment is affected by atomic processes which took place at rather distant terraces in rather earlier moments. The reason is that an adatom needs time to cross many terraces before attaching to a kink position. That is why the theory of crystallization with non-local kinetics should account for the time dependence of the adatom concentrations on the terraces. Such a transient growth model (going beyond the quasi-static approximation of the BCF theory of crystal growth) is developed here for the limit of slow kinetics at the steps and fast surface diffusion. This model predicts instability of the vicinal surface (in agreement with the earlier studies) but rather different expression for the wavelength of the most unstable mode, which depends only on the ratio between the step transparency and the step kinetic coefficients.

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1. Introduction

The most intriguing feature of the step bunching, induced by the direct electric current flowing through the Si wafer, is that it occurs at different directions of the current in the different temperature intervals [1–6]. Step bunching at step-down direction of the electromigration of adatoms was satisfactorily explained by generalizing the Burton Cabrera Frank (BCF) model [7–9] to account for the drift of the adatoms [10,11]. For the step bunching at step-up direction of the electromigration, Stoyanov [12,13] proposed a mechanism based on the transparency of the steps. This feature of the crystal growth kinetics is involved in the model through the boundary conditions of the differential equation describing the diffusion of the atoms adsorbed on the terraces of a vicinal crystal surface [14]. In the case we analyze here (electromigration of the adatoms) the boundary conditions read

\[ D_s \frac{d}{dx} \left( \frac{F n}{kT} \right) = -K [n_i(x_i) - n^*_i(x_i)] + P [n_{i-1}(x_i) - n_i(x_i)] \] (1a)

at \( x = x_{i+1} \). Here \( D_s \) is the coefficient of surface diffusion, \( F \) is the electromigration force and \( n_i \) is the concentration of mobile atoms, adsorbed on the \( i \)th terrace (see Fig. 1). The boundary conditions (1a, 1b), accounting for both crystal – adlayer exchange and the inter-terrace exchange, were first formulated in Ref. [14] for \( F = 0 \) and later used in the general case \( F \neq 0 \) [15].

The terms in the right hand side of these equations have a clear physical meaning – the first term describes the exchange of atoms between the crystal phase and the two-dimensional dilute layer of adsorbed atoms. This exchange is characterised by the step kinetic coefficient \( K \). The second term describes the inter-terrace exchange. The coefficient \( P \) characterises the transparency of the steps – \( P = 0 \) means zero transparency, i.e. no atoms can cross the step without attaching to a kink position. Non-zero transparency \( P > 0 \) means that the adatoms have a chance to either jump directly from one terrace to the neighbouring one, or effectively cross the step by attachment to the step edge and subsequent detachment from it before visiting a kink position. Considerable transparency takes place when the kink density is low and the migration of atoms along the step edge is slow. Under these conditions the atoms have high probability to detach from the edge before arriving to a kink position. In other words \( K \) is small and \( P \) is large.

The coefficients \( K \) and \( P \) have a dimension of velocity but only \( K \) is directly related to the crystallization kinetics and the motion of the elementary steps on the crystal surface through the equation

\[ \nu(x_i) = \frac{dx_i}{dt} = -K \Omega [n_i(x_i) - n^*_i(x_i)] - K \Omega [n_{i-1}(x_i) - n^*_i(x_i)] \] (2)
Here \( \Omega \) 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 \( n_i(x_i) < n^*(x_i) \).

The research activity on the crystal growth for many years has been focussed on the BCF model [7–9] with zero transparency. Thus the instabilities (step bunching and wandering) induced by various physical factors have been explored [10,11,15–20] for the local kinetics of growth and evaporation, i.e. when \( P = 0 \). In the special case of instability, induced by the electromigration of adatoms, however, the transparency of steps is expected to change dramatically the kinetics of surface processes. In the case \( P \gg K \) a new mechanism of step bunching (induced by electromigration) operates as shown first by Stoyanov [12,13]. The model of Stoyanov was later studied by Sato et al. [21,31] who performed linear stability analysis. It is essential to note, however, that these authors [13,21] analyzed a continuum model of a crystal surface so that the step transparency coefficient \( P \) does not explicitly appear in the theoretical considerations. Substantial progress in the understanding of kinetic instabilities was made by Pierre-Louis [15]. He analyzed the step bunching at a vicinal crystal surface in a presence of adatom electromigration and step transparency. The onset of bunching and step meandering instability was studied for general kinetics and also an instability towards a train of stable pairs was discovered [22].

The present paper addresses the problem of electromigration induced instability of a vicinal surface with transparent steps from a different point of view. Our philosophy is to approach this phenomenon by non-steady state treatment similar to the considerations in our recent papers [23,24]. We think such a treatment is a different point of view. Our philosophy is to approach this problem. That is why we focus our attention on the limit of very fast surface diffusion. In this limit the adatom concentration field on a given terrace reaches very quickly its steady state profile and the advection effect is negligible. As far as the average concentration of adatoms on the terrace is concerned, it cannot change very quickly since the inter-terrace exchange is assumed to be substantially slower than the surface diffusion, whereas the attachment–detachment processes are the slowest. In our approximate treatment the concentration field on every terrace is assumed to have its steady state profile (and the advection effect is neglected) whereas the time evolution of the average concentrations is governed by a set of ordinary differential equations.

### 2. A model of surface processes

The external force \( F \) acting on the adatoms induces a gradient of their concentration on every terrace. Intuitively, one expects the step transparency to decrease the concentration gradient. To evaluate the gradient we analyze the simplest case of crystal annealing with negligible desorption and zero deposition rate. Then the surface transport on each terrace is described by the Eq. (10)

\[
D_s \frac{d^2 n_i}{dx^2} - \frac{D_s F}{K} \frac{dn_i}{dx} = 0
\]

with \( x \) being an axis, perpendicular to the step edges (a system of equidistant parallel steps with straight edges is under consideration).

The solution of the Eq. (3) with boundary conditions (1a, 1b) reads

\[
n_i(x) = \frac{n^*_i \exp \left( \frac{l}{ds} \right)}{1 + \frac{F \tau_i}{kT}}
\]

where \( d_s = D_s/K \) and \( d_s = D_s/P \) are characteristic lengths for step attachment–detachment kinetics and step transparency, whereas \( l \) is the terrace width. For the concentration gradient at \( x = 0 \) the Eq. (4) gives

\[
\text{grad}(n_i) = \frac{n^*_i \frac{d_s}{l}}{1 + \frac{F \tau_i}{kT}}
\]

Since we focus our attention on the dynamics of strongly transparent steps (where the adatoms have much higher probability to jump to the next terrace than to visit a kink at the step, i.e. \( d_s \gg l \) and \( d_s \ll 1 \)) the expression (5) can be simplified to

\[
\text{grad}(n_i) \approx n^*_i \frac{2Fd_s}{kTl}
\]

Strictly speaking this expression is valid only in an absence of any desorption. Since we are looking for an explanation of the experiments in the temperature interval 1040–1190 °C the desorption should not be ruled out. Introducing in Eq. (3) a term \( \frac{n_i}{l} \) accounting for the desorption flux (\( \tau_i \) is the life time of an adatom in a state of mobile adsorption) and solving the relevant boundary problem, one obtains an expression for the concentration gradient which contains the diffusion distance \( \Delta_s = \sqrt{D_s \tau_i} \). The series expansion of \( \text{grad}(n_i) \) (we make use of the well-established fact that \( \Delta_s \gg l \) in the case of Si evaporation) has a leading term which coincides with Eq. (6).

### 3. Kinetic equations

When the crystal grows or evaporates the adatom concentration deviates from its equilibrium value \( n^*_i \). In analogy with Eq. (6) we assume the gradient of the adatom concentration on the \( i \)th terrace to be

\[
\text{grad}(n_i) = n_i \frac{2Fd_s}{kTl}
\]

where \( n_i \) is the average concentration on this terrace. The use of this expression for the adatom concentration gradient requires some comments. The expression (5) is obtained for a system of equidistant parallel steps with straight edges. For this configuration the expression (5) is an exact result. It could be a rea-
reasonable approximation when the step configuration slightly deviates from the equidistant one (as in the linear stability analysis given in Section 4). In the later stages of the step bunching instability, however, the terrace distribution is far from being uniform (neighbouring terraces could have rather different size). That is why the expression (5) is no more a good approximation for the adatom concentration gradient on the terraces at the vicinal crystal surface. Therefore, the late stages of step bunching instability require special considerations which are beyond the scope of this paper.

Here we shall make use of the expression (6) and write a differential equation for the time evolution of the concentration of adatoms on the ith terrace during sublimation. In the framework of this approximation we obtain

$$\frac{dn_i}{dt} = -\frac{n_i}{\tau_i} - 2K \eta_i + K \left| n_i(i + 1) + n_i(i) \right| - 2P \eta_i + \frac{P}{\tau_i} n_i \left( 1 - \frac{F_d \eta_i}{K \tau_i} \right)$$

(7)

The terms in the right hand side of this equation have clear physical meaning – the adatom concentration decreases because of desorption of adatoms from the vicinal surface. Finally, the jumps of the adatoms from the neighbouring terraces to the ith terrace lead to an increase of the concentration $n_i$ (see the last two terms).

Accounting for the dependence of the equilibrium concentration on the size of the neighbouring terraces [25,26]

$$n_i^* = n_i^* \left[ 1 + A \left( \frac{1}{\tau_i - 1}, \frac{1}{\tau_j} \right) \right]$$

(8)

where

$$A = \frac{2 \Omega g}{K t_i}$$

(9)

we can write the final form of the Eq. (7) (Here $g(T)$ is defined [26] through the expression $f(\rho) = f(0) + k \rho + g \rho^2$ for the surface free energy per unit projected area of a vicinal surface with a density of steps $\rho$). In dimensionless variables $\tau = k t_i / l_i$, $\tau_j = k t_j / l_j$, $\eta_i = l_i / l_j$, $c_i = n_i / n_j^*$, $A = \sqrt{a_i}$ and $P_a = P / K t_i$ we obtain

$$\frac{dc_i}{d\tau} = -c_i - 2 \eta_i c_1^* \left( \frac{1}{\eta_i - 1} \right) + \frac{P_a}{\eta_i} (c_i - 1)$$

(10)

The time evolution of the terraces is governed by the equations

$$\frac{dc_i}{dt} = \frac{dc_{i-1}}{dt} + \frac{dc_i}{dt}$$

(11)

In dimensionless variables the last set of equations reads

$$\frac{d\eta_i}{d\tau} = -n_i^* \left( c_{i-1} - c_i \right) + 2n_i \left( \frac{1}{\eta_i - 1} - 2 \right) \left( \frac{1}{\eta_i - 1} \right)$$

(12)

$$- \frac{F_d \eta_i}{K t_i} (c_i - 1)$$

4. Linear stability analysis

The simplest solution of the Eqs. (10) and (12) is

$$\eta_i = 1, c_i = c_0 = \frac{1}{1 + 1/2 \tau_i}$$

(13)

which is an equidistant step distribution and the corresponding average concentration of adatoms during sublimation. To check the stability of this solution with respect to small fluctuations of the terrace size and adatom concentration we consider small deviations from $\eta_i = 1$ and $c_i = c_0$, i.e. $\eta_i = 1 + \Delta \eta_i(t)$ and $c_i = c_0 + \Delta c_i(t)$ (with the additional requirement $\Delta \eta_i(t) < 1$ and $\Delta c_i(t) < c_0$). Substituting these expressions into Eqs. (10) and (12) we make use of series expansion to obtain linear equations for $\Delta \eta_i(t)$ and $\Delta c_i(t)$.

Following the routine we look for a solution of the type

$$\Delta \eta_i = e^{\eta(\tau)} \Delta \eta_i(0), \quad \Delta c_i = e^{\eta(\tau)} \Delta c_i(0)$$

(14)

where $q$ is a wave number and we already use $i$ to denote the imaginary unit and $j$ to denote the sequence number of the terrace. In addition we allow for a phase shift $\phi$ of the wave describing the adatom concentrations $\Delta \eta_i$ with respect to the wave describing the terrace widths $\Delta \eta_i$. For the amplitude of the fluctuations in the terrace size distribution we find $\eta_i(\tau) \approx q^2$ and, therefore, the uniform terrace size distribution is stable when the real part of the parameter $s$ is negative. For small wave numbers $q \ll 1$ and high transparency $P_a \gg 1$ the real part of $s$ is given approximately by

$$s_{real} = B_2 q^2 - B_4 q^4$$

(15)

$$B_2 = \frac{V}{K^2} \left( \frac{V_{drift} + V_{cr}}{2} - V_{cr} \right)$$

$$B_4 = \frac{V_{cr}}{K^2} \left( 3 V_{drift} + \frac{3V}{4} + V_{cr} K \Omega \eta^2 \right)$$

(16)

where $V_{drift} = D \eta / \tau$ is the drift velocity of the adatoms, $V = \sqrt{4 \kappa}$ is the velocity of a train of equidistant steps during sublimation and $V_{cr} = 12 K \Omega g / K t_i$ is exactly the same critical velocity that appears in the problem of instability due to a very fast motion of the non-transparent steps (fast sublimation or growth) [23].

When the coefficient $B_2$ is positive the step train is unstable for fluctuations with wave number $0 < q < \sqrt{B_2 / B_4}$. The parameter $s$ reaches its maximum at a wave number $q_{max} = \sqrt{\frac{B_2}{B_4}}$ (see Eq. (15)). A very simple expression for $q_{max}$ is obtained in the case of strong electromigration (high drift velocity) and weak repulsion between the steps. Under this condition one gets $q_{max} = 1 / 2 V_{cr}$ and therefore the most unstable mode has a wave length (expressed as a number of terraces)

$$\lambda_{max} = 2 \pi \sqrt{2 V_{cr}}$$

(17)

The Eqs. (15) show the vicinal surface with transparent steps to develop instability when either the drift velocity of the adatoms is larger than the critical velocity $V_{cr}$ or the rate of step motion $V$ is larger than $2 V_{cr}$. The first criterion $V_{drift} > V_{cr}$ has already been obtained by Sato et al. [21] on the basis of linear stability analysis of the continuum model proposed by Stoyanov [13]. The second type of instability is induced by the fast motion of the transparent steps ($V > 2 V_{cr}$) and it is very similar to the instability found to exist in the case of non-transparent steps [23,24].

In the case of crystal growth the Eq. (7) contains one more term – the deposition rate $R$ which is larger than its equilibrium value $R_e = n_j^* / \tau_j$. Linear stability analysis of the modified equation results in an instability criterion

$$B_2 = \frac{V}{K^2} \left( \frac{V_{drift} + V_{cr}}{2} + \frac{V_{cr}}{2} \right) > 0$$

(18)

which is valid when the parameter $c_0 = K t_i / n_j^* \gg 1$ i.e. when the deposition rate $R$ is much larger than its equilibrium value. Now the velocity $V$ has a negative value (see Fig. 1) and therefore insta-
bility takes place when the expression in the brackets is also negative, i.e. \( V_{\text{drift}} \) has a step-down direction (in agreement with the earlier findings [4,13,15]).

The obtained results for step bunching instability (see Eqs. (15) and (18)) are not new except for the presence of the velocity \( V \) in the brackets in the expression for \( B_2 \) (this leads to a formation of step density waves even in absence of drift velocity of the adatoms). Apart from this the same instability criterion was obtained by Sato et al. [21,31]. These authors performed linear stability analysis of the model proposed by Stoyanov [13]. A deficiency of the Stoyanov model is the absence of any quantity characterizing the step transparency – the coefficient \( P \) is not explicitly involved in the model. In fact, Sato assumed that an adatom jumps from one terrace to the neighbouring one as easily as between two neighbouring adsorption sites. Because of this deficiency of the model Sato et al have not derived the Eq. (17).

5. Non-linear dynamics of transparent steps

The expression (6) for the electromigration induced gradient of the adatom concentration was obtained for equidistant configuration of the steps. The use of this expression in the linear stability analysis is justified since only small fluctuations of the step density \( \langle \Delta n_s(t) \rangle \ll 1 \) were allowed in these considerations. The Eqs. (10) and (12) are not applicable to the late stages of the non-linear dynamics where bunches of steps are separated by large terraces (i.e. the fluctuations in the step density are large). One can numerically integrate the Eqs. (10) and (12), but one should keep in mind that this procedure is justified only in the early stages of step bunching instability. The results for the late stages of the non-linear dynamics are not reliable since the real gradient of the adatom concentration on a given terrace could differ significantly from the value predicted by Eq. (6).

For the integration of Eqs. (10) and (12) we need numerical values of the parameters \( \tau_s = K \tau_s / l \), \( \tau_f = A / l \), \( P_i = P / K \), \( f = F_{\text{drift}} / kT \) and \( \eta \Omega \). These values should be in agreement with the assumptions already made in this model. For instance, the characteristic lengths are assumed to satisfy the inequalities \( d_i \ll l \) and \( d_p \ll 1 \) in order to reduce the expression (5) to \( \text{grad} (n_s) = n_s \Delta s \). These inequalities, however, immediately show that \( d_i / d_p = P / K = P_i > 10 \) (it is reasonable to remind that Tanaka et al. [27] estimated from their experimental results \( P_i = 36 \) for the steps at Si(0 0 1) surface). In the numerical integration of the Eqs. (10) and (12) we used values of the parameter \( P_i \) between 10 and 50.

The values of the parameter \( \tau_s = \tau_s K / l \) are restricted by the requirements \( l / L \ll \tau_s \). As mentioned above the characteristic length \( d_i \) is assumed to be \( d_i \gg l \) which immediately means \( \tau_s \gg 1 \). The parameter \( \tau_f \) determines the deviation of the real concentration of adatoms (in the case of sublimation) from its equilibrium value since (see Eq. (13)) \( c_0 = \frac{\tau_f}{\tau_f} = \frac{\tau_f}{\tau_f} \). We shall study the step dynamics at \( \tau_f > 5 \) (which means \( \tau_f \gg n_s \gg 0.9 n_s \), i.e. near to equilibrium). For the case of growth, however, one can go well away from the equilibrium by increasing the deposition rate while keeping the value \( \tau_f > 5 \). The parameter \( \varepsilon \) describes the step-step repulsion and values in the interval \( 10^{-6} < \varepsilon < 10^{-4} \) will be used in the numerical integration of the equations (the large interval of values of \( \varepsilon = A / l \) is used to see the impact of the surface orientation on the instability).

The parameter \( f = F_{\text{drift}} / kT \) is estimated on the basis of the experimental results of Fujita et al. [3] for the shape of the step bunches. This interpretation [3] provides the value \( \frac{f}{s} = 2 \times 10^{-6} \text{ nm}^{-2} \) at 1250°C. Making use of the value \( g = 0.1 \text{ eV nm}^{-1} \) and assuming \( d_i = D_i / K = 10 \) we estimate \( f = 0.6 \times 10^3 \) for a temperature 1230°C and a vicinal surface with a terrace width \( l = 100 \text{ nm} \). As will be seen below the main difficulties in reproducing the experimental observations are related to the values of the parameter \( f \) - step bunching occurs at unrealistically high values of the electromigration force \( F \). Finally, we shall explore the step dynamics at \( n_s \Omega = 0.1 \) and \( n_s \Omega = 0.01 \) in agreement with the experimental findings [28].

The numerical integration of the Eqs. (10) and (12) for \( \frac{V_{\text{drift}}}{\tau_f} = 5 \times 10^4 \) and \( \frac{\varepsilon}{\tau_f} = 5 \times 10^5 \) produces the step trajectories shown in Fig. 2.

As seen the step dynamics manifests formation of relatively small step density waves which disappear at some moment but soon after that reappear in a place close to the place of disappearance.

The next figure shows the step trajectories when the dominating physical phenomenon which induces instability is the drift of the adatoms. Now one has \( \frac{V_{\text{drift}}}{\tau_f} = \frac{l}{s} = 10^4 \) and \( \frac{\varepsilon}{\tau_f} = 1 \times 10^5 \). The step bunches in Fig. 3 are strongly compressed – the minimum interstep distance is \( s_{\text{min}} = 0.04 l \). This is probably a result of the unrealistically high value of the electromigration force \( f = 1 \).
Fig. 4 shows the trajectories of the steps during crystal growth when the two destabilizing factors have the same order of magnitude ($\frac{\Omega}{\omega} = \frac{2}{5}$ and $\frac{\lambda}{\sigma} = \frac{2}{5}$).

As seen step density waves propagate at the vicinal surface. The step trajectories manifest space and time periodicity characteristic for the instability induced by the fast motion of the steps.

6. Concluding remarks

We believe it is essential to account for the non-steady state effects when treating a non-local electromigration model for sublimation and growth of crystal surfaces with transparent steps. The reason is that one atom, landing on a given terrace, can cross 10 or 20 steps before attaching to a kink position. Such a long trip requires considerable time. In other words, what is happening is a given step in a given moment depends on the “history” of a considerable part of the crystal surface around this step. The basic idea of our approach is to account for the “history” of the growing (or evaporating) crystal surface. The considerations are restricted to the case of slow kinetics at the steps and fast diffusion on the terraces.

Our approach reproduces the instability criterion $|V_{rel}| > V_{cr}$ reported by earlier authors [21,31]. The new result we obtained is for the most unstable mode – it has a wave length (expressed as a number of terraces) $\lambda_{\text{max}} = 2\pi\sqrt{2P_k}$, i.e. $\lambda_{\text{max}}$ depends only on the relative transparency of the steps (this is true only for strong electromigration of the adatoms). Another new result is the instability of the train of transparent steps induced by the very fast motion of the steps ($V > 2V_{cr}$). This kind of instability is more likely to take place at very high deposition rate where the instability criterion reads $V > 2V_{cr}/\sigma$ (here $\sigma = R_s/\eta s \gg 1$).

It is tempting to try to explain the step bunching experiments at step-up direction of the electric current (through the Si crystal) on the basis of the model developed in this Letter. This attempt, however, meets some difficulties as seen from the confrontation with the reported [1–6,29,30] observations. The linear stability analysis and the numerical integration of Eqs. (10) and (12) predicts step bunching instability at step-up electromigration of the adatoms during sublimation whereas step-down adatom drift induces instability during growth. Our model, however, cannot reproduce the observed [5] step bunching during vapour-crystal equilibrium (according to Eq. (15) $B_2 = 0$ at $V = 0$). Here one should also mention the experiments of Pelz et al. [29] who claim the step bunching in the temperature interval (1040–1190 °C) to occur at step-up direction of the electric current during sublimation, equilibrium and growth of (1 1 1) Si crystal face. These findings contradict our results for equilibrium and growth.

As far as the wave length of the most unstable mode is concerned our formula (17) is in contradiction with the reported [30] unique wavelength $\lambda = 4 \mu$m. Our result $\lambda_{\text{max}} = 2\pi\sqrt{2P_k}$ should be multiplied by the average terrace width $l$ in order to obtain the wavelength $\lambda$ discussed in Ref. [30]. Calculated in this way $\lambda$ increases with the increase of $l$ in clear contradiction with the unique wavelength reported by Leroy et al. [30] for samples with variation of $l$ by two orders of magnitude. This contradiction might be due to the fact that our model does not include the elastic interaction between the developed facets via their different surface stresses (this interaction is a key feature of the considerations of Leroy et al. [30]).

Another weak point of our model is related to the unrealistically high values of the electromigration force necessary to obtain bunching with coarsening (see Fig. 3) by numerically integrating Eqs. (10) and (12).

In conclusion, the non-local electromigration can destabilize the vicinal surface but some results of our considerations contradict the reported experimental observations in temperature interval (1040–1190 °C). Our work by no means puts an end of the story of bunching of transparent steps. We believe, however, that writing down the kinetic Eqs. (10) and (12) we open a pathway to involve new physics in the model – for instance, the elastic interaction between the developed facets via their different surface stresses [30].

Acknowledgements

This work was partly supported by Projects TK-X-1713, IRC-CoSiM and MADARA granted from Bulgarian National Science Fund.

References


Fig. 4. Growth in a presence of electromigration force. Model parameters: $\Omega = 0.1$, $f = -5 \times 10^{-6}$, $\varepsilon = 10^{-5}$, $P_k = 20$, $\gamma_s = 10$, $c_d = 5$. 