New mechanism for impurity-induced step bunching

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Abstract. – Codeposition of impurities during the growth of a vicinal surface leads to an impurity concentration gradient on the terraces, which induces corresponding gradients in the mobility and the chemical potential of the adatoms. Here it is shown that the two types of gradients have opposing effects on the stability of the surface: Step bunching can be caused by impurities which either lower the adatom mobility, or increase the adatom chemical potential. In particular, impurities acting as random barriers (without affecting the adatom binding) cause step bunching, while for impurities acting as random traps the combination of the two effects reduces to a modification of the attachment boundary conditions at the steps. In this case attachment to descending steps, and thus step bunching, is favored if the impurities bind adatoms more weakly than the substrate.

Introduction. Step bunching is a morphological instability of a vicinal crystal surface, in which a regular train of equally spaced steps separates into regions of high step density – the step bunches – and large flat terraces. The process can be driven energetically by an attractive step-step interaction, or by a variety of kinetic mechanisms, which all share the common feature of breaking the symmetry between the ascending (upper) and descending (lower) step bordering the vicinal terrace. In growth or sublimation, the symmetry breaking is provided by the different kinetic rates for the attachment and detachment of adatoms (or some other species required for growth) at the upper and the lower step; step bunching occurs under growth if atoms attach preferentially to the descending step. For electromigration-induced step bunching, the asymmetry is introduced by the electric field, and the step train is unstable if the adatom motion is biased in the down-step direction.

It has been appreciated for a long time that in many cases step bunching must be attributed to the presence of impurities. The traditional view is that impurities pin the steps. Once a step is slowed down relative to its neighbors, more impurities accumulate in front of it and delay it even further, leading to a feedback mechanism which drives the instability. A different kind of impurity-mediated step bunching was suggested in recent work on Si_{1−y}Cy layers grown on Si(100) by molecular beam epitaxy, in which C plays the role of a codeposited impurity. The key observation is that different parts of the vicinal terrace have been exposed to the impurity flux for different durations. Therefore the impurity concentration is smallest on the freshly created part near the descending step, and largest near the ascending...
step. To the extent that the impurities couple to the energetics and kinetics of the adatoms on the terrace, this causes corresponding gradients in the adatom chemical potential and mobility which break the symmetry between ascending and descending steps, and hence may lead to step bunching\(^1\).

For the SiC system, the experimentally observed step bunching could be reproduced in simulations in which the Si-C binding was assumed to be weaker than the Si-Si binding. This was interpreted in terms of an increase of the adatom mobility due to the impurities: The low concentration of impurities near the descending step was argued to lead to an accumulation of adatoms in these low-mobility regions, and hence to a preferential attachment to the descending step. However, the adatom flux onto a step depends not only on the adatom density gradient, but also on the adatom mobility, which is lower near the descending step. The explicit calculations presented below show that the latter effect overcompensates the increase in the adatom concentration gradient. Impurities which increase the adatom mobility are found to stabilize the step train, while step bunching is induced if the adatoms are slowed down by the adsorbates.

On the other hand, the chemical potential gradient induced by the impurities acts in the opposite direction. For impurities which bind the adatoms more strongly than the clean substrate, and which would therefore be expected to lower the adatom mobility, the chemical potential is decreased near the ascending step edge, where the impurities accumulate. This implies an uphill force on the adatoms, which, as is well known from studies of electromigration-induced step bunching, stabilizes the step train\(^1\). Similarly, for impurities that bind more weakly than the substrate, the chemical potential gradient is destabilizing and the mobility gradient stabilizing. The net outcome of the two competing effects can be determined only if the modification of the adatom potential energy landscape caused by the impurities is precisely specified. Two limiting cases will be considered in detail: Random barriers which modify only the adatom mobility, and random traps for which binding energies and diffusion barriers are modified by the same amount (see Fig. 1). Random barriers and random traps are standard models in the theory of diffusion in disordered media\(^10\).

Model and general solution. Figure 2 illustrates the geometry employed in the calculation. I consider a train of straight steps with spacing \(l\). The deposition flux is \(F\) and the impurity flux \(F'\). Impurities are immobile, they do not desorb, and they are incorporated into the crystal when a step moves over them. The steps move with speed \(v = Fl\). The exposure time at a distance \(x\) from the descending step is \(x/v\), hence the stationary impurity coverage profile

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\(^1\)A similar mechanism for step equalization was proposed in Ref. 4.
Fig. 2 – Schematic of the unperturbed step train and the linear impurity concentration profile [1].

is

$$\theta(x) = F'x/v = \phi x/l,$$

where $\phi = F'/F$ is the flux ratio. The spatial variation of the impurity concentration implies a corresponding variation of the effective chemical potential $\mu_{\text{eff}}(x)$ and the adatom diffusion coefficient $D(x)$, which will be specified later. Assuming that the adatom concentration $n(x)$ adapts rapidly to changes in the step spacing and in the impurity profile, it can be computed from the inhomogeneous, stationary diffusion equation [11]

$$\frac{d}{dx}D(x) \left( \frac{dn}{dx} + \beta n \frac{d\mu_{\text{eff}}}{dx} \right) + F = 0,$$

(2)

where $\beta = 1/k_B T$. This is supplemented by boundary conditions for the mass fluxes $j_-$ and $j_+$ to the descending ($x = 0$) and ascending ($x = l$) step [2,4],

$$j_- = D(0)[n'(0) + \beta n(0)\mu_{\text{eff}}'(0)] = k_-n(0)$$

(3)

$$j_+ = -D(l)[n'(l) + \beta n(l)\mu_{\text{eff}}'(l)] = k_+n(l).$$

(4)

The attachment rates $k_-$, $k_+$ are chosen such that the attachment probability is symmetric in the absence of impurities. Specifically, I will consider two types of boundary conditions: Type I with $k_- = k_+ = k$ (attachment rates independent of the impurity concentration) and type II with $k_-/D(0) = k_+/D(l) = \lambda^{-1}$ (attachment rate proportional to the adatom mobility at the step).

The mass fluxes $j_-$ and $j_+$ govern the dynamics of the vicinal surface. The two are related through mass conservation, $j_- + j_+ = Fl$. To probe the stability of the uniform step train, consider a period-2 perturbation in which the length of every second terrace is increased by an amount $\epsilon$ and every second terrace length is decreased by $\epsilon$. In the absence of impurities this does not affect the speed of the steps, since the attachment rates $k_\pm$ are symmetric, and hence the total flux feeding each step remains $Fl$. The impurity profile associated with the perturbed step train is therefore still given by (1). When the coupling of the impurities to the adatom concentration is turned on, the larger terraces either shrink, restoring the uniform step train, or grow, leading to step doubling and, eventually, to step bunching. The large terraces shrink, if the speed of the corresponding ascending step is larger than that of the descending step, i.e. if

$$j_+(l + \epsilon) + j_-(l - \epsilon) > j_+(l - \epsilon) + j_-(l + \epsilon).$$

(5)
In the limit $\epsilon \to 0$ this becomes $dj_+/dl > dj_-/l$ or, using mass conservation,

$$dj_-/(l)dl < F/2,$$

which has to be evaluated at fixed $\theta(x)$, i.e. without taking into account the $l$-dependence of the impurity concentration gradient. When the stability criterion (8) is violated, the growth rate of the perturbation determines the time scale for step bunching, which is given by

$$\tau = (4dj_-/dl - 2F)^{-1}.\quad (7)$$

Following [11], the mass flux $j_-$ to the descending step is obtained from Eqs.(2,3,4) in the general form

$$j_- = Fl \left( \frac{M_1 + 1/\tilde{k}_+}{M_0 + 1/k_+ + 1/k_-} \right), \quad (8)$$

where

$$M_\nu = l^{-\nu} \int_0^l dx x^\nu e^{\beta \mu_{\text{eff}}(x)} D(x)^{-1}$$

and

$$\tilde{k}_- = e^{-\beta \mu_{\text{eff}}(0)} k_-, \quad \tilde{k}_+ = e^{-\beta \mu_{\text{eff}}(l)} k_+.\quad (10)$$

Random barriers. Consider first the case where the impurities affect only the mobility of the adatoms. This corresponds to the random barrier energy landscape illustrated in Fig.1 (a), where the binding energies remain unaffected while the diffusion barriers are modified by an amount $\Delta E_D$, which can be positive (as in Fig.1 (a)) or negative. An exact analytic expression for the effective diffusion coefficient in two dimensions is not available for the random barrier model [10], but some general conclusions can be drawn from Eqs.(8,9), which are to be evaluated with $\mu_{\text{eff}} = 0$. Since $D(x)$ is a monotonic function of $x$, we have that $l/D(0) < M_0 \leq l/D(l)$, $l/2D(0) < M_1 \leq l/2D(l)$ and $M_1/M_0 \geq 1/2$ for $\Delta E_D > 0$, and the converse inequalities for $\Delta E_D < 0$. Using these relations it is straightforward to prove that attachment is primarily to the descending step ($j_- \geq F l/2 \geq j_+$) when $\Delta E_D > 0$, and to the ascending step when $\Delta E_D < 0$, for both types of boundary conditions.

For the explicit calculation of $j_-$ I use the expression [12, 13]

$$D(x) = \frac{D_0}{1 + \left( e^{\beta \Delta E_D - 1}\theta(x) \right)} \equiv D_0 \frac{1}{1 + bx},\quad (11)$$

which is exact for the one-dimensional random barrier model [10]. Here $D_0$ is the diffusion coefficient on the clean surface, and $b = \phi(e^{\beta \Delta E_D - 1})/l$ is a dimensionless parameter describing the strength and the sign of the mobility gradient[2]. For type I boundary conditions the flux to the descending step reads

$$j_- = \frac{Fl}{2} \frac{1 + l/2\lambda_0 + bl^2/3\lambda_0}{1 + l/2\lambda_0 + bl^2/4\lambda_0},\quad (12)$$

where $\lambda_0 = D_0/k$. Taking the derivative of (12) at fixed $b$, one finds that the stability criterion (8) is satisfied (violated) when $b < 0$ ($b > 0$). Thus step bunching is induced by impurities which slow down adatom diffusion ($\Delta E_D > 0$). The instability is directly linked to the preferential feeding of the steps from above, i.e. the stability criterion (8) is equivalent to $j_- < F l/2$. This need not be true in general.

\(^2\)Note that $bl > -\phi$ with $\phi = F'/F \ll 1$, hence $D(x)$ is positive and finite everywhere.
The corresponding adatom density profile is given by

$$n(x) = \frac{F}{D_0} \left( A(\lambda_0 + x) + \frac{1}{2}(Ab - 1)x^2 - \frac{1}{3}bx^3 \right),$$  \hspace{1cm} (13)$$

where $A = j_-/F = kn(0)/F$. The examples depicted in Fig. 3 show how the density maximum shifts towards the ascending (descending) step for $b > 0$ ($b < 0$), as would be expected intuitively. Consequently the density gradient is enhanced near the ascending (descending) step. As was mentioned already, this effect is however overcompensated by the spatial dependence of the adatom mobility. The boundary values of the adatom density vary in the opposite direction to the density gradients, so that the mass flux is predominantly to the descending (ascending) step for $b > 0$ ($b < 0$).

For type II boundary conditions the flux to the descending step is given by

$$j_- = \frac{Fl}{2} \frac{1 + l/2\lambda_0 + bl + bl^2/3\lambda_0}{1 + l/2\lambda_0 + bl/2 + bl^2/4\lambda_0},$$  \hspace{1cm} (14)$$

which behaves similar to (12): Attachment is primarily to the descending (ascending) step and the step train is unstable (stable) when $b > 0$ ($b < 0$). This shows that step bunching caused by random barrier impurities is a robust phenomenon which is independent of the detailed model assumptions.

**Random traps.** In general, the influence of the impurity-induced chemical potential gradient has to be taken into account as well. The effective chemical potential $\mu_{\text{eff}}$ is obtained from a thermodynamic argument. We assume that the impurities modify the adatom binding energy by an amount $\Delta E_b$, $\Delta E_b > 0$ corresponding to stronger binding. The equilibrium adatom density in a region with impurity concentration $\theta$ is then given by $n_0(\theta) = n_0(0)(1 - \theta + \theta e^{\beta \Delta E_b})$, since the occupation of impurity sites is enhanced or suppressed by the Boltzmann factor $e^{\beta \Delta E_b}$. Writing $n_0(\theta) = n_0(0)e^{-\beta \mu_{\text{eff}}}$ and inserting the linear impurity profile (1), we obtain

$$\mu_{\text{eff}}(x) = -k_B T \ln(1 + fx)$$  \hspace{1cm} (15)$$

Fig. 3 – Adatom density profile (13) for $l/\lambda_0 = 10$ and $bl = 2, -1/2$ and 0, respectively. The adatom density has been scaled by the overall factor $F/D_0$. 
where $f = (e^{\beta \Delta E_b} - 1)(\phi/l)$ is the analogue of $b$ in (1). The effective force entering (3) is then given by $-\beta \mu_{\text{eff}}/dx = f/(1 + fx)$, which points uphill (stabilizing the step train (4)) when $\Delta E_b > 0$, and downhill (destabilizing the step train) when $\Delta E_b < 0$.

In contrast to the impurity-induced mobility gradient, the gradient in the chemical potential cannot occur in isolation (at constant $D(x)$), because an energy landscape in which the impurities modify the adatom binding energy without affecting the diffusion barriers is not conceivable. A simple yet realistic situation where both effects are present simultaneously is provided by the random trap model, illustrated in Fig.3(b). In this model it is assumed that the transition states between diffusion sites remain unaffected by the impurities, so that the binding energies and the diffusion barriers (for jumps away from an impurity site) are modified by the same amount, $\Delta E_b = \Delta E_D \equiv \Delta E$. The effective diffusion coefficient is then given exactly by (11) in all dimensions (9). Combining (15) and (11) with $b = f$, the integrand $e^{\beta \mu_{\text{eff}} D(x)x^{-1}}$ in (3) is seen to become constant. Hence $M_0 = l/D_0$, $M_1 = l/2D_0$ and (8) reduces to the familiar expression (2) for the clean surface, but with modified attachment rates $k_- = k_-$, $k_+ = k_+(1 + bl)$.

This is a consequence of the fact that for unbiased potential landscapes, in which the jump rates away from a given site are everywhere symmetric, the inhomogeneous diffusion equation (8) can be written as (14)

$$\frac{d^2}{dx^2}[D(x)n(x)] + F = 0,$$

which implies that $\tilde{n}(x) \equiv D(x)n(x)$ satisfies a diffusion equation with constant coefficients and standard boundary conditions $D(0)\tilde{n}'(0) = k_-\tilde{n}(0)$, $D(l)\tilde{n}'(l) = -k_+\tilde{n}(l)$. For type II boundary conditions $k_+/D(l) = k_-/D(0)$ so that attachment remains symmetric in the presence of impurities, and the two competing impurity effects precisely cancel. In contrast, for type I boundary conditions the impurities are seen to induce a preference for attachment at the ascending step for $\Delta E > 0$, and at the descending step for $\Delta E < 0$. This implies a tendency towards step bunching for $\Delta E < 0$. The effect is however quite feeble, since $|bl| \ll \phi$ for $\Delta E < 0$.

Summary. In conclusion, I have described a novel mechanism through which co-deposited adsorbates may destabilize a growing vicinal surface. The kinetic and energetic couplings between adsorbate atoms and adatoms were shown to have competing effects. Impurities which slow down the adatom diffusion without affecting adatom binding energies (random barriers) generically cause step bunching. When the impurities act as random traps, and provided the attachment rates at the steps are not modified by the impurities (type I boundary conditions), the net result of the two effects was found to be destabilizing for impurities that bind adatoms more weakly than the substrate. This is consistent with the simulations of SiC growth (8) that inspired the present study. However, the precise cancellation of the two effects for type II boundary conditions also suggests that predicting the stability of the surface may be difficult if the details of the adsorbate-adatom-interaction are not known.

The observation that barrier-like and trap-like impurities may have qualitatively different effects on the stability of a growing surface, because they affect the symmetry of the surface diffusion process in different ways, was made previously in the context of growth on singular surfaces (4). It is interesting to note that also in this case the barrier-like impurities induce a downhill diffusion bias, favoring attachment to the descending step, through a mechanism that however does not involve any impurity concentration gradient.

Future work should address the competition between the impurity-induced instability and the stabilizing effect of conventional step edge barriers (3). Going beyond the linear stability analysis presented here will be difficult because the dynamics becomes nonlocal in time when
the impurity profile is nonstationary \[7\]. Further underpinning for the proposed mechanism from KMC simulations would therefore be highly desirable.

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