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Influence of adsorption on thin film thermodynamics

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The thermodynamics of a system composed of a substrate, a deposit, and an adsorbed layer is considered with a lattice model in the framework of Gibbs ensemble statistics. Expressions for the thermodynamic functions (free energy, chemical potential, etc.) are derived. The thermodynamic condition for equilibrium in such a multicomponent multiphase system (equality of chemical potentials of each component in all phases), combined with the requirement of minimal free energy, leads to a criterion for stability of the two-dimensional (2D) phase of the deposit. It is shown that an adsorbate could invert the relative thermodynamic stability of both possible deposit phases. It is found also that the adsorbate drastically influences the chemical potential of the 2D phase, and on whatever substrate it becomes practically equal to the chemical potential of the bulk phase at high adsorbate coverages. The influence of the foreign substrate on the layerwise separation in the adlayer is discussed, along with some peculiarities that arise, by defining surface and interfacial free energies of the thin films. [S0163-1829(96)09948-1]

I. INTRODUCTION

The morphology of deposits on foreign substrates has attracted much attention for a long time now. When a given material is placed on a substrate, it usually forms either a thin uniform film or three-dimensional (3D) crystallites.[1–4] The first case is called the Frank–van der Merwe (FM) growth mode. In the second case the crystallites can be formed directly onto the bare substrate [the Vomer-Weber (VW) growth mode] or can lie on some uniformly distributed monolayers [Stranski-Krastanov (SK) growth mode of their own]. According to the well-known Bauer's criterion,[1] an *A* monolayer is formed on substrate *B* (FM growth) if the condition

$$\sigma_a - \sigma_b + \sigma_{ab} \leqslant 0 \tag{1}$$

is satisfied, where σ_a and σ_b are the deposit and substrate surface free energies, and σ_{ab} is the interfacial free energy. If this inequality does not hold, then formation of 3D *A* islands on the bare substrate takes place (VW growth). Simply speaking, if the surface free energy of the deposit is lower than that of the substrate (the interfacial energies are usually much lower than the corresponding surface energies) the deposit covers the substrate uniformly and lowers the total energy of the system. In the opposite case the complete wetting would increase the energy, so that the deposit prefers to minimize its own surface by forming 3D crystallites.

Pure FM growth is rarely observed in real systems. Owing to the difference of the lattice parameters (misfit), elastic strains arise in the overlayer.[5,6] In the first several monolayers they are accommodated by homogeneous distortion. After a certain thickness, however, the elastic energy becomes very large. A nonuniform relaxation takes place in the topmost layer, resulting in the appearance of small areas with structure more or less close to the structure of the deposit. The layer growth is terminated, and the growth of 3D islands begins (SK growth).[7–9] Obviously, Bauer's rule does not distinguish between FM and SK growth modes.

In the early days of epitaxy in poor vacuum, the surfaces must have been contaminated. The assumption that impurities hinder a good epitaxial overgrowth (by blocking of the growth sites and/or by including irregularities in the crystal lattice) forced the tendency to maintain the growth condition as ''clean'' as possible. The using of ultrahigh vacuum (UHV) and carefully cleaned substrates, however, did not always yield the expected result. On the contrary, in some cases the epitaxy in poor vacuum was better than in UHV.[10] Apparently, in such cases, epitaxy could be achieved because the surfaces *were not clean.*

An example of adsorbate influence on the growth mode are rare-gas systems (Xe, Kr, Ar) on graphite. On air-cleaved graphite, without cleaning in vacuum, Venables and Ball[11] observed a 3D growth, irrespective of vacuum conditions. However, when the substrate was cleaned in UHV prior to deposition, a 2D growth (multilayer adsorption isotherms) was found in all the above systems.[12–16] On the other hand, recent experiments involving the deliberate introduction of adsorbates in a variety of VW epitaxial systems [Fe and Ni on Cu(100), Fe on Ag(100), Si/Ge(100)],[17–22] showed that some of the adsorbates (O, N, CO, As, Sb) are able to suppress the island growth, and to induce ML films to spread out on the substrate.

Most authors presumed qualitatively that the change of the surface free energies is the origin of the observed changes in the growth mode.[3,17–19] Assuming a more general validity of Eq. (1), one could evaluate quantitatively the adsorbate influence by calculating the simultaneous change of the substrate and deposit surface free energies, provided the corresponding adsorption isotherms are known. This approach, although quite reasonable, has the disadvantage that it does not allow a deeper insight into the thermodynamics of the system.

As a matter of fact the chemical potential of a bulk adsorbent is not changed upon adsorption. This is due to its vanishing surface-to-volume ratio. In the case of a thin film, however, this ratio is close to unity. The surface free energy contribution to the total free energy is significant, so that every change in the surface state of the film leads consequently to a change of its thermodynamic functions as well. To the best of our knowledge no quantitative consideration of the problem has been presented till now.

Therefore, the aim of the present paper is to derive expressions, by means of a lattice model, for the thermodynamic functions of an adsorbate-deposit-substrate system and to answer the question of whether there are thermodynamic reasons to expect an inversion of the order of the stability of the 2D and 3D phases of the deposit under the adsorbate influence. This paper is organized as follows. The model and the partition functions are described, and the free energies are calculated in Sec. II. The criterion for 2D deposit stability is derived in Sec. III. It takes a very simple form for a nearly complete adsorbate layer. An expression for the chemical potential of the thin film in the presence of an adsorbate is derived in Sec. IV. The change of the thin-film thermodynamics due to adsorption is illustrated in Sec. V. The definition of the surface energies of thin-film substrates and interfaces is discussed in this section as well. Finally interlayer demixing in a binary adsorbate induced by a foreign substrate is exemplified in Sec. VI.

II. MODEL, PARTITION FUNCTIONS, AND FREE ENERGIES

For sake of simplicity we assume that the deposit (A), substrate (B) and adsorbate (S) have arbitrary but like crystal lattices with equal lattice parameters, and with first-neighbor interactions only. The coordination number of the 3D lattice is $2Z$, and the bond energies between like and unlike atoms are E_{ii} and E_{ik} (taken as negative with $i,k=a,b,s$). The substrate is a crystal face with $2Z_p$ number of bonds in the plane (lateral bonds) and $2Z_o$ number of bonds out of the same plane, so that an atom on the top of this plane has Z_o first neighbors in it.

Let us now consider a system which consist of a substrate B with $M \approx 10^{15}$ adsorption sites, N_a atoms of type A, and N_s atoms of type S. All N_a atoms are situated on B, part of the S atoms of order of magnitude M are adsorbed, and the rest of them are in a vapor phase with volume V. It is assumed that

$$N_s \gg M \gtrsim N_a . \tag{2}$$

This inequality means that all phases in the system are large enough in order to apply the Gibbs ensemble statistics. The system does not exchange mass with its surroundings, i.e., the number of both A and S particles is constant.

Two configurations are possible with respect to component A. The first one is realized when all N_a atoms form a large 3D crystal, N_{3s}^b and N_{3s}^a S atoms are adsorbed on B and on the surface of the 3D A phase, while the rest of them, $N_{3s}^v = N_s - N_{3s}^b - N_{3s}^a$ are in the vapor phase. The canonical partition function Q_3 of this configuration is

$$Q_3 = Q_{3s}^v Q_{3a}^b Q_{3s}^b Q_{3s}^a , \tag{3}$$

where Q_{3s}^v is the partition function of the vapor phase, Q_{3a}^b that of component A, and Q_{3s}^b and Q_{3s}^a those of both S phases adsorbed on B and A, respectively. Because of the large dimensions of the A phase, the surface/volume ratio $\approx N_a^{2/3}/N_a$ is vanishing so that its shape is not exactly defined by Wulff's theorem as in the case of small crystals.

In the second configuration the N_a atoms form a compact (but not necessary full) 2D layer on B, both A and unoccupied B surfaces are covered with N_{2s}^a and N_{2s}^b S atoms, so that $N_{2s}^v = N_s - N_{2s}^b - N_{2s}^a$ S atoms remain in the gas phase. Similarly to Eq. (3), the partition function Q_2 is

$$Q_2 = Q_{2s}^v Q_{2a}^b Q_{2s}^b Q_{2s}^a . \tag{4}$$

The counterparts in the second system are naturally indexed with a 2. It should be underlined that both above configurations are actually two independent systems. Therefore, one has to equilibrate them separately and after calculating of the corresponding free energies, to decide which of them is more stable.

The free energy F and the chemical potential μ in the canonical ensemble are

$$F = -kT \ln Q, \tag{5}$$

$$\mu = \partial F / \partial N, \tag{6}$$

so that from Eqs. (4) and (3) one obtains

$$F_2 = F_{2s}^v + F_{2a}^b + F_{2s}^b + F_{2s}^a , \tag{7}$$

$$F_3 = F_{3s}^v + F_{3a}^b + F_{3s}^b + F_{3s}^a , \tag{8}$$

where the free energies are indexed as the corresponding partitions functions. To calculate the free energies, one now needs a concrete form for the partition functions.

Let the chemical potential of a gas phase with N_s particles in volume V at temperature T be

$$\mu_{se}(N_s, V, T) = -\frac{kT \partial \ln Q(N_s, V, T)}{\partial N_s} .$$

According to Eq. (2) the amount of adsorbed S atoms $(\lesssim M)$ is infinitesimal as compared to N_s. Consequently, the chemical potentials of the gas phase in both systems are equal,

$$\mu_{se} \equiv \mu_{se}(N_s, V, T) = \frac{\partial F_2}{\partial N_{2s}^v} = \frac{\partial F_3}{\partial N_{3s}^v}$$

and are not changed upon adsorption, so that we can express the corresponding free energies as

$$F_{2s}^v = N_{2s}^v \mu_{se} = (N_s - N_{2s}^b - N_{2s}^a) \mu_{se} , \tag{9}$$

$$F_{3s}^v = N_{3s}^v \mu_{se} = (N_s - N_{3s}^b - N_{3s}^a) \mu_{se} . \tag{10}$$

Assuming that the temperature is below the two-dimensional critical temperature of A, we consider both 2D and 3D A phases as Einstein crystals with partition functions

$$Q_{2a}^b(N_a, T) = q_a^{N_a} \exp\left(-\frac{Z_o E_{ab} + Z_p E_{aa}}{kT} \right)^{N_a} , \tag{11}$$

$$Q_{3a}^b(N_a, T) = q_a^{N_a} \exp\left(-\frac{Z E_{aa}}{kT} \right)^{N_a} , \tag{12}$$

where q_a is the internal partition function of the A atoms. Denoting

$$\eta_k^i = -kT\ \ln q_k + Z_o E_{ki} + Z_p E_{kk} \tag{13}$$

for the layer k on the substrate i, one obtains the free energies of the component A

$$F_{2a}^b = N_a \eta_a^b, \tag{14}$$

$$F_{3a}^b = N_a \eta_a^a. \tag{15}$$

For the partition functions of adsorbed S phases (N adatoms on M sites) we use an expression known from the lattice statistics of adsorption,[23]

$$Q(N,M,T) = q_s^N \exp\left(-\frac{N Z_o E_{si}}{kT} \right) \times \sum_j g_j \exp\left(-\frac{E_j(Z_p, E_{ss}, N, M, T)}{kT} \right), \tag{16}$$

where $Z_o E_{si}$ is the bond energy of an S atom to the underlying substrate i ($N Z_o E_{si}$ is the total nonconfigurational energy), E_j are all allowed configurational energy levels of the system, and g_j those of the corresponding degeneracy factors. Keeping in mind that $\Sigma g_j = M!/N!(M-N)!$, the sum in Eq. (16) is replaced by its maximal term $g_j^* \exp(-E_j^*/kT)$, so that for the free energy one can write

$$F = M[kTS_c(\theta) + \theta \eta_s^i - \theta Z_p E_{ss} + E_c(\theta)]. \tag{17}$$

In the last equation $\theta = N/M$ is the coverage and $S_c(\theta) = -\ln g_j^*/M$ and $E_c(\theta) = E_j^*/M$ are the configurational entropy and energy per adsorption site. Of course both S_c and E_c also depend on Z_p, E_{ss}, and T, but they are omitted for convenience. As is evident from the general form of the expressions for the configurational quantities, no concrete approximation is used to obtain Eq. (17) from Eq. (16).

With Eq. (17) the free energies of the S phases are

$$F_{2s}^b = (M - N_a) f_{2s}^b(\theta_{2s}^b) = (M - N_a)[kTS_c(\theta_{2s}^b) + \theta_{2s}^b \eta_s^b - \theta_{2s}^b Z_p E_{ss} + E_c(\theta_{2s}^b)], \tag{18}$$

$$F_{2s}^a = N_a f_{2s}^a(\theta_{2s}^a) = N_a[kTS_c(\theta_{2s}^a) + \theta_{2s}^a \eta_s^a - \theta_{2s}^a Z_p E_{ss} + E_c(\theta_{2s}^a)], \tag{19}$$

$$F_{3s}^b = M f_{3s}^b(\theta_{3s}^b) = M[kTS_c(\theta_{3s}^b) + \theta_{3s}^b \eta_s^b - \theta_{3s}^b Z_p E_{ss} + E_c(\theta_{3s}^b)], \tag{20}$$

$$F_{3s}^a = N_a^{2/3} f_{3s}^a(\theta_{3s}^a) = N_a^{2/3}[kTS_c(\theta_{3s}^a) + \theta_{3s}^a \eta_s^a - \theta_{3s}^a Z_p E_{ss} + E_c(\theta_{3s}^a)]. \tag{21}$$

In the above expressions,

$$\theta_{2s}^b = \frac{N_{2s}^b}{M - N_a}, \quad \theta_{2s}^a = \frac{N_{2s}^a}{N_a}, \quad \theta_{3s}^b = \frac{N_{3s}^b}{M}, \quad \theta_{3s}^a = \frac{N_{3s}^a}{N_a^{2/3}} \tag{22}$$

are the coverages of S on A and B in both systems, and f denotes the free energy per adsorption site. The number of adsorption sites in F_{3s}^a (proportional to the surface of the 3D A crystal) is taken to be $\approx N_a^{2/3}$ and, according to Eq. (2), the number of adsorption sites on B in F_{3s}^b is $M - pN_a^{2/3} \approx M$, with p being a coefficient slightly lower than 1.

The free energies from Eqs. (18)–(21) have to be calculated under the general condition for equilibrium in a multiphase multicomponent system—equality of the chemical potentials of each component in all phases. In our case this means that the chemical potentials of all S phases should be equal to μ_{se}. Denoting the equilibrium coverages at μ_{se} with $\theta_{se}^b \equiv \theta_{se}^b(\mu_{se})$, and $\theta_{se}^a \equiv \theta_{se}^a(\mu_{se})$ and putting $\theta_{3s}^b = \theta_{2s}^b = \theta_{se}^b$ and $\theta_{3s}^a = \theta_{2s}^a = \theta_{se}^a$ in Eqs. (18)–(21), one obtains the equilibrium free energies of adsorbed S phases.

III. THERMODYNAMIC STABILITY OF THE 2D PHASE OF THE DEPOSIT

The thermodynamic condition that the 2D system is more stable than the 3D system is

$$F_2 - F_3 = \Delta F \leqslant 0. \tag{23}$$

Let us see now how this condition looks in the particular case of a ''clean'' substrate (without an adsorbate). All free energies in Eq. (23) containing S bonds are absent, and taking into account Eqs. (14) and (15), it reduces to

$$(\eta_a^b - \eta_a^a)/Z_o = (\mu_a^b - \mu_a^a)/Z_o = E_{ab} - E_{aa} \leqslant 0, \tag{24}$$

where μ_a^b and μ_a^a are the chemical potentials of the 2D and 3D phases of A on B [the equality $\eta = \mu$ is obvious from Eq. (6)].

We now define the specific surface and interfacial free energies of the bulk phases in the model as

$$\sigma_i = -M Z_o E_{ii}/2, \quad \sigma_{ik} = \sigma_i + \sigma_k - \beta_{ik}, \quad \beta_{ik} = -M Z_o E_{ik} \tag{25}$$

where β_{ik} is the so-called specific adhesion energy (the energy gain when putting two bare i and k substrates together). Thus Eq. (24) becomes

$$M Z_o (E_{ab} - E_{aa}) = 2\sigma_a - \beta_{ab} = \sigma_a - \sigma_b + \sigma_{ab} \leqslant 0. \tag{26}$$

The last result shows that the Bauer's 3-σ rule (1) is strictly valid for temperatures below the two-dimensional critical temperature of the deposit, i.e., when both 3D and 2D phases could be considered as Einstein crystals. Although it contains only surface free energy terms, i.e., only a part of the total free energy, it is identical to the most general thermodynamic condition (23). It should be noted that the transition from a small crystal to an infinite large compact monolayer, used in Ref. 1 to derive Eq. (1), includes the assumption of zero configurational entropy and energy of both 3D and 2D phases, i.e., they are implicitly regarded by Bauer as Einstein crystals as well.

Let us now calculate the remaining free energies included in F_2 and F_3. Keeping in mind Eq. (22), from Eqs. (9) and (10) one obtains

$$\begin{aligned} F^v_{2s}-F^v_{3s}&=(-N^b_{2s}-N^a_{2s}+N^b_{3s}+N^a_{3s})\mu_{se}\\ &=N_a(\theta^b_{se}-\theta^a_{se})\mu_{se}. \end{aligned} \tag{27}$$

In the same way Eqs. (18)–(21) yield

$$F^b_{2s}+F^a_{2s}-F^b_{3s}-F^a_{3s}=N_a[f^a_{se}(\theta^a_{se})-f^b_{se}(\theta^b_{se})]. \tag{28}$$

$N_a^{2/3} \ll N_a, M$, as evident from Eq. (2), is used to obtain both last equations. Combining Eqs. (27) and (28), we write

$$\begin{aligned} &F^v_{2s}-F^v_{3s}+F^b_{2s}+F^a_{2s}-F^b_{3s}-F^a_{3s}\\ &\quad=N_a[\theta^b_{se}\mu_{se}-f^b_{se}(\theta^b_{se})]-N_a[\theta^a_{se}\mu_{se}-f^a_{se}(\theta^a_{se})]\\ &\quad=N_a[\varphi^a_s(\mu_{se})-\varphi^b_s(\mu_{se})], \end{aligned} \tag{29}$$

where the relation

$$f^i_{se}(\theta^i_{se})-\theta^i_{se}\mu_{se}=\Delta f^i_{se}(\mu_{se})=\varphi^i_s(\mu_{se}) \tag{30}$$

is used. The quantity $\varphi^i_s(\mu_{se})$ is also a thermodynamic function called two-dimensional spreading pressure. It is just the free energy change $\Delta f^i_{se}(\mu_{se})=f_{\mathrm{adsorbate}}-f_{\mathrm{gas}}$ by isothermal reversible adsorption at chemical potential μ_{se}.

Finally, the thermodynamic condition (23) for stability of the two-dimensional phase A on B in the presence of an adsorbate becomes

$$\frac{\Delta F}{N_a}=\eta^b_a-\eta^a_a-\varphi^b_s(\mu_{se})+\varphi^a_s(\mu_{se})\leq 0. \tag{31}$$

We now want to point out the simple physical sense of last equation. According to Eq. (24), the free energy change by the 3D-2D transition in the ''clean'' case is $\eta^b_a-\eta^a_a$. Equation (31) means that, to perform this transition in the presence of an adsorbate, extra work has to be done, to readsorb S from B on A. Obviously, if this work is negative (energy is gained), it could compensate for the positive energy difference $\eta^b_a-\eta^a_a$ (stable 3D islands without an adsorbate) and thus to stabilize the 2D phase of A.

Let us analyze now Eq. (31) in more detail. Suppose we know the adsorption isotherms, i.e., the partial derivatives of the free energy with respect to the number of adsorbed particles,

$$\mu^b_s(\theta)=\frac{\partial F_2}{\partial N^b_{2s}}=\frac{\partial F_3}{\partial N^b_{3s}}, \tag{32}$$

$$\mu^a_s(\theta)=\frac{\partial F_2}{\partial N^a_{2s}}=\frac{\partial F_3}{\partial N^a_{3s}}. \tag{33}$$

The free energy f could also be expressed as

$$f^i_{se}(\theta^i_{se})=\int_0^{\theta^i_{se}}\mu^i_s(\theta)d\theta,$$

so that the 2D spreading pressure from Eq. (30) becomes

$$\varphi^i_s(\mu_{se})=\int_0^{\theta^i_{se}}\mu^i_s(\theta)d\theta-\theta^i_{se}\mu_{se}. \tag{34}$$

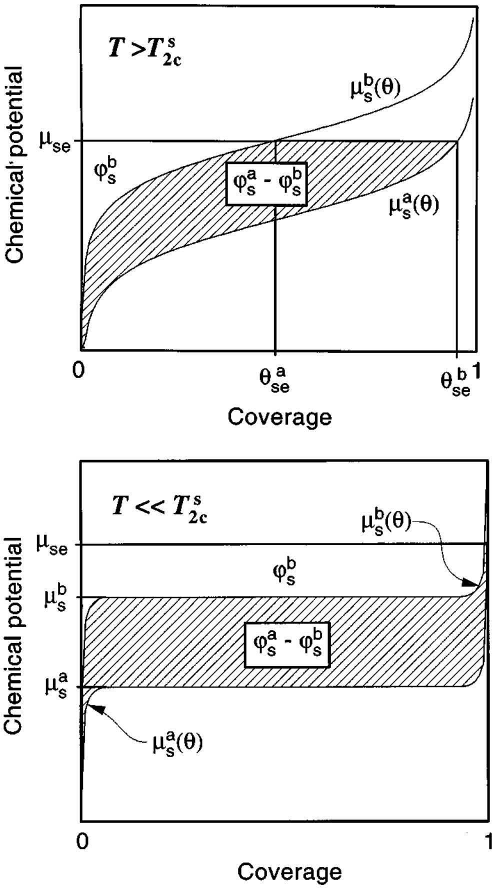

FIG. 1. Adsorption isotherms of S on A and B substrates. (a) For temperatures higher than the two-dimensional critical temperature T^s_{2c} of S. (b) For temperatures lower than T^s_{2c}. The dashed areas are proportional to the difference of the 2D spreading pressures $\varphi^a_s-\varphi^b_s$ and increase with rising μ_{se}. Above a certain value of μ_{se} in both cases, $\theta^b_{se}\rightarrow\theta^a_{se}\rightarrow 1$ and $\varphi^a_s-\varphi^b_s\rightarrow\eta^b_s-\eta^a_s$.

The adsorption isotherms $\mu^b_s(\theta)$ and $\mu^a_s(\theta)$ are presented schematically in Fig. 1 for two extreme cases: (a) at temperatures higher than the two-dimensional critical temperature T^s_{2c} of component S, and (b) for $T\ll T^s_{2c}$. The area between μ_{se} and the isotherm $\mu^b_s(\theta)$ equals $\varphi^b_s(\mu_{se})$, and the dashed area is just the energy $\varphi^a_s(\mu_{se})-\varphi^b_s(\mu_{se})=\Delta\varphi(\mu_{se})$, gained by readsorption of S from B on A. It is obvious that energy is gained if $E_{sa}<E_{sb}$. With a rising chemical potential (coverage) of the adsorbate, $\Delta\varphi(\mu_{se})$ increases, and after a certain value of μ_{se} practically does not change any longer. As evident from the same figure, the energy gain is maximal for $\mu_{se}\gtrsim\eta^b_s$ when $T\ll T^s_{2c}$, while for $T>T^s_{2c}$ chemical potentials, significantly higher than η^b_s, are necessary to obtain the maximal effect. The quantity η, as defined in Eq. (13), is equal to the chemical potential μ only in some special cases, e.g., by Einstein crystals and for adsorbed phases at $T<T_{2c}$ in the coverage region of the van der Waals wave. Above T_{2c} by the symmetrical adsorption isotherms, obtained from Eq. (16) with mean-field or quasichemical approximations, μ equals η only for $\theta=0.5$.

Now using Eqs. (13) and (25), one can rewrite Eq. (31) as

$$\sigma_a-\sigma_b+\sigma_{ab}+M\varphi_s^a(\mu_{se})-M\varphi_s^b(\mu_{se})$$
$$=\sigma_a^*(\mu_{se})-\sigma_b^*(\mu_{se})+\sigma_{ab}\leqslant 0, \tag{35}$$

where

$$\sigma_i^*(\mu_{se})=\sigma_i-\Delta\sigma_i(\mu_{se}) \tag{36}$$

is the reduced surface free energy in the presence of an adsorbate with chemical potential μ_{se} in the system, and

$$\Delta\sigma_i(\mu_{se})=-M\varphi_s^i(\mu_{se}) \tag{37}$$

is the free energy change per unit surface due to adsorption, i.e., the surface free energy change. The similarity of Eq. (35) and (1) is evident.

In order to obtain a more concrete form of Eq. (35), one needs to assume a certain approximation for calculating φ, which leads to more or less complicated expressions. For the maximal effect, however, it is possible to obtain a very simple form of Eq. (35), evading the use of approximations. One can see from Fig. 1 that with rising chemical potential θ_{se}^b and θ_{se}^a come more and more closely together, and approach unity. For that limiting case ($\theta_{se}^a\approx\theta_{se}^b\approx 1$)

$$S_c(\theta\approx 1)\rightarrow 0 \quad \text{and} \quad E_c(Z_p,E_{ss},\theta\approx 1,T)\rightarrow Z_pE_{ss}. \tag{38}$$

Then

$$f_{se}^i(\theta_{se}^i\approx 1)\rightarrow\eta_s^i, \quad \varphi_s^i(\mu_{se})\rightarrow\eta_s^i-\mu_{se}, \quad \Delta\varphi_{\max}=\eta_s^a-\eta_s^b, \tag{39}$$

and, keeping in mind Eq. (30), Eq. (31) is reduced to

$$(\eta_a^b-\eta_a^a+\eta_s^a-\eta_s^b)/Z_o=E_{ab}-E_{aa}+E_{sa}-E_{sb}\leqslant 0 \tag{40}$$

and

$$MZ_o(E_{ab}-E_{aa}+E_{sa}-E_{sb})=\sigma_a^*(\mu_{se})-\sigma_b^*(\mu_{se})+\sigma_{ab}$$
$$=\sigma_{sa}-\sigma_{sb}+\sigma_{ab}\leqslant 0. \tag{41}$$

From Eq. (35) one can conclude that simultaneous adsorption on two substrates lowers the difference of their surface free energies. This effect increases with a rising chemical potential (coverage) of the adsorbate. The maximal effect is obtained practically for adsorbate coverages close to unity, whereby the difference of the surface free energies is reduced to the difference of the corresponding substrate-adsorbate interfacial energies. According to (41) in that particular case the three interfacial energies remain solely responsible for the thermodynamic stability of the 2D phase of the deposit.

IV. CHEMICAL POTENTIAL OF THE DEPOSIT

Let us now consider the chemical potential of deposit A in the multicomponent system. For the 2D configuration of A the partial derivative of F_2 with respect to N_a is

$$\mu_{2a}^b(\mu_{se})=\frac{\partial F_2}{\partial N_a}=\frac{\partial F_{2a}^b}{\partial N_a}+\frac{\partial F_{2s}^b}{\partial N_a}+\frac{\partial F_{2s}^a}{\partial N_a}, \tag{42}$$

while, in the 3D system,

$$\mu_{3a}^b(\mu_{se})=\frac{\partial F_3}{\partial N_a}=\frac{\partial F_{3a}^b}{\partial N_a}+\frac{\partial F_{3s}^a}{\partial N_a}. \tag{43}$$

The notation $\mu_a(\mu_{se})$ means that the chemical potential μ_a of component A is taken at the chemical potential μ_{se} of component S. The first summands in the right-hand sides of both above equations are the chemical potentials of the 2D and 3D phases respectively, without adsorption (partial derivatives of the free energies with respect to the number of adsorbed particles). The remaining terms are partial derivatives of the free energies with respect to the adsorption sites, which are just the two-dimensional spreading pressures φ of the corresponding adsorbates, so that

$$\mu_{2a}^b(\mu_{se})=\mu_a^b-\varphi_{se}^b(\mu_{se})+\varphi_{se}^a(\mu_{se}), \tag{44}$$

$$\mu_{3a}^b(\mu_{se})=\mu_a^a+\frac{N_a^{2/3}}{N_a}\left[\varphi_{se}^a(\mu_{se})-\tfrac{1}{3}f_{se}^a(\theta_{se}^a)\right]\approx\mu_a^a. \tag{45}$$

The more complicated form of the last equation arises from the fact that the number of adsorption sites in F_{3s}^a is not N_a but $N_a^{2/3}$. According to Eq. (2) the multiplier $N_a^{2/3}/N_a$ is an infinitesimal quantity, so that the chemical potential of the 3D A phase is not changed by adsorption. This is true until its surface-to-volume ratio remains negligible. In the opposite case $\mu_{3a}^b(\mu_{se})$ becomes an adsorption-dependent quantity, because the contribution of the surface free energy (and also its change) to the total free energy becomes significant.

Concerning Eq. (44), it is evident that the chemical potential of the two-dimensional phase A is strongly dependent on μ_{se}. It seems as if this conclusion contradicts the well-known fact that an adsorbed layer does not change the chemical potential of the underlying substrate. As discussed above, however, this is not true when the surface-to-volume ratio of the substrate phase becomes different from zero. It is hardly possible to speak about ‘‘surface’’ of an adsorbed layer above the two-dimensional critical temperature, where the adatoms are almost randomly distributed on the supporting substrate. Below this temperature, however, the adatoms form a more or less compact layer. This layer has still its ‘‘own surface’’ because it is able to adsorb other particles, i.e., it can act as a substrate. The surface-to-volume ratio of this compact layer is unity, so that every change of its ‘‘own surface’’ (adsorption on it) should change its free energy (and chemical potential) as well. Keeping in mind that the chemical potential of one of the components in a multicomponent system is *the free-energy change of the whole system (not only of the component under consideration) per particle*, it is obvious that every change of the number of A particles is accompanied with a redistribution of the adsorbed S atoms between both A and B surfaces, i.e., as compared to the adsorbate free surface the chemical potential is changed just with the free energy for readsorption per site.

With Eq. (44) the general condition (31) obtains a very simple form,

$$\mu_{2a}^b(\mu_{se})-\mu_a^a=\frac{1}{M}\left[\sigma_a^*(\mu_{se})-\sigma_b^*(\mu_{se})+\sigma_{ab}\right]\leqslant 0. \tag{46}$$

It turns out that in the presence of an adsorbate, similarly to the ''clean'' case, the 2D configuration of the deposit is more stable when its chemical potential is lower than those of the bulk phase. Therefore it is interesting to analyze the dependence of $\mu_{2a}^{b}(\mu_{se})$ on the particular choice of S. Keeping in mind Eqs. (38), (39), and (40), it is obvious that for the limiting case $\theta_{se}^{a}\approx\theta_{se}^{b}\approx 1$,

$$\mu_{2a}^{b}(\theta_s\approx 1)-\mu_a^a=Z_o(E_{ab}-E_{aa}+E_{sa}-E_{sb}). \qquad (47)$$

As one can see the S-dependent quantity in Eq. (47) is the difference $E_{sa}-E_{sb}$, so that the question is how it depends on E_{ss}. The relation $E_{ik}=(E_{ii}+E_{kk})/2$ is widely used as a first approximation for the bond energy of two unlike atoms. In the real case, of course, the quantity

$$W_{ik}=E_{ii}+E_{kk}-2E_{ik}=-\sigma_{ik}/Z_oM \qquad (48)$$

is usually not zero. Nevertheless, both theoretical consideration and experiment[7,24] showed that, as a rule, W_{ik} is at least about one order of magnitude lower than all three energies. As a consequence, every change of E_{ii} or E_{kk} will shift E_{ik} in the same direction. Evidently, different values of E_{ss} (different adsorbates) will shift both unlike bond energies E_{sa} and E_{sb} in one and the same direction, thus making the difference $E_{sa}-E_{sb}$ almost insensitive on E_{ss}. Therefore, the difference $\mu_{2a}^{b}(\theta_s=1)-\mu_a^a$ is practically one and the same whatever the adsorbed layer S is.

On the other hand one can rewrite Eq. (47) in the form

$$\mu_{2a}^{b}(\theta_s=1)-\mu_a^a=Z_o(-W_{ab}+W_{sb}-W_{sa}). \qquad (49)$$

Keeping in mind that μ_a^a is an arbitrary quantity, the sum on the right-hand side of this equation is very low as compared to both summands in the left-hand side. The conclusion is that the chemical potential of a 2D compact phase in the presence of a complete adsorbed layer deviates, in general, negligibly from the chemical potential of the 3D A phase. On the other hand, the attachment/detachment of a single A particle to/from the substrate B is associated with energy $Z_o(E_{ab}+E_{sa}-E_{sb})$ (neglecting the lateral bonds). It is obvious that this energy differs also little from Z_oE_{aa}, and is very insensitive with respect to E_{bb} (bond strength to the substrate), because of the difference $E_{ab}-E_{sb}$. Thus if the substrate contains different type of atoms, e.g., impurities or dopants, then the differences in the local bond energies are much smaller in the presence of adsorbate than without it. That is why the adlayer additionally equalizes the local bond energies and renders the substrate energetically homogeneous.

Strictly speaking, the above considerations are valid for volatile adsorbates, i.e., for adsorbates with low mean residence times (as compared to the experimental time), for which a vapor phase is absolutely necessary to maintain a certain coverage. On the contrary, the adlayers of nonvolatile adsorbates are very stable in time because of the low desorption rate. Without presenting concrete calculations we note that the same general conclusions could be drawn as for volatile adsorbates. What is more, all expressions for the limiting case of a complete adsorbate monolayer are fully identical with those derived for the former case. That is because the difference $F_{2s}^{v}-F_{3s}^{v}$ from Eq. (27) vanishes when $\theta_{se}^{a}\approx\theta_{se}^{b}\approx 1$, which is equivalent to excluding the vapor phase from consideration.

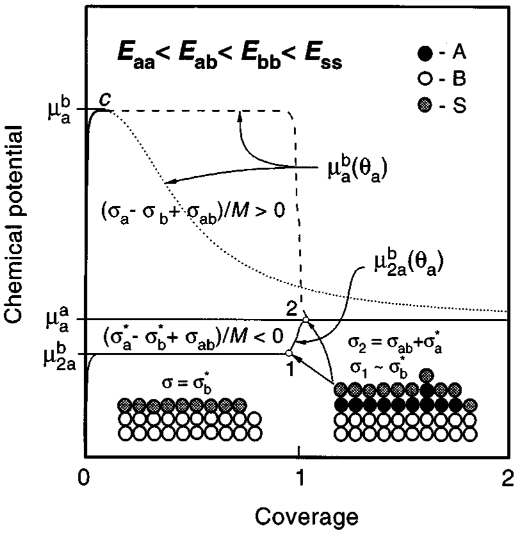

FIG. 2. Schematic representation of the deposition process and the adsorbate influence in a system growing in the VW mode $(\sigma_a-\sigma_b+\sigma_{ab}>0)$. Note that the surface energy of the sandwich system 1 differ significantly from the apparent surface and interfacial energies refined by Eq. (25).

V. SURFACE AND INTERFACIAL FREE ENERGIES OF THE THIN FILMS

Let us now also consider the initial stages of deposition of A on B as an adsorption phenomenon.[2,3,25,26] When condition (1) is satisfied, both FM and SK growth modes are associated with stepped isotherms, quite similar to the multilayer adsorption isotherms obtained for gases on foreign substrates. On the contrary, the VW isotherm displays a maximum at coverages significantly lower than 1 ML, followed by an experimentally unobservable decreasing part, where an unstable equilibrium should exist. The latter case is represented schematically in Fig. 2. The VW isotherm $\mu_a^b(\theta_a)$ is drawn by a full line up to the maximum c (stable adsorption equilibrium) and by a dotted line after c, where the equilibrium is unstable. At point c the VW growth of A on B (three-dimensional nucleation) begins, which requires relatively high supersaturations—$\mu_a\gtrsim\mu_a^b\gg\mu_a^a$. The dashed curve, also denoted by $\mu_a^b(\theta_a)$, is a hypothetical isotherm of A on B, which would be obtained if one initially suppresses the adsorption on the top of the first monolayer and allows it only after the first monolayer is completed. Although it is not possible to realize this isotherm at all, it is depicted only to show that the area between it and μ_a^a is just $(\sigma_a-\sigma_b+\sigma_{ab})/M>0$.

The introduction of an adsorbate S into the system (with chemical potential μ_{se}, which is lower than the bulk chemical potential μ_s^s and at which a nearly complete S ML on B is adsorbed) changes the surface energy σ_b of the initial clean B substrate to $\sigma_b^*=\sigma_b^*(\mu_{se})$ according to Eqs. (52) and (37). If condition (46) is satisfied, then the ''clean'' isotherm $\mu_a^b(\theta)$ is transformed to a stepped isotherm, denoted in Fig. 2 as $\mu_{2a}^{b}(\theta_a) \equiv \mu_{2a}^{b}(\theta_a, \mu_{se})$. According to Eq. (47) the chemical potential of the step is $\mu_{2a}^{b} = \mu_{2a}^{b}(\mu_{se})$.

Let us now calculate the surface energies in the system. Starting with an S-preadsorbed B substrate, the deposition of A now follows the isotherm $\mu_{2a}^{b}(\theta_a)$, so that at point 1 one obtains the sandwich, depicted in the lower right-hand corner of the figure. The free-energy change by the deposition of A by chemical potential $\mu_a = \mu_{2a}^{b}$ is

$$\Delta f_1 = \int_0^{\theta_a} \mu_{2a}^{b}(\theta) d\theta - \theta_a \mu_{2a}^{b},$$

and with $\theta_a \approx 1$ one obtains, for the change of the surface free energy of σ_b^*,

$$\Delta \sigma_b^*(\mu_{2a}^{b}) = -M \Delta f_1 \approx 0.$$

Hence the surface free energy of the whole sandwich in point 1 is

$$\sigma_1 = \sigma_b^* - \Delta \sigma_b^*(\mu_{2a}^{b}) \approx \sigma_b^*, \tag{50}$$

i.e., the surface free energy of the S preadsorbed B substrate is practically unchanged after the deposition of a nearly complete A ML *at the chemical potential* μ_{2a}^{b}. If additionally the adsorption isotherm on S on B is similar to those depicted in Fig. 1(b) and $\mu_{se} = \mu_s^{b}$ ($\theta_s \approx 1$), then $\sigma_1 \approx \sigma_b^* \approx \sigma_b$.

The free-energy change at point 2 of the isotherm $\mu_{2a}^{b}(\theta_a)$ is

$$\Delta f_2 = \int_0^{\theta_a} \mu_{2a}^{b}(\theta) d\theta - \theta_a \mu_a^{a}.$$

With $\theta_a \approx 1$, and taking into account Eq. (46), the surface free energy σ_b^* is changed now with

$$\Delta \sigma_b^*(\mu_a^{a}) \approx M(\mu_a^{a} - \mu_{2a}^{b}) = -\sigma_a^*(\mu_{se}) + \sigma_b^*(\mu_{se}) - \sigma_{ab},$$

so that for the total surface free energy of the sandwich in point 2, 1 becomes

$$\sigma_2 = \sigma_b^* - \Delta \sigma_b^*(\mu_a^{a}) = \sigma_{ab} + \sigma_a^*(\mu_{se}). \tag{51}$$

From a macroscopical point of view both sandwiches have one A/B interface, one S/A interface, and one S surface, and it could be expected that $\sigma_1 \approx \sigma_2 \approx \sigma_{ab} + \sigma_{sa} + \sigma_s$, which is evidently not true. The reason is that the surface energies in Eq. (25) are implicitly defined for the bulk chemical potentials of the corresponding phases. For sandwich 1, only the chemical potential of B is the bulk potential, while the chemical potentials of both A and S phases differ from the bulk values, so that neither the energy of the interfaces A/B and S/A nor the energy of the surface S could be defined by Eq. (25). For sandwich 2, however, the energy of the A/B interface is just σ_{ab}, because the chemical potentials of both B and A phases are the bulk potentials. For the same reason, the energies of the interface S/A and of surface S could not be expressed by Eq. (25), because μ_{se} is different from the bulk chemical potential μ_s^{s}, which explains why the total energy of both above interfaces is $\sigma_a^*(\mu_{se}) \neq \sigma_{sa} + \sigma_s$. Similarly if $\mu_{se} \neq \mu_s^{s}$ then $\sigma_b^*(\mu_{se}) \neq \sigma_{sb} + \sigma_s$ as well.

However, as evident from (41), $\sigma_a^*(\mu_{se}) - \sigma_b^*(\mu_{se}) = \sigma_{sa} - \sigma_{sb}$ even for $\mu_{se} \neq \mu_s^{s}$, when $\theta_{se}^{a} \approx \theta_{se}^{b} \approx 1$. This result confirms once again that the only way to calculate correct surface free energies in the case of thin films on a substrate is to make use of the general expression

$$\sigma^* = \sigma + M \int_0^{\theta_d} \mu_d(\theta) d\theta - M \theta_d \mu_{de}, \tag{52}$$

in which σ is the surface free energy of a clean substrate, σ^* the total surface free energy of a system deposit/substrate, which includes the substrate-deposit interface and the deposit surface, μ_{de} the equilibrium chemical potential of the deposit at coverage θ_d; and $\mu_d(\theta)$ the dependence of the chemical potential of the deposit on coverage (adsorption isotherm). Thus even by macroscopically well-defined surfaces and interfaces with negligible entropy, solely internal energetic calculations (bond-counting procedure) could lead to an erroneous result if one does not account for the chemical potentials of the components. An obvious and important consequence from Eq. (52) is that there is no way to separate the individual contributions of the substrate-deposit interface and of the deposit surface to the total free-energy change. As a matter of fact both interfaces above are always simultaneously created by thin-film deposition. Therefore, from a thermodynamical point of view it is impossible to define the corresponding free energies singly. Until the chemical potential of the thin film is still lower than its bulk value, one can speak solely about the reduced surface free energy of the initial substrate. Strictly speaking, the interfacial energy and the surface energy of the deposit lose physical sense as separate quantities, while the chemical potential of the deposit is lower than those of the bulk material.

VI. SUBSTRATE-INDUCED DEMIXING BETWEEN DEPOSIT AND ADSORBATE

In all above considerations it was implicitly assumed that no mixing between the deposit and adsorbate takes place. According to the thermodynamics of binary systems, bulk separation of the components occurs, roughly speaking, if $-W_{sa} \gtrsim kT$. So it seems reasonable to assume that the same inequality justifies the neglecting of mixing in two dimensions as well. This is absolutely true in the case of one monolayer only (when the occupation of the next monolayer is prohibited)—the partition functions of the 3D- and 2D-mixed phases do not differ except in the value of the lattice coordination number Z (cf., for example, the 3D binary isotherm[23,27] and 2D binary isotherm.[28]) In the case of multilayer adsorption, however, the content in the different monolayers may deviate significantly from the average content of binary adsorbate. This effect is also closely related to the surface segregation phenomena in binary alloys.[24]

In a recent paper[29] a binary multilayer adsorption isotherm was proposed and used to determine the mechanism of the displacement of unmixable layers. Unfortunately, no analysis of the dependence of demixing phenomena near the substrate, i.e., in the first several adlayers, on the bond strength to the substrate is carried out. Therefore, our purpose in this section is, avoiding a comprehensive presentation and detailed calculations of an exact treatment, solely to illustrate the influence of the foreign substrate on the miscibility of binary adsorbates in general.

For that purpose we consider two configurations of an A-S binary adsorbate on substrate B—the first one is a sandwich (a pure A layer on B, covered by a pure S layer), while in the second one all particles are arranged in one monolayer. Assuming, for the sake of simplicity, that the temperature is below the 2D critical temperatures of both components, the free energy of the sandwich is

$$F_{\mathrm{bilayer}}=N_a\eta_a^b+N_s\eta_s^a.$$

The free energy of the mixed single layer in the Bragg-Williams approximation is

$$F_{\mathrm{mix}}=kT(N_a\ln X_a+N_s\ln X_s)+N_a\eta_a^b+N_s\eta_s^b-\frac{Z_pW_{sa}N_aN_s}{N_a+N_s},$$

where $X_a=N_a/(N_a+N_s)$ and $X_s=N_s/(N_a+N_s)$ are the relative contents of the components. Similarly to the bulk compounds the binary monolayer is considered as a compact (but not necessary full) layer without holes. $N_s\leqslant N_a$ and $N_s+N_a\leqslant M$ are evidently also assumed.

Thus for the difference of the free energies, one obtains

$$\Delta F=\frac{F_{\mathrm{bilayer}}-F_{\mathrm{mix}}}{N_a+N_s}=Z_pW_{sa}X_aX_s-kT(X_a\ln X_a+X_s\ln X_s)+Z_o(E_{sa}-E_{sb}). \tag{53}$$

The first two terms in this expression are actually the free energy of 2D interlayer mixing, which obviously does not depend on the bond strength of the substrate. The last term, however, being substrate dependent, reveals its influence on the interlayer demixing in the adlayer. Thus, if $E_{sa}<E_{sb}$ (which is usually the case when $E_{aa}<E_{bb}$), this additional internal energy term in ΔF favors the decomposition of the mixed adlayer to a sandwich bilayer (interlayer demixing). Moreover, it could overcompensate for the free energy of interlayer mixing, so that even components, miscible in all proportions in three dimensions, on a foreign substrate become separated into two practically pure, superimposed layers (but not as different phases in one monolayer).

In the case of strongly bonding substrates ($E_{aa}>E_{bb}$) the additional energy term, induced by the substrate, changes its sign: ΔF becomes positive and the binary monolayer configuration becomes more stable. Hence, in the submonolayer range only intralayer mixing/demixing could take place, which is not affected by the substrate. Only after the total coverage exceeds one monolayer does the mixed adlayer begins to ''feel'' the substrate. It could be shown that the layerwise separation, as in the former case, becomes energetically favored, but that goes beyond the scope of the present paper.

VII. CONCLUSION

It was shown that, unlike in the case of a bulk adsorbent, adsorption substantially alters the thermodynamic functions of a thin film. A negligible amount of foreign components could inverse the thermodynamic stability of the 2D and 3D phases of the deposit, as compared to the ''clean'' system. The criterion for 2D stability depends on the adsorbate coverage. In the particular case of one adsorbate monolayer, the interfacial energies are solely responsible for the 2D stability. The chemical potential of the adsorbate-covered deposit monolayer on whatever substrate differs little from the chemical potential of the corresponding bulk phase. This implies that heteroepitaxial growth on adsorbate-precovered surfaces could be considered to take place practically on an ''own'' substrate. The foreign substrate could induce a layerwise demixing in the first several monolayers of a binary adsorbate even when both components are miscible in all proportions in the bulk. It was shown that care must be taken when defining surface and interfacial energies of thin films and sandwich structures.

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