

ELASTICITY-DRIVEN INSTABILITY IN MOLECULAR BEAM
EPITAXY¹Christophe Dupont[†], Philippe Nozières[‡], Jacques Villain[†][†]CEA, Département de Recherche Fondamentale sur la Matière Condensée,
SPSMS, MDN, CENG, 17 rue des Martyrs, F-38054 Grenoble Cédex 9, France[‡]Institut Laue-Langevin, Grenoble, France

Received 14 April 1994, accepted 2 May 1994

A new, step bunching instability in growth of stepped surfaces by molecular beam epitaxy (MBE) is described. It is produced by the elastic interaction between steps and adatoms. The local strain due to an adatom is mainly due to broken bonds and the local strain due to a step is mainly due to the natural misfit with the substrate. Depending on whether the two strains have the same sign or not, the instability takes place or not. This is in contrast with the instability discovered by Asaro and Tiller and by Grinfeld, which depends only on the misfit mechanism, and which in principle always takes place if the growth rate is slow enough. In practice, the Schwoebel effect (asymmetric sticking at steps) is probably sufficient to stabilize step flow in most cases.

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 all the same uniform velocity, due to sticking of diffusing adatoms.

However, instabilities of the step flow motion are frequently observed. 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 [1,2,3], the mechanism of which is briefly recalled below. The driving force of that instability is proportional to the square δa^2 of the natural misfit δa between the lattice constants of the substrate and the adsorbate. We are going to describe here a new, different instability for which the driving force is proportional to δa .

Let the mechanism of elastic interaction be recalled first for a single 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 neighbours, but the effect is of

¹Invited lecture at MECO (Middle European CoOperation) 19, Smolenice, Slovakia, April 11-15, 1994

course general. An isolated adatom is seen to exert forces \vec{f}_R on the other atoms, the location of which is designated by R . The total force is zero at equilibrium, but the dipole moments

$$m_{\alpha\gamma} = \sum_R R_{\alpha} f_{\gamma}^R \quad (1)$$

are not equal to 0 if $\alpha = \gamma$. If the x and y axes are chosen parallel to the surface, symmetry imposes

$$m_{xx} = m_{yy} = m \quad (2)$$

At a long distance r of an atom, the strain induced by this atom depends only on the dipole moment, and is proportional to $1/r^3$ for a given direction and a given dipole moment. Quadrupolar and higher effects will be neglected, as is correct if the distance between steps is large.

The broken bond effect is not additive: for instance, if many adatoms form a half-monolayer, the resulting strain is not obtained by attributing to each atom of the half-monolayer the dipole moment of an isolated adatom. Indeed the stress exerted by the half monolayer on the rest of the crystal (hereafter called "substrate") can be approximately evaluated by neglecting the elastic strain of the substrate (Fig. 3). If the half-monolayer is at equilibrium, the forces exerted by the substrate on the half-monolayer decay exponentially with the distance to the boundary, and the force per unit length of boundary is zero. From the action and reaction principle, it is seen that the forces exerted on the substrate by the half-monolayer is also localised near the step, and the force per unit length of boundary is zero. Therefore the elastic effect of half-monolayer, or more generally a terrace, is that of a distribution of force dipoles along its edge.

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, in that sense that the stress exerted by a large terrace is uniform at long distance from the edge, and that the stress exerted by n terraces is n times the stress exerted by one terrace. 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 [1,2,3]

$$\eta_{\alpha\gamma} = \frac{\delta a}{a} \frac{E}{1-\sigma} (\delta_{\alpha\alpha} + \delta_{\gamma\alpha}) \delta_{\alpha\gamma} \quad (3)$$

where a positive value of δa corresponds to adsorbate atoms bigger than substrate atoms.

If there is a substrate, 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 to the misfit effect of 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 Grinfeld instability [1,2,3] which takes place for any sign of δa .

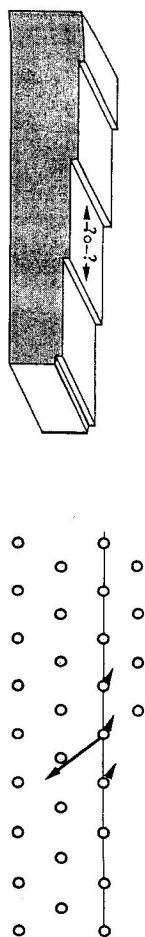


Fig. 1. A stepped surface grown by M.B.E. Due to elasticity, the freshly landed adatom is attracted to the the upper terrace or to the lower terrace. In the former case, the step flow is unstable with respect to step bunching.

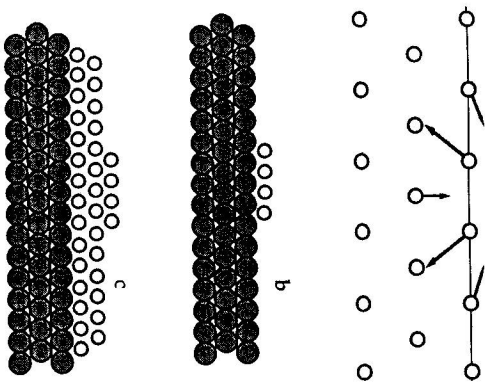


Fig. 2. a) The broken bond mechanism, represented in the special case of pairwise interactions between nearest and next-nearest neighbour atoms. The adatom exerts on the rest of the crystal a force dipole tensor, the nonvanishing components of which are $m_{xx} = m_{yy}$ and m_{zz} (all negative in the present case). b) The misfit mechanism: smaller adatoms apply a negative stress on the substrate. This mechanism also works through one or several layers of smaller atoms (c). For bigger adatoms the stress would of course be positive.

The argument is the following. Assume first that the stresses associated to both mechanisms (i.e. m and δa) have the same sign, for instance (Fig. 4 a) adatoms favor an expansion of the substrate ($m > 0$) and the substrate itself would like to expand with respect to the substrate ($\delta a > 0$) then an adatom is attracted to the outer edge of its terrace, where expansion is less efficiently hindered by the substrate. From there, it jumps more easily to the lower terrace. Thus, atoms go preferably to the lower terrace. The same occurs if both m and δa are negative. It results that broad terraces become broader - an obviously destabilizing effect. Conversely, if the stress associated to both mechanisms have opposite signs an adatom is attracted to the upper end of its terrace, a broad terrace becomes narrower (as in the usual so-called Schwoebel effect [4,5]) 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 takes place irreversibly. The crucial

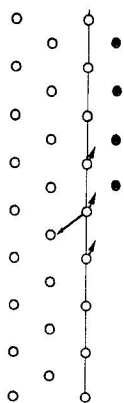


Fig. 3. Forces applied by an extra half-layer on the rest of the crystal, assuming the latter to be rigid. Pairwise interactions between nearest and next-nearest neighbour atoms are assumed. The forces are localized near the terrace edge, their sum is zero, but their dipole moment is not.

point is whether an adatom goes to the upper ledge 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 distances. The present model is different from that of Spencer et al [6] which ignores the atomic structure of matter, and does not seem to be appropriate in usual MBE growth.

We wish to investigate the linear stability of a regular array of steps. For this purpose, we write the time derivative of the width l_n of the n 'th terrace as

$$\frac{dl_n}{dt} = -D_n P_{-M,n} + D_{n-1} P_{-M,n-1} + D'_n P_{M,n} - D'_{n+1} P_{M,n+1} \quad (4)$$

where $P_{q,n}(t)$ is the probability per site to have an adatom on the q 'th atomic row of the n 'th terrace at time t . $q = 0$ corresponds to the middle of each terrace, and $M = l_n/2 - 1$ and $-M$ correspond to the terrace edges (Fig. 4 b). D_n is the probability per unit time for an adatom near an upward step to stick that edge, and D'_n is the same probability for a downward step. D_n and D'_n may depend on n if the terrace widths are slightly different. The fact that D'_n may be different from D_n (even for equal widths) characterizes the so-called Schwoebel effect [4].

The next task is to write the equation of motion for $P_{q,n}(t)$. Assuming the time variation of this probability to be very slow in comparison with adatom motion, a master equation can be written in a stationary form, namely

$$\frac{d}{dt} P_{q,n} = \gamma_{q,n}^{q-1} P_{q-1,n} - (\gamma_{q-1,n}^q + \gamma_{q+1,n}^q) P_{q,n} + \gamma_{q,n}^{q+1} P_{q+1,n} + F = 0 \quad (5)$$

Here, F is the beam intensity and $\gamma_{q,n}^q$ is the probability per unit time to jump from the row q' of the terrace n to the row q of the same terrace. It results from (3) that the quantity

$$\gamma_{q+1,n}^{q+1} P_{q,n} - \gamma_{q,n}^{q+1} P_{q+1,n} - F^q = -J_n \quad (6a)$$

is independent of q on any terrace n . On the edges of a terrace, one of the γ 's vanishes because unsticking is neglected, and equation (6 a) is to be replaced respectively for $q = M = l_n/2 - 1$ by

$$D' P_{M,n} - F l_n/2 + F = -J_n \quad (6b)$$

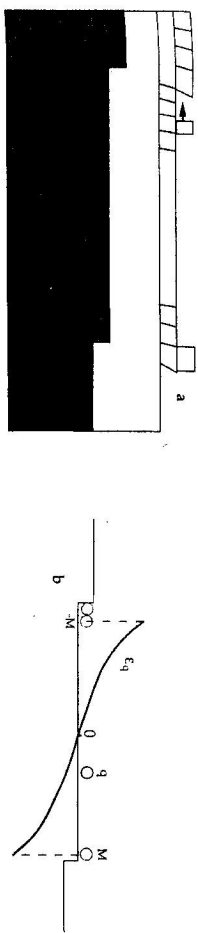


Fig. 4. a) Schematic sketch showing destabilization when m and δa have identical signs (in the case $\delta a > 0$, i.e. adsorbed atoms bigger than substrate atoms). The incorporated atoms are expanded on the higher side of a step, and contracted on the lower side. Consequently, if the quantity m (related to the broken bond mechanism of Fig. 2) is positive, an adatom is attracted to the right and eventually goes downstairs. If $m < 0$, the adatom is attracted to the upper terrace. For larger δa , the misfit effect of an isolated atom may become important, and the usual Grinfeld effect results. b) Labelling the adatom positions. The curve shows the energy of an adatom as given by (18).

and for $q = -M$ by

$$-D_n P_{-M,n} + F l_n/2 = -J_n \quad (6c)$$

We now come back to equation (4). For broad terraces, it may be approximately written as

$$\frac{dl_n}{dt} = (l_{n-1} - l_n) \frac{d}{dt} (D P_{-M}) + (l_n - l_{n+1}) \frac{d}{dt} (D' P_M)$$

or, using (3.b) and (3.c):

$$\frac{dl_n}{dt} = (l_{n-1} - l_n) \left[\frac{F}{2} + \frac{dJ}{dt} \right] (l_n - l_{n+1}) \left[\frac{F}{2} - \frac{dJ}{dt} \right] \quad (7)$$

For large l , (7) may be approximately written as

$$\left(\frac{\partial l}{\partial t} \right)_n = -F \left(\frac{\partial l}{\partial n} \right)_t \frac{dJ}{dt} \left(\frac{\partial^2 l}{\partial^2 n} \right)_t \quad (8)$$

It is convenient to make the change of variable $u = n - Ft$, so that (8) reads

$$\left(\frac{\partial l}{\partial t} \right)_u = \frac{dJ}{dl} \left(\frac{\partial^2 l}{\partial^2 u} \right)_t \quad (9)$$

One can now check the stability of the step flow regime with respect to step bunching. We assume that the profile is: $l_u = l_0 + \varphi(t) \cos(ku)$, with $l_0 \gg \varphi(t)$. Equation (9) yields

$$\frac{d\varphi}{dt} = -k^2 \frac{dJ}{dl} \varphi$$

The step flow is stable if the perturbation φ relaxes to zero. The condition of stability is therefore

$$\frac{\partial J}{\partial l} > 0 \quad (10)$$

In order to make this condition explicit, one has to calculate dJ/dl by solving the set of $(2M+1)$ linear equations (6), where the unknowns are the P_q 's and J . The value of J obtained by standard methods is given by

$$\begin{aligned} (J/D) \exp[\beta(\varepsilon_{-M} - \varepsilon_M)] + J \sum_{q=1}^{2M} \frac{1}{\gamma_{-M+q}^{2M+q}} \exp[\beta(\varepsilon_{-M+q} - \varepsilon_M)] \\ + F \frac{M+1}{D} \exp[\beta(\varepsilon_{-M} - \varepsilon_M)] + F \sum_{q=1}^{2M} \frac{M-q+1}{\gamma_{-M+q}^{2M+q}} \exp[\beta(\varepsilon_{-M+q} - \varepsilon_M)] \\ = (FM - J)/D' \end{aligned} \quad (11)$$

where ε_q is the interaction free energy of an adatom at position q . The detailed balance condition

$$\gamma_q^{q-1} \exp[-\beta \varepsilon_{q-1}] = \gamma_{q-1}^q \exp[-\beta \varepsilon_q] \quad (12)$$

has been taken into account. It will now be assumed that

$$\gamma_{m'}^m = \frac{2D}{1 + \exp[\beta(\varepsilon_{m'} - \varepsilon_m)]} \quad (13)$$

It results from (11) and (13) that

$$\begin{aligned} \frac{J}{D} \left[\sum_{q=0}^{2M} \exp[\beta(\varepsilon_{-M+q} - \varepsilon_M)] + \frac{1}{2} \{ \exp[\beta(\varepsilon_{-M} - \varepsilon_M)] - 1 \} \right] + \frac{J}{D'} = \frac{FM}{D'} \\ - \frac{F}{D} \left[\sum_{q=0}^{2M} (M-q+1/2) \exp[\beta(\varepsilon_{-M+q} - \varepsilon_M)] + \frac{1}{2} \{ (M+1) \exp[\beta(\varepsilon_{-M} - \varepsilon_M)] + M \} \right] \end{aligned} \quad (14)$$

It will be assumed that, for any q , elastic energies are much smaller than $k_B T = 1/\beta$:

$$\beta |\varepsilon_{-M+q} - \varepsilon_M| \ll 1 \quad (15)$$

Moreover, as will be seen later, the case of interest is when M is large with respect to D/D' , and therefore with respect to 1. Only the terms of highest order in M among the terms of order β , and the terms of the two highest orders in M among the terms of order 0 in β , will be retained. Under these assumptions, formula (14) reads, to first order in β :

$$J = F \left(\frac{D}{2D'} - 1 \right) - \frac{F}{2M} \left(\frac{D^2}{2D'^2} - \frac{D}{2D'} \right) - \frac{\beta F}{2M} \sum_{q=0}^{2M} [M-q] \varepsilon_{-M+q} \quad (16)$$

The final step is the evaluation of the energy ε_q . This has to be done, as explained at the beginning, under the assumption [7,8,9,10] 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} , 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} , m_{zz} (the nonvanishing elements of the force dipole corresponding to an adatom) is purely local and can therefore be neglected. 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} [8]. However, it can be shown that the interaction of m_{xz} with m_{zz} is purely local and that the interaction of m_{xx} with a dipole of type m_{xz} at distance r decays as r^{-4} , and can therefore be neglected in comparison with the interaction between two dipoles of type m_{xx} . Summing the various contributions and taking only nearest steps into account (a qualitatively correct approximation) one obtains for large M

$$\varepsilon_q = C [(q+M+3a/2)^{-1} - (M-q+a/2)^{-1}] \quad (17)$$

where

$$C = \frac{2m \delta a}{\pi} (1 + \sigma) \quad (18)$$

a is the atomic distance to the surface, m is the value of $m_{xx} = m_{yy}$ for an isolated adatom, σ is the Poisson coefficient and E is the Young modulus. Relation (3) has been used.

In formula (17), only the misfit mechanism of the terraces, which dominates at long distances has been taken into account.

Insertion of (17) into (16) yields

$$J = F \left(\frac{D}{2D'} - 1 \right) - \frac{F}{2M} \left(\frac{D^2}{2D'^2} - \frac{D}{2D'} \right) - \beta F \sum_{q=0}^{2M} \frac{C}{q+3a/2} + 2\beta F$$

and the derivative, to be inserted into (10), is

$$\frac{dJ}{dM} = 2 \frac{dJ}{dL} = \frac{F}{2M^2} \left(\frac{D^2}{2D'^2} - \frac{D}{2D'} \right) - \frac{\beta FC}{M} = \frac{F}{l^2} \left(\frac{D^2}{D'^2} - \frac{D}{D'} \right) - \frac{2\beta FC}{l} \quad (19)$$

Insertion into (10) shows that an instability appears if C is positive and large enough, when l is larger than l_c , with

$$l_c \approx \frac{\pi k_B T}{4m(1+\sigma)} \left(\frac{D^2}{D'^2} - \frac{D}{D'} \right) \frac{\delta a}{a} \quad (20)$$

where (18) has been used. For lower values of l , the Schwoebel effect stabilizes the step flow.

It is also possible to take into account all the steps and not only the nearest, the second term of the right hand side of (19) becomes $\beta FC/l$. Then l_c is twice the value (20).

We now give a rough evaluation of the values of the parameters which appear in (18). For the activation energy of the Schwoebel effect in a typical metal, the value 2000 K found for $W(110)$ [11] will be accepted. Then, at a temperature of 900K, the ratio D/D' is about $\exp(2000/900) = 9.2$. An order of magnitude of m may be obtained assuming a pair potential between nearest and next-nearest neighbours (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 $W_{coh}/k_B T = 35000$ K, l_c is found to be several thousands of interatomic distances at 900K. This is much larger than usual distances between steps. We conclude that step bunching is generally made impossible by the Schwoebel effect. Note that, if there is no Schwoebel effect and if C is positive, the step bunching instability always occur. It never occurs if C is negative, and C depends, for a given adsorbate, on the nature of the substrate. The present instability dominates the Asaro-Tiller-Grinfeld instability, because the driving force (19) is of order δa instead of δa^2 as in the Asaro-Tiller-Grinfeld instability. This will not be true at very low flux, because adatom detachment from steps has to be taken into account.

To conclude, the importance of mechanisms which have been ignored in this note will be briefly discussed. The step flow may 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, equations (6 b, c) are no longer valid since atoms may have time to detach from steps. Therefore, the island formation rate cannot be reduced beyond a certain limit. A final remark is that the possibility of instability with respect to step distortion has not been taken into account although it is known to be important [12].

References

- [1] Asaro, R.J., Tiller, W.A., *Metallurgical Transactions* 3, 1789 (1972)
- [2] Grinfeld, M.A., *J. Nonlinear Science* Vol. 3, 35 (1983)
- [3] Nozières, P., Lectures at the Beg Rohu Summer School (1989), in "Solids far from equilibrium" C. Godrèche Ed. (Cambridge Univ. Press, 1991) and *J. Phys.* 1, 3, 681 (1993)
- [4] Schwoebel, R.L., *Journal of Applied Physics* 40, 614 (1969).
- [5] Villain, J., *J. Physique* 1, 1, 19 (1991)
- [6] Spencer, B.J., Voorhees, P.W., Davis, S.H., *Phys. Rev. Lett.* 67, 3696 (1991)
- [7] Lau, K.H., Kohn, W., *Surface Science* 65, 607 (1977)
- [8] Marchenko, V.I., Parshin, Ya., *Sov. Phys. JETP* 52 (1) (1980), Andreev, A.F., Kosevich Yu.A., *Sov. Phys. JETP* 54 (4) (1981)
- [9] Van der Merwe, Jan H., Shuttle, G.J., *Surface Science* 256, 171 (1991)
- [10] Solorovitz, D.J., *Acta metal.* 37, 621 (1989); Rickman, J.M., Solorovitz, D.J., *Surface Science* 284, 211 (1993).
- [11] Wang, S.C., Tsong, T.T., *Surface Sci.* 121, 85 (1982)
- [12] Bales, G.S., Zangwill, A., *Phys. Rev.* B41, 5500 (1990)