

Kinetics of nucleation in surfactant-mediated epitaxy

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The theory of atomistic nucleation is developed to account for the presence of surface active species (surfactants) on the crystal surface. A cluster consisting of surfactant atoms is formed on top of the crystal nucleus owing to segregation of the surfactant on the crystal surface. In effect, two factors account for the presence of the surfactant. The first is the decrease of the edge energy of the nucleus owing to the saturation of the dangling bonds at the nucleus periphery by the atoms of the surfactant. The second is the edge energy of the cluster consisting of surfactant atoms. The two factors influence inversely the process of nucleation. The decrease of the nucleus edge energy requires less work for nucleus formation and a smaller number of atoms in the critical nucleus. The edge energy of the surfactant cluster leads to larger work of nucleus formation and a greater number of atoms in the critical nucleus. Thus the presence or absence of a surfactant may result in a different number of atoms in the critical nucleus at one and the same supersaturation. An expression for the nucleation rate is derived and the saturation nucleus density is calculated on the assumption that the latter is determined by overlapping of nucleation exclusion (depleted) zones around the growing nuclei. The work needed for formation of kinks at the steps edges is calculated. It is shown that the latter, as well as the step free energy and the roughening temperature are determined by the surfactant efficiency. That efficiency is defined as the relative difference of the interfacial energy per bond and the energy of the dangling bonds and can be evaluated directly from the slope of an Arrhenius plot of the kink density.

I. INTRODUCTION

Fabrication of devices based on heterojunctions between single-crystal substrates and epitaxial films requires the epitaxial interface to be as smooth as possible. Epitaxial films, however, often grow with formation and growth of isolated three-dimensional (3D) islands either from the very beginning of the deposition (island or Volmer-Weber growth), or after the deposition of several (one, two, or three) monolayers in a layer-by-layer mode (Stranski-Krastanov mechanism). The reason for islanding in the first case is the incomplete wetting of the substrate by the film material. It was expressed by Bauer¹ in terms of interrelation $\sigma_s < \sigma + \sigma_i$ of the specific surface energies of the substrate, σ_s , overgrowth, σ , and the interface, σ_i , respectively. In the second case islanding is caused by the nonzero lattice mismatch of both materials in addition to the complete wetting, $\sigma_s > \sigma + \sigma_i$.¹⁻⁶ It was established long ago that the mode of growth of thin epitaxial films is also strongly affected by the substrate temperature and the deposition rate (for a review see Ref. 6). Islanding is observed in the case of Volmer-Weber or Stranski-Krastanov growth at high temperatures (near-equilibrium conditions) whereas below a certain critical temperature the growth proceeds by consecutive formation of monolayers (layer-by-layer growth) or by simultaneous growth of several monolayers (multilayer growth). In other words, a 2D or planar growth is observed in both cases. However, the as-grown films are unstable and aggregate into 3D islands upon annealing at higher temperatures. Films grown at low temperatures are often of poor quality. They contain many defects and even could be amorphous. That is why using the temperature as a tool to avoid islanding is not a solution to the problem in a series of cases.

According to recent findings the mode of epitaxial growth

is strongly influenced by the presence of a third, surface active element (surfactant). The latter alters the wetting of the substrate by the film and thus suppresses islanding.⁷⁻⁹ Copel *et al.*⁷ established that predeposition of 1 monolayer (ML) of As suppressed islanding in Stranski-Krastanov growth of Ge on Si(001). van der Veegt *et al.*¹⁰ found later that 1 ML of Sb deposited on Ag(111) caused strong oscillations of the x-ray reflection to appear. This showed that Sb changed the growth mode from multilayer growth that is characteristic of homoepitaxial growth to layer-by-layer growth. Rosenfeld *et al.*¹¹ carried out a model study of the Ag/Ag(111) system. They deposited an anomalously high density of nuclei in the absence of a surfactant and showed that the greater the island density the stronger the tendency for layer-by-layer growth was. Voigtländer *et al.*^{12,13} carried out detailed scanning tunneling microscopy (STM) studies of 2D nucleation of Si on a clean Si(111) surface, and in the presence of Ga, In, As, and Sb as surfactants. They found, first, that the saturation island density steeply increased when group-V elements As and especially Sb were used as surfactants. On the contrary, In decreased the number density of the islands. Second, the nucleation exclusion (depleted) zones around the growing islands and the steps decreased in width in the presence of As and Sb, and strongly increased in the case of In. Third, the islands shape and the form of the steps were irregular compared to the triangular shape and straight steps under clean conditions.

It follows from the above that the nucleation plays a prominent role in the kinetics of surfactant-mediated epitaxy. As is well known from the classical theory of nucleation, the adsorption of surface active species decreases the surface energy of the 3D nuclei (or the edge energy of the 2D nuclei). This leads to smaller nuclei, less work for nucleus formation, and higher nucleation rate.¹⁴ However, far from

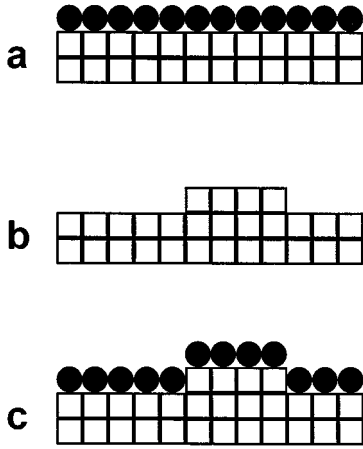


FIG. 1. The calculation of Gibbs free energy for nucleus formation. (a) The initial surface covered with surfactant atoms denoted by filled circles; (b) the surfactant atoms are evaporated and a cluster consisting of i atoms is created; (c) the surfactant atoms are condensed back.

equilibrium the classical theory of nucleation is not applicable as the nuclei consist of a very small number of atoms. Then such macroscopic thermodynamic quantities as specific surface (or edge) energies cannot be applied to describe the process of nucleation. The aim of this paper is to develop the atomistic theory of nucleation, which deals with small clusters of atoms^{15,16} in the case of surfactant-mediated epitaxy. The paper is organized as follows. The work needed for nucleus formation is derived in Sec. II. An expression for the nucleation rate is derived in Sec. III. The saturation nucleus density is considered in Sec. IV assuming that it is determined by overlapping of depleted zones as observed by Voigtländer and Zinner.¹² The calculations are carried out for close-packed crystals with central interatomic forces. The work of formation of kinks along the steps in the presence of a surfactant is calculated in Sec. V. It is shown that measurements of the kink density can be used to determine the value of the energetic parameter, which defines quantitatively the efficiency of the surfactant. The results are discussed in Sec. VI.

II. WORK FOR NUCLEUS FORMATION

The Gibbs free energy for nucleus formation can be easily evaluated by using the following imaginable process (see Fig. 1). The initial state is a surface covered by 1 ML of surfactant (S) atoms [Fig. 1(a)]. First we evaporate all surfactant atoms reversibly and isothermally. Then on the clean surface we produce a cluster consisting of i atoms [Fig. 2(b)]. The Gibbs free energy needed to form a cluster of an arbitrary shape on the clean surface reads (for a review see Ref. 16)

$$\Delta G_0(i) = -i\Delta\mu + \Phi, \quad (1)$$

where $\Delta\mu$ is the supersaturation (the difference of the chemical potentials of the infinitely large ambient and new phases), and Φ is the excess surface (or edge) energy. In case of small supersaturations, when the cluster is large enough,

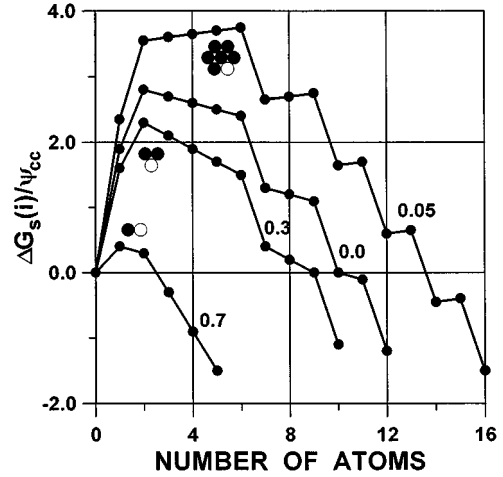


FIG. 2. The change of Gibbs free energy for cluster formation relative to the work needed to disjoin two crystal atoms, $\Delta G_s(i)/\psi_{cc}$, vs the number of atoms on the (111) surface of a fcc crystal. The values of the surfactant efficiency s are denoted by figures at each curve. The structure of the nucleus is given by the filled circles. The empty circles denote the atoms that turn the critical nuclei into stable clusters. The supersaturation $\Delta\mu = 1.1\psi_{cc}$ for all curves. As it could be seen the increase of efficiency of the surfactant leads to a decrease of the critical nucleus size and the work needed for its formation. The only exception is at small values of s at which the edge energy of the surfactant cluster, Φ_s , overcompensates for the decrease of the edge energy of the crystalline cluster. In this case i^* and $\Delta G_s(i^*)$ are larger than in the clean case.

Φ can be expressed in terms of surface, edge, and apex energies. For a cluster of any size and particularly for small clusters the surface energy is expressed in terms of the energy of unsaturated dangling bonds in the form^{16,17}

$$\Phi = iE_k - U(i), \quad (2)$$

where E_k is the energy needed to detach an atom from a kink (or a half-crystal) position¹⁷ (the bulk energy per atom of the crystal) and $U(i)$ is the energy of dissociation of the cluster into single atoms, including also the bonds with the substrate. In fact Φ gives the number of dangling bonds multiplied by the energy, $\psi_{cc}/2$, of one dangling bond [ψ_{cc} is the work needed to disjoin two crystal (C) atoms]. As written above, Φ is equally valid for any 3D or 2D clusters with arbitrary shape and size. In case of 2D clusters Φ gives the energy of the dangling bonds at the periphery of the cluster, or in other words, the edge energy. It is worth noting that E_k and, in turn, the chemical potential of the infinitely large crystal do not depend on the presence of a surfactant on its surface.¹⁴

Finally we condense back all the surfactant atoms [Fig. 1(c)] and for the work of formation of a cluster consisting of i atoms we obtain

$$\Delta G_s(i) = -i\Delta\mu + [iE_k - U(i)](1-s) + \Phi_s, \quad (3)$$

where

$$\Phi_s = [iE_k - U(i)]\alpha_s \quad (4)$$

is the edge energy of the cluster consisting of S atoms formed on top of the crystalline cluster [Fig. 1(c)] assuming that the surfactant cluster has the same size and shape as the crystalline cluster,

$$\alpha_s = \psi_{ss} / \psi_{cc},$$

ψ_{ss} being the work needed to separate two S atoms, and

$$s = 1 - \omega / \omega_0 \quad (5)$$

accounts for the presence of the surfactant where

$$\omega = \frac{1}{2}(\psi_{cc} + \psi_{ss}) - \psi_{sc} \quad (6)$$

and

$$\omega_0 = \psi_{cc}/2 \quad (7)$$

is the energy of a dangling bond. In the above equations ψ_{sc} is the work needed to disjoin a S atom from a C atom.

In fact Eq. (6) represents the relation of Dupré,¹⁸ $\sigma_i = \sigma + \sigma_s - \gamma$, with the specific surface energies, σ , σ_s , σ_i , and the specific adhesion energy, γ , taken per atom. This can be easily verified if we multiply Eq. (6) by the area occupied by one atom. It turns out that the parameter ω represents the interfacial energy per atom. In other words, the energy, $\omega_0 = \psi_{cc}/2$, of the dangling bonds at the cluster periphery under clean conditions is replaced by the smaller interfacial energy per bond ω . The energy -2ω is also the energy per bond gained when an adatom joins the cluster. Note also that in fact ω is the energetic parameter that determines the enthalpy of mixing the two species C and S . It must be positive in order to allow the growth of the crystal and the segregation of the mediate. As will be shown below $\omega > 0$ is the necessary condition for layer growth of the crystal. At $\omega \leq 0$ the crystal surface will be thermodynamically rough and will grow by direct incorporation of atoms to kink sites from the vapor.^{19,20} Moreover, the mediate will tend to mix with the crystal. Therefore, we consider the nucleation process as taking place in a two-dimensional solution on the crystal surface in which the surfactant plays the role of a solvent.

In the absence of a surfactant $\psi_{ss} = \psi_{sc} = 0$, $\omega = \psi_{cc}/2$, and $s = 0$. At the other extreme of complete efficiency of the surfactant ($\psi_{cc} + \psi_{ss})/2 = \psi_{sc}$ and $s = 1$. In general, $(\psi_{cc} + \psi_{ss})/2$ could be smaller than ψ_{sc} , which leads to $s > 1$. However, this means a negative value of ω or a negative enthalpy of mixing. Thus the parameter s varies from 0 at complete inefficiency to 1 at complete efficiency and is always positive. We call the parameter s a *surfactant efficiency*. It could be calculated on the basis of thermodynamic data but, as will be shown below, can be also experimentally measured as it determines the equilibrium structure of the steps in the presence of a surfactant.

Substituting Eq. (1) in Eq. (3) gives

$$\Delta G_s(i) = \Delta G_0(i) - s[iE_k - U(i)] + \Phi_s.$$

It immediately becomes obvious that in the case of surfactant-mediated growth the Gibbs free energy for nucleus formation contains two more terms that have opposite signs and thus compete with each other. The s -containing term accounts for the decrease of the edge en-

ergy of the cluster due to saturation of the dangling bonds by the surfactant atoms. The energy, Φ_s , of the dangling bonds of the periphery of the cluster, consisting of surfactant atoms, which is *unavoidably* formed on top of the nucleus due to segregation of the mediate, increases the work of cluster formation. It is important to note that the parameters s and α_s are independent of each other, although both equal zero by definition in the absence of a surfactant. This means that at nearly complete inefficiency of the surfactant, $s \approx 0$, α_s has a finite value and the work for nucleus formation and the rate of nucleation change discontinuously.

Figure 2 shows the dependence of $\Delta G_s(i)$ relative to the crystal bond strength ψ_{cc} on cluster size i for the (111) surface of fcc metals with $\alpha_s = 0.2$, different values of the surfactant efficiency, s , and at a constant supersaturation $\Delta\mu = 1.1\psi_{cc}$. s is denoted by figures at each curve. As it could be seen, $\Delta G_s(i)$ represents a broken line (as should be expected for a small number of atoms) displaying a maximum at $i = i^*$. The latter represents the size of the critical nucleus. Under clean conditions ($s = 0$) the critical nucleus consists of 2 atoms. When s approaches zero ($= 0.05$), the number of atoms in the critical nucleus equals 6 due to the contribution of the edge energy of the surfactant cluster, Φ_s . The work of formation of the critical nucleus also increases. Increasing surfactant efficiency to 0.3 leads to a decrease of the nucleation work and i^* again becomes equal to 2. At some greater value of s ($= 0.7$) i^* equals unity and the work of nucleus formation decreases drastically. In the case of 2D nucleation and close-packed lattices

$$U(i^*) = E^* + i^* E_{des}, \quad (8)$$

where E_{des} is the activation energy for desorption from the clean surface and E^* is the work required to dissociate the cluster into single atoms without accounting for the bonds with the underlying crystal plane.

The work of formation of the critical nucleus then reads

$$\Delta G_s(i^*) = -i^* \Delta\mu + (1-s)(E_k - E_{des}) - (1-s)E^* + \Phi_s. \quad (9)$$

We will use this expression to derive the rate of nucleation, bearing in mind that the supersaturation does not depend on the presence of a surfactant on the crystal surface.

Figure 3 shows the work needed to form the critical nucleus $\Delta G_s(i^*)$ relative to the work for nucleus formation, $\Delta G_0(i^*)$, under clean conditions as a function of surfactant efficiency, s , at two different values of α_s . A decreasing broken line is seen, which is due to the change of i^* at some particular values of s . At $s \approx 0$ $\Delta G_s(i^*)$ increases discontinuously and becomes larger than $\Delta G_0(i^*)$ owing to the edge energy, Φ_s , of the surfactant cluster. The larger the value of Φ_s , the stronger this effect. At small values of α_s (small Φ_s) the plot of $\Delta G_s(i^*)$ on s tends to cross zero at some value of s close to unity. This means that at low edge energy of the surfactant cluster the supersaturation overcompensates the former at the very beginning of nucleus formation. It follows that at very high efficiencies of the surfactants the crystallization will take place without any need to overcome a barrier for nucleus formation. On the contrary, at high values of α_s the supersaturation cannot overcompensate

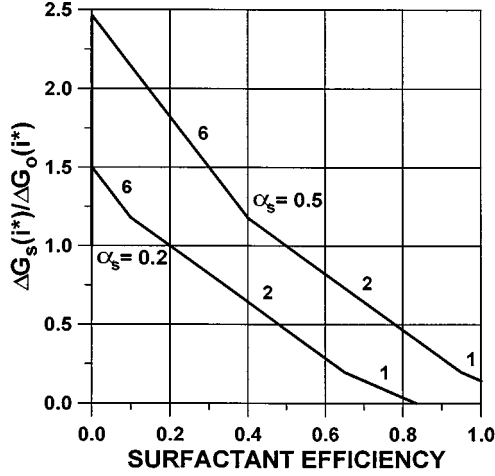


FIG. 3. Variations of the Gibbs free energy with the surfactant efficiency of formation of a critical nucleus relative to the same quantity under clean conditions at two different values of α_s . The jump at $s=0$ is due to the finite value of Φ_s . The singular points divide regions with a different number of atoms in the critical nucleus denoted by the figures at each part. $\Delta\mu = 1.1\psi_{cc}$ for both curves.

the edge energy of the surfactant cluster and the work for nucleus formation has a finite value even at $s = 1$.

III. NUCLEATION RATE

In order to calculate the nucleation rate we follow the usual procedure.¹⁵ The nucleation rate is given by

$$J_s = \beta^* N_0 \Gamma \exp[-\Delta G_s(i^*)/kT], \quad (10)$$

where β^* is the flux of atoms joining the critical nucleus, N_0 is the density of adsorption sites on the crystal surface, and Γ ($\cong 0.1$) is the nonequilibrium Zeldovich factor. The flux of atoms β^* is given by

$$\beta^* = \alpha \nu \left(\frac{n_s}{N_0}\right) \exp[-(E_{sd} \pm \Delta E_{sd} + \Delta U)/kT]. \quad (11)$$

In the above equation α is the number of ways by which an adatom can join the critical nucleus,¹⁶ ν is the vibrational frequency of the adatoms, n_s is the adatom concentration, ΔU is the kinetic barrier an adatom should overcome to displace a surfactant atom in order to join the critical nucleus, E_{sd} is the activation energy for surface diffusion on a clean surface in the absence of a mediate, and ΔE_{sd} is the additional energy an atom has to overcome when diffusing on a surface covered by a monolayer of surfactant atoms. The plus sign refers to the case of inhibited diffusion (diffusion in-between the surfactant atoms) whereas the minus sign refers to the case of surfactant-facilitated diffusion (diffusion on top of the energetically smoother surfactant layer).

It seems reasonable to argue that the energies ΔE_{sd} and ΔU depend on the interrelation of the works needed to break C-C, S-S, and S-C bonds, or in other words, on the value of s . The greater the value of s , the more difficult the displacement processes and the larger the values of ΔE_{sd} and ΔU should be. The simplest way to express the s dependences of

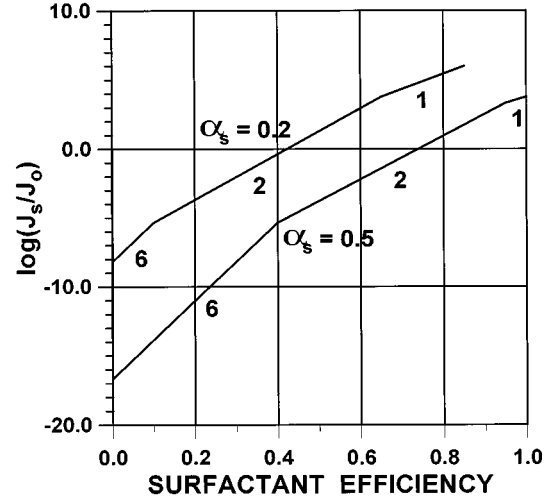


FIG. 4. Dependence of the nucleation rate, J_s , relative to the rate, J_0 , under clean conditions on the surfactant efficiency. The broken line reflects the s variation of the Gibbs free energy. $\Delta\mu = 1.1\psi_{cc}$ for both curves, n_s is determined from $\Delta\mu$ by Eqs. (12) and (13).

ΔE_{sd} and ΔU is to write $\Delta E_{sd} = s\Delta E_{sd}^0$ and $\Delta U = s\Delta U^0$ where ΔE_{sd}^0 and ΔU^0 are some maximum values of ΔE_{sd} and ΔU at $s = 1$. One can assume that ΔE_{sd}^0 and ΔU^0 could have values even greater than that of E_{sd} .

Combining Eqs. (9), (10), and (11) gives

$$J_s = \alpha N_0 \nu \Gamma \left(\frac{n_s}{N_0}\right)^{i^*+1} \exp\{[i^*(E_k - E_{des})s + (1-s)E^* - \Phi_s - (E_{sd} \pm s\Delta E_{sd}^0) - s\Delta U^0]/kT\}. \quad (12)$$

In deriving Eq. (12) we used the fact that the supersaturation is given by

$$\Delta\mu = kT \ln(n_s/n_{se}), \quad (13)$$

where the equilibrium adatom concentration, n_{se} , reads²⁰

$$n_{se} = N_0 \exp[-(E_k - E_{des})/kT]. \quad (14)$$

It immediately becomes obvious that in the absence of a surfactant $s = 0$, $\Phi_s = 0$, Eq. (12) takes the familiar form¹⁶

$$J_0 = \alpha \nu N_0 \Gamma \left(\frac{n_s}{N_0}\right)^{i^*+1} \exp[(E^* - E_{sd})/kT]. \quad (15)$$

Comparing Eqs. (12) and (15) shows that the presence of the surfactant leads above all to a sharp decrease by orders of magnitude of the nucleation rate owing to the edge energy, Φ_s , of the surfactant cluster (Fig. 4). After that the nucleation rate increases with s , which stems from the decrease of the edge energy as in the classical theory of nucleation. The dependence is represented again by a broken line, which reflects the discontinuous decrease of the number of atoms in the critical nucleus.

Note that in Eqs. (12) and (15) the nucleation rate is expressed as a function of the adatom concentration, n_s . In the case of incomplete condensation (adsorption-desorption

equilibrium) the latter is given by $n_s = R\tau_s$ where τ_s is the mean residence time before desorption of the adatoms on the crystal surface and R ($\text{cm}^{-2} \text{s}^{-1}$) is the atom arrival rate. At the other extreme of complete condensation (absence of reevaporation) the adatom concentration increases linearly with time, $n_s = Rt$, or is given by $n_s = R\tau$ where τ is the mean free time of the adatoms before incorporation into islands or steps. As given above the equations for the nucleation rate are suitable for any particular case mentioned above.

IV. SATURATION NUCLEUS DENSITY

Once the supersaturation is "switched on" the adatom concentration increases linearly with time. At sufficiently high temperature a dynamic adsorption-desorption equilibrium is gradually reached and $n_s = R\tau_s$ so that the nucleation process takes place at a constant supersaturation. At low temperatures (which is usually the case) the adatom concentration increases with time during the nucleation process. If the surface diffusion is still fast enough, depleted zones appear around the growing islands and in the near vicinity of the steps. The system in them is undersaturated and the nucleation process is arrested. After some time the depleted zones overlap and cover the surface completely. This results in saturation of the number density of the nuclei.²¹ If the surface diffusion is slow, a large number of islands are formed at the start of the process and they begin to coalesce in an early stage of deposition. The saturation nucleus density is then determined by coalescence of the islands.^{22,23} Adatom concentration is again constant, $n_s = R\tau$, and is determined by the balance of atoms arriving from the vapor and joining the islands and/or the steps on the crystal surface (for a review see Ref. 23). We consider here the saturation of the island density, which is due to the overlapping of depleted (nucleation exclusion) zones. There are two reasons for this. First, it has been shown in numerous papers that surface diffusion has a considerable rate at extremely low temperatures (for example, see Ref. 24). Second, the overlapping of the depleted zones always precedes the coalescence process in time.

We assume that there is no reevaporation; i.e., we consider the case of complete condensation and follow the procedure developed by Stowell.²¹ A depleted zone is formed around each growing nucleus with a radius following the time law $r \cong (D_s t)^{1/2}$, where D_s is the surface diffusion coefficient.²¹ Outside the depleted zones the adatom concentration increases linearly with time, $n_s = Rt$. Nuclei are progressively formed outside the depleted zones at a rate $J(t) \propto t^{i^*+1}$. The saturation nucleus density is given by²⁵⁻²⁷

$$N_s = \int_0^\infty J(t) \exp\left\{-\pi \int_0^t J(\tau) [r(t-\tau)]^2 d\tau\right\} dt. \quad (16)$$

Substituting Eq. (12) into (16) and making the integration gives

$$N_s = qN_0^{-(i^*-1)/(i^*+3)} \left(\frac{R}{D_s}\right)^{(i^*+1)/(i^*+3)} \exp\{[i^*(E_k - E_{\text{des}})s + (1-s)E^* - \Phi_s - s\Delta U^0]/(i^*+3)kT\}, \quad (17)$$

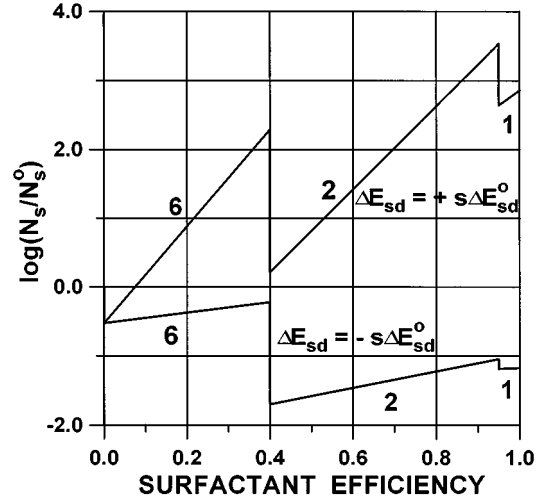


FIG. 5. Variations of the saturation island density, N_s , relative to the same quantity, N_s^0 , under clean conditions at a different impact of the surfactant on the rate of surface diffusion. The number of atoms in the critical nucleus is denoted by figures at each section of the curve. The number of atoms in the critical nucleus in the absence of a surfactant is $i^* = 2$. $E_{sd} = \Delta E_{sd}^0 = \Delta U^0 = 0.4$ eV, $\psi_{cc} = 0.44$ eV, $R = 2 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$, $N_0 = 1 \times 10^{15} \text{ cm}^{-2}$, $\nu = 1 \times 10^{13} \text{ sec}^{-1}$, $\alpha_s = 0.5$.

where q is nearly a constant and has a value of about 0.1.

Under clean conditions ($s = 0$) Eq. (17) becomes

$$N_s^0 = qN_0^{-(i^*-1)/(i^*+3)} \left(\frac{R}{D_s^0}\right)^{(i^*+1)/(i^*+3)} \times \exp[E^*/(i^*+3)kT]. \quad (18)$$

Note that in the absence of a surfactant the surface diffusion coefficient, D_s^0 differs from that in a surfactant mediated growth, D_s , by a factor of $\exp(\pm s\Delta E_{sd}^0/kT)$.

Equations (17) and (18) are compared in Fig. 5. As it could be seen the increase of s up to 0.8 leads to an increase of N_s by about three orders of magnitude in cases when surface diffusion is inhibited by the presence of the surfactant. In the opposite case the nucleus density remains of the same order of magnitude. The change of the number of atoms in the critical nucleus leads to some characteristic discontinuities. Figure 6 represents Arrhenius plots of the nucleus density under clean conditions (the line denoted by N_s^0) and mediated by surfactants that either facilitate or inhibit the surface diffusion. The intervals of the temperature are chosen so that $i^* = 2$ for all curves.

V. WORK FOR KINK FORMATION

The work for kink formation determines the roughness of the steps and in turn the state of the crystal surfaces and the mechanism of growth²⁰ (for a review see Ref. 19). Modern techniques for surface analysis like STM allow direct observation of steps and measurement of step roughness. Burton and Cabrera²⁸ were the first to define and calculate the work for kink formation by thermal excitation in the case of growth in vapors. They considered a straight step and removed consecutively two adjacent atoms embedded in the

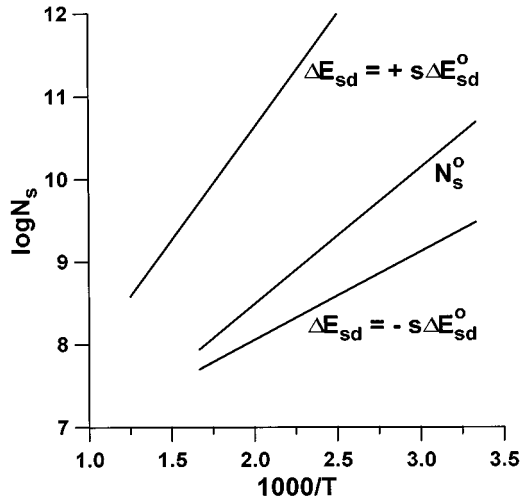


FIG. 6. Arrhenius plots of the saturation nucleus density, N_s , at a different influence of the surfactant on the rate of surface diffusion. N_s^0 denotes the curve obtained under clean conditions. The values of the quantities are the same as in Fig. 5.

step and placed them at the step edge thus producing four kinks. The spent work was $2\psi_{cc}$ and the work, ω_0 , for kink formation was equal to half the work needed to break a nearest-neighbor bond, or $\omega_0 = \psi_{cc}/2$. A generalization was later given for the case in which the crystal surface was in contact with its own melt (for a review see Ref. 29). The latter can be directly used for the case of surfactant-mediated growth. As it can be seen from Fig. 7 simple calculations based on the principle of conservation of bonds and the lattice model of the surfactant layer show that the work of kink formation is given precisely by the parameter ω . Following Burton, Cabrera, and Frank,²⁰ we can write an approximate expression for the density ρ of kinks in the presence of a surfactant

$$\begin{aligned} \rho &= (2/a)\exp(-\omega/kT) \\ &= (2/a)\exp[-\omega_0(1-s)/kT], \end{aligned} \quad (19)$$

where a is the interatomic distance.

Neglecting the kink-kink interaction the Gibbs free energy of the step reads²⁰

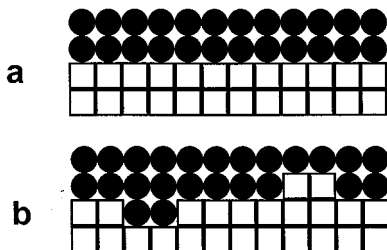


FIG. 7. To the calculation of the work needed for kink formation. (a) A straight step without kinks; (b) a step with four kinks. The crystal and surfactant atoms are denoted by empty squares and filled circles, respectively. The energetic difference between both configurations yields the work, $4\omega = 2\psi_{cc} + 2\psi_{ss} - 4\psi_{sc}$, required to create four kinks.

$$G_{st} = -(kT/a)\ln\left(\eta\frac{1+\eta}{1-\eta}\right), \quad (20)$$

where $\eta = (a/2)\rho = \exp(-\omega/kT)$.

What follows is that the surfactant efficiency must be always positive (positive enthalpy of mixing, $\omega > 0$). If $s \geq 1$ the work for kink formation and in turn the free energy of the step will equal zero. The steps will disappear and the crystal surface will become rough. Then the crystal surface will grow by direct incorporation of atoms from the vapor phase without any need to form 2D nuclei.^{19,20}

VI. DISCUSSION

As shown above the formation of a 2D nucleus in a surfactant medium leads unavoidably to the formation of a cluster consisting of surfactant atoms due to the segregation of the latter. As a result the work for nucleus formation contains in addition the edge energy, Φ_s , of the surfactant cluster. The work for nucleus formation decreases as a result of the lower "edge energy" but increases as a result of the surfactant cluster formation. The latter increases the number, i^* , of atoms in the critical nucleus at lower values of surfactant efficiency. Thus at one and the same temperature i^* can be larger or smaller in the presence of surfactant in comparison with the clean case depending on the interrelation of s and α_s . The greater the value of α_s , the greater the possibility that i^* will be larger in surfactant-mediated epitaxy and vice versa. It is important to note that the parameter Φ_s will equal zero if the concentration of the surfactant is much less than one monolayer. If this is the case the surfactant atoms will prefer to join kink sites at the island edges where the bonding is stronger than at other sites.³⁰

The value of α_s can be evaluated qualitatively as a ratio of the energies of the dangling bonds of the C and S crystals

$$\alpha_s \cong \frac{(\sigma v^{2/3})_s}{(\sigma v^{2/3})_c},$$

calculated from the respective specific surface energies, σ , and molar volumes, v . Thus in the case of Sb-mediated growth of Ag(111) with $\sigma_{Sb} = 395$ erg/cm² and $\sigma_{Ag} = 1140$ erg/cm² one obtains $\alpha_s \cong 0.5$. In the case of Sb-mediated growth of Si(111) ($\sigma_{Si} = 1240$ erg/cm²)² $\alpha_s \cong 0.42$. These values are large enough (see Fig. 3) and the contribution of Φ_s should not be overlooked when comparing the experimental data with the theory even at very low temperatures. However, one should bear in mind how unreliable the measurements of the surface energies are and should consider the above values as approximate. In any case, they should be of the order of 0.5.

One very important consequence of the decrease of the work for kink formation due to the presence of a surfactant is the change of shape of the growing islands. Steps that are straight under clean conditions will become rough in surfactant-mediated growth. As a result the well polygonized islands under clean conditions will be rounded in the presence of a surfactant. The above prediction is in agreement with the observations of Voigtländer and Zinner¹² on the growth of Si(111). The shape of the islands and the form of the steps are irregular in Sb-mediated growth compared to the triangular island shape and straight steps under clean

conditions. A comparison of experimental observations on the structure of single steps in the absence and presence of a surfactant such as the STM studies carried out by Swartzentruber *et al.*,³¹ with Eq. (19) can give direct information about the value of the surfactant efficiency. This is particularly important in the case of S_A steps on the Si(001) 2×1 surface, which are straight under clean conditions. Thus the presence of a surfactant in the growth of Si(001) can drastically change the mechanism of growth by step flow and to prevent the formation of double steps.

The saturation nucleus density is derived under the assumption of overlapping nucleation exclusion (depleted) zones around the growing nuclei. It is valid before the occurrence of significant coalescence. An indication of applicability of the expressions derived above are stripes observed around the steps without islands in them as in the case of Si(111) growth.^{12,13} Thus surface diffusion plays a dominant role in the determination of the saturation nucleus density. Due to the influence of the presence of surfactant on surface diffusion the saturation nucleus density can become much greater or smaller in comparison with growth under clean conditions. The schematic Arrhenius plot shown in Fig. 6 is in a good qualitative agreement with the data on nucleation on Si(111),¹³ although Eqs. (17) and (18) are not valid for (111) surfaces of crystals with diamond lattice. There are two reasons for that. First, Si(111) grows by complete bilayers³² and Eq. (14) is not valid because only half of the atoms of the bilayer are bound to the atoms of the underlying crystal plane. Second, a clean Si(111) surface is reconstructed in 7×7 unit cells below 830°C , whereas a surface covered with Sb or As recovers the 1×1 bulk structure.^{12,13} The latter means that we have to deal with two completely different crystal surfaces on which the mechanisms and the activation energies for surface diffusion differ considerably. Thus the experimental results obtained for both surfaces are incomparable. The case of nucleation on Si(111) 7×7 will be considered in a further study.

The increase of the saturation nucleus density in the presence of a surfactant easily explains the experimentally observed transition from multilayer to layer-by-layer growth in

Sb-mediated growth of Ag(111).¹⁰ The rate of nucleation on top of 2D islands depends on their size through the adatom concentration.^{3,6} The bigger the island is the higher the adatom concentration on top of it will be and the higher the nucleation rate. When a large population of small islands is formed as a result of the present surfactant, the nucleation rate on top of them remains negligible up to the beginning of coalescence and the critical surface coverage for nucleation in the upper monolayer is large.^{3,33} This results in a layer-by-layer growth. In the absence of a surfactant a small population of big islands is formed and nucleation on top of them begins long before the surface is completely covered by them. Consequently, two and more monolayers grow together and a multilayer growth takes place.

The main problem in the comparison of theory with experimental data is the evaluation of the surfactant efficiency, s , or in other words, of the energetic parameter ω . In principle it could be evaluated if the enthalpy of mixing of the two species is known. However, ω is, in a general case, dependent upon both composition and temperature.³⁴ Moreover, it is not clear whether a value of ω that is evaluated from the equilibrium phase diagram of a three-dimensional alloy and thus depends on the environment could be applied to treat a two-dimensional problem. It seems that the best way to measure ω is by studying the equilibrium structure of single steps. It is the surfactant efficiency that determines the kink density. The slope of an Arrhenius plot of kink density should directly give the value of surfactant efficiency and a comparison with the experiment can be carried out without unnecessary speculations. On the other hand the problem of kink density in the presence of a surfactant is very important in itself. The equilibrium structure of the steps determines the mechanism of growth and the transition from step-flow growth to growth by 2D nucleation.

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