

Kinetics of surfactant-mediated epitaxial growth

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A kinetic model for surfactant-mediated epitaxial growth is suggested. The surfactant atoms join kinks predominantly at steps as the latter are the energetically most favored sites on the crystal surface. The deposited atoms must displace them in order to join the crystal lattice. This gives rise to additional kinetic barriers the atoms have to overcome when they join the ascending steps. The asymmetry of incorporating atoms in ascending and descending steps is reversed and a diffusion gradient that drives the atoms to join the descending steps appears. The thermodynamic driving force for the two-dimensional–three-dimensional transformation to occur is suppressed and layer-by-layer growth takes place.

It has recently been found that the deposition of 1 ML (or less) of surface-active species (surfactants) before film deposition drastically changes the growth mode of the latter from island (or Stranski-Krastanov) growth to layer-by-layer (LBL) growth.^{1,2} It has been suggested that the surfactant changes the interrelation between the surface energies of the substrate and deposited materials and, in turn, the mode of growth.¹ Further studies of the growth of Si mediated by Sb showed that the mediate suppresses the surface diffusion of the Si adatoms and stimulates the formation of two-dimensional (2D) nuclei.³ van der Vegt *et al.*⁴ found that a submonolayer of Sb deposited on Ag(111) changes the growth mode from ordinary multilayer growth to LBL growth. They suggested that the mediate decreases the barrier for interlayer diffusion.⁴ Similar ideas have been explored by Zhang and Lagally.⁵ On the other hand, in order to explain the low-temperature LBL growth Tersoff, Denier van der Gon, and Tromp⁶ assumed an additional (Schwoebel) barrier, which the atoms have to overcome when joining a descending step. In this paper we show that the effect of the mediate on the mode of growth can be explained by assuming it creates additional kinetic barriers at ascending steps and thus reverses the asymmetry in incorporating adatoms to kinks at ascending and descending steps surrounding the growing 2D islands.

Schwoebel assumed some time ago that incorporating adatoms to kinks is asymmetric, being easier at ascending rather than at descending steps.⁷ Whereas an atom approaching an ascending step joins it upon striking, an atom approaching a descending step has to overcome an additional barrier E_s in order to join a kink at the step⁸ as shown in Fig. 1(a). Detailed measurements in the case of Re, Ir, and W on W(110) (Ref. 9) gave values for E_s varying from 0.15 to 0.2 eV. Wang and Ehrlich¹⁰ reported recently that the barrier height depends on the size of the 2D islands and incorporating an adatom to the descending step can take place by exchange mechanism rather than by rolling over the edge. In particular, they found that when the island is large enough (>20 atoms) the adatoms at the step edge become trapped for some time and prefer to join the step rather than to diffuse backwards. Therefore they proposed the potential diagram shown in Fig. 1(b), in which the last barrier that the atoms have to overcome in order to join the step is shifted

downwards by an amount E_a below the level of the surface diffusion barrier. Thus the last potential trough becomes asymmetric and E_a is a measure of its asymmetry. Moreover, the step becomes attractive rather than repulsive for atoms arriving from the upper terrace.

The presence of a surfactant should change the incorporation asymmetry. The surfactant atoms should predominantly join the kinks at the steps as the latter are the energetically most favored sites on the crystal surface.¹¹ Then the deposited atoms must displace them in order to join the crystal lattice. An atom approaching a descending step can join a kink displacing a mediate atom by the exchange mecha-

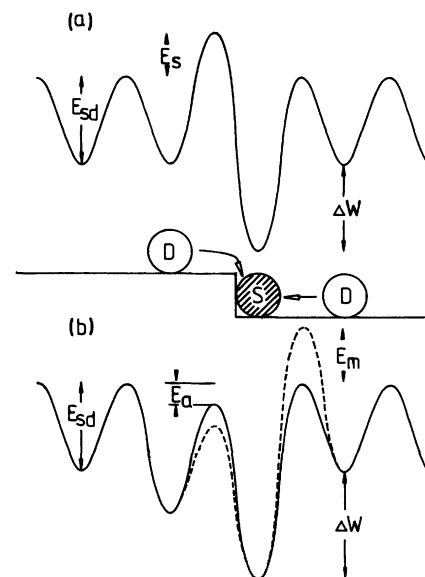


FIG. 1. Schematic potential diagrams for atoms moving toward ascending and descending steps. (a) Traditional view, (b) according to the results of Wang and Ehrlich (the solid line) (Ref. 10); E_s is the Schwoebel barrier. The additional barrier E_m at the ascending step in the presence of a mediate is shown by the dashed line. ΔW is the work to transfer an atom from a kink site at the step on the terrace. Note that the measure of asymmetry E_a is accounted for from the level of the surface diffusion barrier. S and D denote surfactant and deposited atoms, respectively.

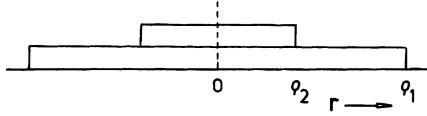


FIG. 2. Pyramid of growth consisting of two monolayer islands with radii ρ_1 and ρ_2 and chemical potentials μ_1 and μ_2 ($\mu_2 < \mu_1$).

nism.¹⁰ One could expect that the Schwoebel barrier will be reduced by an amount $2(U_{DD} - U_{SD})$ ($U_{DD} > U_{SD}$) as shown in Fig. 1(b) by the dashed line.³ Thus the measure of asymmetry E_a will increase. An atom that approaches an ascending step [Fig. 1(b)] should displace a surfactant atom in the same plane. This will give rise to an additional kinetic barrier of amount E_m as shown by the dashed line in Fig. 1(b).¹¹ One can speculate that the additional barrier E_m is of the order of the amount of work to break a bond U_{SD} between a mediate and a deposited atom.

We consider now the kinetics of deposition of the epitaxial films. Atoms strike the substrate surface, accommodate thermally, migrate over the surface, and collide with each other to give rise to 2D nuclei. The latter grow further as 2D islands. Atoms arrive on their surface and an adatom population is formed whose concentration has a maximum value on the middle of the islands.^{12,13} The maximum value of the adatom concentration on top of the 2D islands increases with the square of the island size and at some moment 2D islands of the second monolayer will most probably form around the middle of the lower islands, thus giving rise to flat pyramids of growth as shown in Fig. 2.^{12,13} The upper islands grow at the expense of the atoms arriving on their own surfaces and on the terraces, whereas the lower islands grow at the expense of the atoms on the terraces and the atoms on the surface between the pyramids. Island growth will be observed when the surface transport on the terrace is directed towards the edges of the upper islands.¹³ As a result they will grow faster and will catch up with the steps surrounding the lower islands, thus transforming the pyramids into bilayer (3D) islands. The thermodynamic driving force for the surface transport towards the upper islands' edges is the difference of the chemical potentials of both monolayers.¹³⁻¹⁶ The latter is due to the difference in bonding of the deposited atoms to kink sites at the different steps, on one hand, and to the distribution of the misfit strain, on the other. Such a mechanism of formation of 3D islands was recently observed by Corcoran, Chakarova, and Sieradzki¹⁷ in the case of Stranski-Krastanov growth of Ag on Au(111). LBL growth will be observed when the surface transport on the terrace is directed downwards towards the descending steps surrounding the lower islands. We conclude that it is the *direction of transport* of atoms on the terrace that is responsible for the growth mode^{12,13} rather than the interlayer transport in general.

We consider a pyramid of growth consisting of two 2D islands with radii ρ_1 and ρ_2 , one on top of the other (Fig. 2). We assume that the chemical potential μ_2 of the upper island is smaller than that, μ_1 , of the lower one. In fact, the inequality $\mu_2 < \mu_1$ represents the thermodynamic criterion for island growth.¹³⁻¹⁶ We further assume that adatoms joining a descending step have to overcome a barrier higher than that

for surface diffusion E_{sd} by an amount E_s minus an amount due to the presence of a surfactant as shown in Fig. 1(b). Adatoms that join an ascending step in the absence of surfactant have to overcome only the surface diffusion barrier. In the presence of a mediate an additional amount E_m should be overcome.

The adatom concentration $n_s(r)$ on the terrace in the case of complete condensation (absence of reevaporation) can be found by solving the diffusion equation

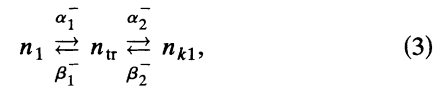
$$\frac{d^2 n_s(r)}{dr^2} + \frac{1}{r} \frac{dn_s(r)}{dr} + \frac{R}{D_s} = 0, \quad (1)$$

where R and $D_s = a^2 \nu \exp(-E_{sd}/kT)$ are the atom arrival rate and the surface diffusion coefficient, respectively. The solution reads

$$n_s(r) = C_1 - \frac{R}{4D_s} r^2 + C_2 \ln(r). \quad (2)$$

The integration constants C_1 and C_2 can be found from the boundary conditions $j_i = \pm D_s [dn_s(r)/dr]_{r=\rho_i}$ ($i=1,2$), with the minus sign referring to $i=1$ (Ref. 7), where j_1 and j_2 are the net fluxes of atoms towards the lower and upper steps. In order to join the upper step the atoms have to make a single jump and $j_2 = \alpha_2^+ n_2 - \beta_2^+ n_{k2}$, where n_2 is the adatom concentration on the terrace in the immediate vicinity of the upper step and n_{k2} is the concentration of detachable atoms at the step, $\alpha_2^+ = a \nu \exp[-(E_{sd} + E_m)/kT]$ and $\beta_2^+ = a \nu \exp[-(\Delta W_2 + E_{sd} + E_m)/kT]$ are the rates of attachment and detachment of atoms to and from the ascending step of the upper island, a and ν are the distance between neighboring adsorption sites and atom vibrational frequency, respectively, and ΔW_2 is the work to transfer an atom from a kink position along the step on the terrace (see Fig. 1).¹⁸

The incorporation of the atoms to the descending step takes place in two consecutive stages,



where n_1 , n_{tr} , and n_{k1} are the concentrations of the atoms in the near vicinity of the step, the atoms trapped in the last potential trough before joining the step, and the atoms detachable from the step. The net flux of atoms is

$$j_1 = \alpha_1^- n_1 - \beta_1^- n_{tr} + \alpha_2^- n_{tr} - \beta_2^- n_{k1}. \quad (4)$$

The condition for steady state is the concentration of the intermediate species $n_{tr} = \text{const}$, or

$$\frac{dn_{tr}}{dt} = 0 = \alpha_1^- n_1 - \beta_1^- n_{tr} - \alpha_2^- n_{tr} + \beta_2^- n_{k1}. \quad (5)$$

Combining (4) and (5) and bearing in mind the potential diagram in Fig. 1(b) for j_1 , one obtains

$$j_1 = 2a \nu \exp(-E_{sd}/kT) [n_1 - n_{k1} \exp(-\Delta W_1/kT)] / (1 + A), \quad (6)$$

where $A = \exp(-E_a/kT)$ is the asymmetry factor and ΔW_1 is the work to transfer an atom from a kink site at the lower step on the terrace.¹⁸ Note that $\Delta W_2 > \Delta W_1$, which is equivalent to $\mu_2 < \mu_1$. Thus ΔW_2 and ΔW_1 account not only for the difference in bonding but also, implicitly, for the misfit strain in the corresponding monolayers.¹⁶ Note that the Schwoebel factor $S = \exp(-E_s/kT)$ does not enter the flux when the potential has the shape shown in Fig. 1(b). If the last potential trough is symmetric, $A = 1$, the flux is exactly equal to the flux j_0 in the absence of Schwoebel effect. In the general case, $E_a \neq 0$ and at low temperatures $A \ll 1$ and $j_1 = 2j_0$.

The adatom concentration on top of the upper island, which is surrounded by a descending step, can only be found by the same way from the solution of Eq. (1), $n_s(r) = C - Rr^2/4D_s$, subject to the corresponding boundary condition for the descending step that surrounds the upper island.

The exact expressions for the adatom concentrations are very cumbersome, so we do not give them; instead, we proceed further and calculate the rates of growth of the 2D islands. In order to calculate the rate of growth $d\rho_1/dt$ of the lower island we have to take into account the flux of adatoms diffusing on the substrate. In the case of complete condensation the mean value of this flux is $j_s = R(1 - \pi\rho_1^2 N_s)/N_s$, where N_s is the density of the pyramids. In other words, we assume that all atoms arriving on the bare substrate are equally distributed among the growing pyramids. Through the substitutions $\Theta_i = \pi\rho_i^2 N_s$ ($i = 1, 2$) and $\tau = Rt/n_0$, where n_0 is the atom density of the substrate surface, a set of equations for the surface coverages, Θ_1 and Θ_2 , of the lower and upper monolayers as a function of the number of monolayers deposited, τ , can be written in the form

$$d\Theta_1/d\tau = 1 - F(\Theta_1, \Theta_2) \quad d\Theta_2/d\tau = F(\Theta_1, \Theta_2) \quad (7)$$

with

$$F(\Theta_1, \Theta_2) = \frac{P + \Theta_1 - \Theta_2 + \frac{Q\sqrt{\Theta_2}}{M} \left[1 + \frac{M}{2}(1+A) \left(\frac{\Theta_1}{\Theta_2} \right)^{1/2} \right]}{\ln \left(\frac{\Theta_1}{\Theta_2} \right) + \frac{Q}{M\sqrt{\Theta_2}} \left[1 + \frac{M}{2}(1+A) \left(\frac{\Theta_2}{\Theta_1} \right)^{1/2} \right]}, \quad (8)$$

where $P = 4\pi D_s N_s (n_1^e - n_2^e)/R$,¹³ $Q = 2(\pi N_s/n_0)^{1/2}$, and $M = \exp(-E_m/kT)$ is the mediate factor.

Note that the parameter P contains the thermodynamic driving force $n_1^e - n_2^e$ for the 2D-3D transformation to occur as the equilibrium adatom concentrations n_1^e and n_2^e ($n_1^e > n_2^e$) are determined by the corresponding chemical potentials through $n_i^e = n_e \exp[(\mu_i - \mu_\infty)/kT]$ ($i = 1, 2$) (Ref. 13), where μ_∞ is the chemical potential of the infinitely large deposit crystal and $n_e = n_0 \exp(-\Delta W/kT)$ is the equilibrium adatom concentration on its surface.¹⁸ The parameter P decreases steeply with decreasing temperature but is always smaller than unity.¹³ On the contrary, the parameter Q increases with decreasing temperature varying from approximately 1×10^{-1} at very low (room) temperatures to $1 \times 10^{-3} - 1 \times 10^{-4}$ at high temperatures.

In the absence of a surfactant $M = 1$. At high temperatures $P = 0.2 - 0.3$, $Q \ll 1$, and $F(\Theta_1, \Theta_2)$ turns into^{12,13}

$$F(\Theta_1, \Theta_2) = (P + \Theta_1 - \Theta_2)/\ln(\Theta_1/\Theta_2). \quad (9)$$

The solution of the system (7) with (9) ($P = 0.25$) is shown in Fig. 3 (curves 1' and 2'). As seen at temperatures high enough so that P is large, the solution for the surface coverage of the first monolayer, Θ_1 , increases initially, displays a maximum, and decreases. This means that at some stage of growth the rate of advance of the first monolayer islands, $d\rho_1/dt$, becomes negative or, in other words, the lower islands decay and the atoms feed the upper islands. The edges of the latter catch up with the edges of the former and islands with double height result. The double steps propagate more slowly than the single steps,¹¹ and after some

time the single steps of the third monolayer islands catch up with the edges of the double-height islands, thus producing islands with triple height. As a result, island growth takes place. At low temperatures $P \ll 1$, $Q \cong 0.1$, and $F(\Theta_1, \Theta_2) \cong (\Theta_1 \Theta_2)^{1/2}$. The solution of (7) (not shown) demonstrates the typical behavior of the multilayer growth: Θ_1 reaches unity when Θ_2 reaches a value of about 0.3. The thermodynamic driving force for the 2D-3D transformation is suppressed and the atoms on the terrace are equally shared between both islands. Planar growth is observed.

In the case of surfactant-mediated growth, $M \neq 1$. At

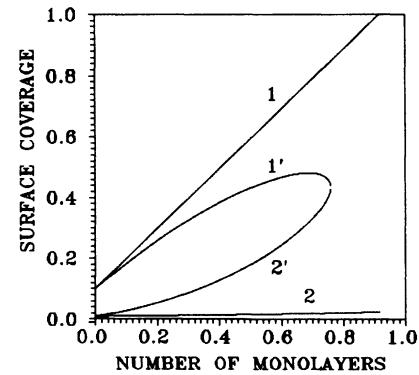


FIG. 3. Dependence of the surface coverages of the first (curves 1 and 1') and second (curves 2 and 2') monolayers on the amount of material deposited measured in the number of monolayers. Curves 1' and 2': growth in the absence of a surfactant or at very high temperature [$F(\Theta_1, \Theta_2)$ is given by Eq. (9)]; curves 1 and 2: surfactant-mediated growth with $F(\Theta_1, \Theta_2) = \Theta_2$ [Eqs. (10)].

very high temperatures $Q \ll 1$ and $M \cong 1$. $F(\Theta_1, \Theta_2)$ is given by Eq. (9) and island growth should be observed irrespective of the presence of the surfactant. As the temperature decreases Q increases and M decreases so that the terms containing Q/M become dominant. Then $F(\Theta_1, \Theta_2) = \Theta_2$ and the solution of Eqs. (7) subject to the initial conditions $\tau = 0$, $\Theta_1 = \Theta_1^0$, and $\Theta_2 = \Theta_2^0$ reads

$$\Theta_1 = \Theta_1^0 + \tau - \Theta_2^0(e^\tau - 1), \quad \Theta_2 = \Theta_2^0 e^\tau. \quad (10)$$

Equations (10) are plotted in Fig. 3 (curves 1 and 2). As seen, Θ_1 reaches unity while Θ_2 is still negligible. The 2D islands grow in a kinetic regime,¹¹ the thermodynamic driving force for the 2D-3D transformation being totally suppressed. The surface transport is directed now in the opposite direction, from the upper to the lower edges. This is due to the fact that the upper step repulses the atoms whereas the lower step attracts them. A diffusion gradient on the terrace appears, which drives the atoms towards the lower step. On one hand, this prevents the transformation of the pyramid to a 3D island. On the other hand, the upper islands in fact grow only at the expense of the atoms adsorbed on their surfaces. They remain small and the nucleation on top of them is also suppressed. As a result, the growth follows a

mode of growth that is nearly LBL due to kinetic reasons. The case of homoepitaxial growth [e.g., Ag/Ag(111)/Sb (Ref. 4)] is treated in the same way with $P = 0$ ($\mu_1 = \mu_2$).

We conclude that the effect of the surfactant for suppression of the island growth can be explained on the basis of the following assumptions: (i) the atoms of the surfactant occupy the kink sites on the crystal surface as they provide the strongest bonding, and (ii) the deposited atoms should displace them in order to join the crystal lattice, which in turn gives rise to an additional energy barrier at ascending steps of a kinetic origin, a fact which is well known in crystal growth,¹¹ and most probably reduces the Schwoebel barrier at descending steps. The descending steps are thus attractive rather than repulsive as believed previously. It should be stressed that the traditional view of the potential diagram as shown in Fig. 1(a) leads in the absence of a surfactant to $F(\Theta_1, \Theta_2) = \Theta_1$ and thus to 3D growth at low temperatures, which contradicts the experimental observations.

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