

New Instability in Molecular Beam Epitaxy

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A new, step bunching instability in the growth of stepped surfaces by molecular beam epitaxy MBE is described. It is produced by an elastic mechanism, and is different from the instability discovered by Asaro and Tiller and by Grinfeld. Unlike the Asaro-Tiller-Grinfeld instability (which is expected to occur only under very low fluxes), the present instability can occur or not, according to the nature of the substrate. This instability is likely to be offset by step barrier asymmetry in many materials.

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Semiconducting devices are usually prepared by molecular beam epitaxy (MBE). The materials which are grown are crystals limited by a surface (Fig. 1) very close to a high symmetry orientation (generally 001). The preferred type of growth is step flow, i.e., all steps have the same uniform velocity, due to sticking of diffusing adatoms.

However, instabilities of the step flow motion are frequently observed [1]. A possible cause of instability is the long range, elastic interaction between the adatoms and the rest of the material. The best-known elastic instability is the Grinfeld mechanism [2,3,4], which is briefly recounted below. The driving force of that instability is proportional to the square $(\delta a)^2$ of the natural misfit δa between the lattice constants of the substrate and the adsorbate. We are going to describe here a new, differ-

ent instability for which the driving force is proportional to δa .

Let the mechanism of elastic interaction be recalled first for an adatom on a high symmetry surface. One can distinguish (Fig. 2) the “broken bond mechanism” and the “misfit mechanism.” The former occurs even if the adatom is of the same chemical species as the substrate. It is described by Fig. 2(a) in the case of central, pairwise interactions between nearest and next-nearest neighbors, but the effect is general. An isolated adatom is seen to exert forces \mathbf{f}_R on the other atoms, the location of which is designated by \mathbf{R} . The total force is zero at equilibrium, but the dipole moments

$$m_{\alpha\gamma} = \sum_R R_\alpha f_R^\gamma \tag{1}$$

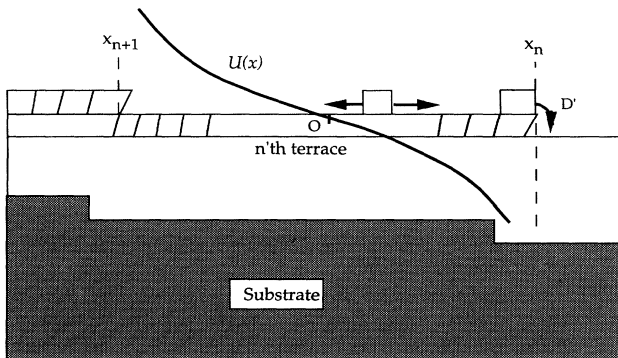


FIG. 1. A stepped surface grown by MBE. Because of elasticity, the freshly landed adatom is attracted to the upper or to the lower terrace. In the former case, which is illustrated, the step flow is unstable with respect to step bunching. In this case $\delta a > 0$, i.e., adsorbed atoms bigger than substrate atoms, then the incorporated atoms are expanded on the higher side of a step and contracted on the lower side. So, if the quantity m (related to the broken bond mechanism of Fig. 2) is positive, an adatom is attracted to the right and eventually goes downstairs. For larger δa , the misfit effect of an isolated atom may become important, and the usual Grinfeld effect results. The curve shows the energy of an adatom as given by (15).

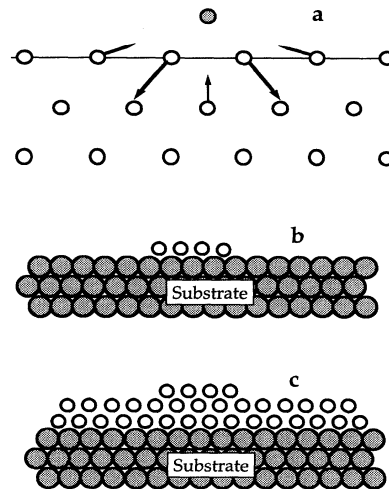


FIG. 2. (a) The broken bond mechanism, represented in the special case of pairwise interactions between nearest and next-nearest neighbor atoms. The adatom exerts a force dipole tensor on the rest of the crystal. (b) The misfit mechanism: smaller adatoms apply a negative stress on the substrate. (c) This mechanism also works through one or several layers of smaller atoms. For bigger adatoms the stress would of course be positive.

are not zero if $\alpha = \gamma$. If the x and y axes are chosen parallel to the surface, symmetry imposes $m_{xx} = m_{yy} = m$.

At a long distance r of an atom, the strain induced by this atom in a given direction is proportional to $1/r^3$ and to the dipole moment m . Quadrupolar and higher effects will be neglected.

The broken bond effect is not additive: For instance, if many adatoms form a cluster, the resulting strain is not obtained by attributing the dipole moment of an isolated atom to each atom of the cluster. Actually, the stress exerted by a large terrace on the rest of the crystal (in the absence of misfit) is localized near the ledge (Fig. 3), so that the elastic effect of a terrace is that of a distribution of force dipoles along its edge [5].

The other mechanism, or misfit mechanism, results from the fact that the adatoms would like to have an interatomic distance different from that of the substrate [(Fig. 2(b)]. This effect is additive, i.e., proportional to the size and the thickness of terraces. However, if the substrate is infinitely deep, the stress exerted by complete layers does not need to be taken into account, because they have no effect, since the size of these layers is fixed by the substrate. The stress per atom is [2,3,4]

$$\eta_{\alpha\gamma} = \frac{\delta a}{a} \frac{E}{1-\sigma} (\delta_{x\alpha} + \delta_{y\alpha}) \delta_{\alpha\gamma}, \quad (2)$$

where σ is the Poisson coefficient, E is Young's modulus, and a positive value of δa corresponds to adsorbate atoms bigger than substrate atoms.

In the case of heteroepitaxy, addressed in this Letter, the misfit mechanism dominates the elastic effect of a large terrace, at least far from its edge. On the other hand, for an isolated adatom, the broken bond mechanism dominates. Thus, the elastic energy of an adatom on a stepped surface is dominated by the misfit effect of the terraces and the broken bond effect of the adatom. The stress associated with both mechanisms may have the same sign or different signs, according to the sign of δa . As will now be argued, the elastic effect is destabilizing in the former case and stabilizing in the latter case, in contrast with the Asaro-Tiller-Grinfeld (ATG) instability [2,3,4] which takes place for any sign of δa . The argument is the following. If the stress associated with both mechanisms has the same sign (Fig. 1) an adatom is attracted to the downward edge

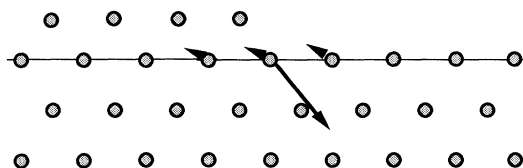


FIG. 3. Forces applied by an extra half layer on the rest of the crystal, assuming the latter to be rigid. Pairwise interactions between nearest and next-nearest neighbor atoms are assumed. The forces are localized near the terrace edge; their sum is zero, but their dipole moment is not.

of its terrace, where it does not feel the substrate very much. From there, it jumps more easily to the lower terrace. Thus, atoms go preferably to the lower terrace. It results that broad terraces become broader—an obviously destabilizing effect. Conversely, if the stress associated with both mechanisms has the opposite sign and an adatom is attracted to the upper end of its terrace, a broad terrace becomes narrower (as in the usual step barrier asymmetry effect [6,7]) and this is stabilizing.

These qualitative ideas will now be applied in a quantitative form to step flow growth. Freshly landed atoms (“adatoms”) diffuse on high symmetry surfaces (Fig. 1) until they meet a step. Then the incorporation is irreversible. The crucial point is whether an adatom goes to the upper or to the lower ledge. This depends partly on the elastic interaction between this atom and the steps, and a qualitative discussion may be restricted to the two steps which bound the terrace where the adatom has landed. The discussion will be restricted to terrace widths much broader than the atomic distance. It differs from the work of Spencer *et al.* [8] where the atomic nature of matter is not taken into account.

We will investigate the linear stability of a regular array of straight, parallel steps. The position x_n of the n th step (labeled as shown by Fig. 1) satisfies

$$\frac{d}{dt} x_n(t) = (D_{n-1}''/a) [p_{n-1}(-l_{n-1}/2, t) - p_{n-1}^-] + (D_n'/a) [p_n(l_n/2, t) - p_n^+], \quad (3)$$

where $l_n = x_n - x_{n+1}$, $p_n(x, t)$ is the adatom density on the n th terrace at time t , a is the atomic distance, D_n''/a is the probability per unit time for an adatom near an upward step to stick to that edge, D_n'/a is the same probability for a downward step, $D_n' p_n^+/a$ is the probability of detachment of an atom per unit time from the n th step to the upper terrace, and $D_{n-1}'' p_{n-1}^-/a$ is the probability of detachment of an atom per unit time from the same step to the lower terrace. The quantities p_n^+ and p_{n-1}^- are close to the equilibrium density of adatoms p_0 on a flat surface, with a small local correction due to elasticity. It will be assumed that the beam intensity F is so high that the adatom density is much larger than p_0 , which will be neglected as well as p^+ and p^- throughout this Letter. The middle of each terrace is taken as origin for this terrace. The step barrier asymmetry [6] is generally such that $D_n' < D_n''$.

The next task is to write the equation of motion for $p_n(x, t)$. It is convenient to introduce the current of adatoms $J_n(x, t)$ and the beam intensity F . Assuming the time variation of this probability to be very slow in comparison with adatom motion, a conservation equation can be written in a stationary form,

$$\frac{\partial}{\partial t} p_n(x, t) = -\frac{\partial}{\partial x} J_n(x, t) + F = 0. \quad (4)$$

From now on, the time dependence of p and J will be ignored. Integration of (4) shows that the quantity

$$A_n = J_n(x) - Fx \quad (5a)$$

is independent of x on any terrace n . On the other hand, the current is related to the density by the Einstein-Fokker-Planck equation [9]

$$J_n(x) = -D \left[\frac{\partial p_n}{\partial x} + \frac{p_n(x)}{k_B T} \frac{\partial U}{\partial x} \right], \quad (5b)$$

where D is the diffusion constant, and U is the energy of an adatom at point x and depends on the elastic mechanisms described above. It will be evaluated later. A boundary condition for $x = l_n/2$ is obtained by writing that the sticking rate is, on one hand, equal to the absolute value of the current, and, on the other hand, proportional to the adatom density:

$$J_n(l_n/2) = (D'_n/a)p_n(l_n/2) = A_n + Fl_n/2. \quad (5c)$$

Similarly, for $x = -l_n/2$:

$$J_n(-l_n/2) = -(D''_n/a)p_n(-l_n/2) = A_n - Fl_n/2. \quad (5d)$$

The current J_n can be eliminated between (5a) and (5b) and the resulting differential equation in $p_n(x)$ can be integrated. The integration constant and A_n can be deduced from (5c) and (5d).

Before doing that, we now come back to Eq. (3). It implies the following equation for large values of $l_n = x_n - x_{n+1}$:

$$\begin{aligned} \frac{dl_n}{dt} = & (l_{n-1} - l_n) \frac{d}{dl} [D''p(-l/2)] \\ & + (l_n - l_{n+1}) \frac{d}{dl} [D'p(l/2)], \end{aligned} \quad (6)$$

or, according to (5c) and (5d),

$$\left(\frac{\partial l}{\partial t} \right)_n = -F \left(\frac{\partial l}{\partial n} \right)_t - \frac{dA}{dl} \left(\frac{\partial^2 l}{\partial n^2} \right)_t. \quad (7)$$

The nearly uniform solution of (7) is $l_n(t) = l_0 + \varepsilon \cos[k(n - Ft)] \exp(dA/dl k^2 t)$. The condition of stability of the step flow regime is therefore $dA/dl < 0$. Now, one has to calculate dA/dl from Eqs. (5). Eliminating J_n between (5a) and (5b) and integrating, one obtains

$$\begin{aligned} p_n(x) = & p_n(-l/2) \exp \frac{U(-l/2) - U(x)}{K_B T} \\ & - \int_{-l/2}^x \frac{dy}{D} (Fy + A) \exp \frac{U(y) - U(x)}{K_B T}, \end{aligned} \quad (8)$$

where $l = l_n$. The function $A(l) = A_n$ can be evaluated by replacing x by $l/2$ in (8) and eliminating $p(l/2)$ and $p(-l/2)$ by means of (5c) and (5d). The result is

$$\begin{aligned} A + Fl/2 = & \frac{D'}{D''} [-A + Fl/2] \exp \frac{U(-l/2) - U(l/2)}{K_B T} \\ & - \frac{D'}{a} \int_{-l/2}^{l/2} \frac{dy}{D} (Fy + A) \exp \frac{U(y) - U(l/2)}{K_B T}. \end{aligned} \quad (9)$$

It will now be assumed that (i) elastic energies are much smaller than $K_B T = 1/\beta$, and (ii) l/a is large with

respect to D/D' , and therefore with respect to 1. Only the terms of highest order in l among the terms of order β , and the terms of the two highest orders in l among the terms of order 0 in β , will be retained. Under these assumptions and after differentiation, formula (9) yields, to first order in β :

$$\begin{aligned} \frac{dA}{dl} = & - \frac{Fa^2}{2l^2} \left(\frac{D^2}{D'^2} - \frac{D^2}{D''^2} \right) \\ & - \beta F \frac{d}{dl} \left(\frac{1}{l} \int_{-l/2}^{l/2} yU(y) dy \right), \end{aligned} \quad (10)$$

where U is assumed to be an odd function in agreement with formula (11) below.

The final step is the evaluation of the energy $U(x)$. This has to be done, as explained at the beginning, under the assumption [5,10–12] that adatoms and steps can be represented as force dipoles acting on a *plane* surface. For straight steps parallel to the y axis, the nonvanishing elements of the force dipole moment per unit length are m_{xx} , m_{xz} , m_{zz} , and m_{zx} . However, it can be checked that the interaction of the last two components with dipole components of the type m_{xx} , m_{yy} , and m_{zz} (the nonvanishing elements of the force dipole corresponding to an adatom) is purely local and can therefore be neglected at long distances. It is therefore sufficient to associate to a step parallel to the y axis force the dipole components per unit length m_{xx} and m_{xz} [9]. However, it can be shown that the interaction of m_{xz} with m_{zz} is purely local and that the interaction of m_{xz} with a dipole of type m_{xx} at a distance r decays as $1/r^4$ and is therefore negligible with respect to the interaction between two dipoles of type m_{xx} . Summing the various contributions, taking only nearest steps into account (a qualitatively correct approximation) and using (2), one obtains for large l

$$U(x) = \frac{2m}{\pi} \frac{\delta a}{a} (1 + \sigma) \left(\frac{1}{x + l/2} - \frac{1}{l/2 - x} \right), \quad (11)$$

where m is the value of $m_{xx} = m_{yy}$ for an isolated adatom, σ is the Poisson coefficient, and E is Young's modulus. In formula (11), only the misfit mechanism of the terraces, which dominates at long distances, has been taken into account.

Insertion of (11) into (10) yields

$$\frac{dA}{dl} = - \frac{Fa^2}{2l^2} \left(\frac{D^2}{D'^2} - \frac{D^2}{D''^2} \right) + (1 + \sigma) \frac{2m}{\pi} \frac{\delta a}{a} \frac{\beta F}{l}. \quad (12)$$

As argued above, an instability appears if $dA/dl > 0$, or alternatively if the product $m\delta a$ is positive, when l is larger than l_c , with

$$l_c = \frac{\pi a}{4m} \frac{K_B T}{1 + \sigma} \left(\frac{D^2}{D'^2} - \frac{D^2}{D''^2} \right) \frac{a}{\delta a}. \quad (13)$$

For lower values of l , the step barrier asymmetry effect stabilizes step flow.

If all steps are taken into account, and not only the nearest ones, the second term of the right-hand side of (12) is multiplied by 2. Then l_c is half the value (13).

We now give a rough evaluation of the parameters which appear in (16). Assuming $D' = D \exp(-T_0/T)$, the value $T_0 = 2000$ K found for W(110) [13] can be accepted in a typical metal. Then, at a temperature of 900 K, the ratio D/D' is about $D/D' = \exp(\frac{2000}{900}) = 9.2$, and we assume that $D/D'' \approx 1$. An order of magnitude of m may be obtained, assuming a pair potential between nearest and next-nearest neighbors [(Fig. 2(a)); m is then found to be about 0.07 times the cohesion energy W_{coh} . A value of $\delta a/a$ of 1% is plausible for coherent growth. Assuming $W_{\text{coh}}/K_B = 35\,000$ K, l_c is found to be several thousands of interatomic distances at 900 K. This is much larger than usual distances between steps. We conclude that step bunching is generally made impossible by the step barrier asymmetry. Note that, if there is no step barrier asymmetry effect and if $m\delta a$ is positive, the step bunching instability always occurs. It never occurs if $m\delta a$ is negative, and $m\delta a$ depends, for a given adsorbate, on the nature of the substrate. The present effect (instability if $m\delta a > 0$, stabilization if $m\delta a < 0$) dominates the ATG instability, because the driving force (11) is of order δa instead of δa^2 as in the ATG instability. This is not true for $F = 0$ or for weak flux, when our treatment fails to describe the tendency to thermal equilibrium and the ATG instability. However, it is also proportional to F . In weak flux, our treatment fails because the quantities p^+ and p^- cannot be neglected in (3). A more careful treatment (to be published) yields an additional term in (12), which is independent of F , but proportional to δa^2 and negligible if F is not too small.

To conclude, mechanisms which have been ignored in this Letter will be briefly discussed. Step flow can also be destabilized by formation of islands between steps. In

that case, the step-adatom interaction by the broken bond mechanism (neglected above) may be important. If the flux F is lowered, the adatom density decreases, and this reduces the island formation rate. However, if F is too low, the kinetic instability described here is dominated by the usual ATG instability as pointed out above. A final remark is the possibility of instability with respect to step distortion has not been taken into account although it is known to be important [14].

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