

## Nucleation calculations in a pair-binding model

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Calculations of the nucleation and growth of thin films are presented. These atomistic calculations depend on adsorption ( $E_a$ ), diffusion ( $E_d$ ), and lateral binding ( $E_b$ ) energies. A simplified pair binding model of small two-dimensional clusters is used to make the calculations explicit for layer-plus-island (or Stranski-Krastanov) growth systems. Within such a model it is found that at least a crude (Einstein) representation of surface vibrations is needed to make reasonable predictions at low supersaturation. The calculations are applied to extract parameter values from nucleation and growth experiments on Ag/W(110), Ag/Mo(100), Ag/Si(111), and Ag/Si(100), and for rare gases onto various (plated) substrates. Comments are made about the parameters obtained for these systems, and about the role of surface crystallography and defects.

### I. INTRODUCTION

Nucleation and growth processes are responsible for the structure of thin films grown on surfaces. It is generally accepted that there are three types of growth possible, in the simplest cases when there is no interdiffusion between deposit and substrate. The extensive experimental work which has been done to test our ideas about these processes has been reviewed.<sup>1</sup>

In the much-studied island, or Volmer-Weber, growth mode, small three-dimensional (3D) clusters form directly on the bare substrate. In the layer, or Frank-van der Merwe, growth mode, it is expected that two-dimensional (2D) clusters will form on each layer, provided that the spacing between nuclei is small in comparison to the spacing between steps on the surface.

In the layer-plus-island, or Stranski-Krastanov (SK), growth mode the simplest picture is that the layers form first, and that the islands grow from two- or three-dimensional clusters on top of the intermediate layer(s). This is illustrated schematically in Fig. 1. This figure also points out that the experimental variables are the substrate temperature  $T$  and the arrival rate  $R$ , and indicates important energy parameters. In practice, it seems that the SK mode is quite close to layer growth, and that the growth of islands can sometimes proceed alongside further layer growth. In this case, it seems reasonable to consider the nuclei to be 2D clusters, with conversion to 3D islands taking place at a later stage.

The purpose of this paper is to present a simplified nucleation theory of 2D clusters which can be applied to layer and SK growth modes. In these modes, the deposits often grow at relatively low supersaturation values,  $S = R/R_e$ , where  $R_e$  is the reevaporation rate of the bulk deposit at the given temperature  $T$ . In such conditions the chemical potential driving force for condensation  $\Delta\mu = kT \ln S$  is also small. It is shown here that to ensure self-consistency for small  $S$  values, explicit account must be taken of surface vibrations. Calculations within the Einstein model are presented to illustrate this

point. These calculations are then used to abstract parameters from both Ag and rare-gas deposition systems. The results for Ag have recently been described in outline, in the context of a recent conference review;<sup>2</sup> here the details needed to understand such results are given and discussed.

The theory is used to make specific predictions for the stable cluster density  $n_x(R, T)$  which can then be compared with the experimental (maximum or saturation) island density  $N(R, T)$ . For complete condensation conditions the predictions depend on diffusion ( $E_d$ ) and lateral binding ( $E_b$ ) energies. The onset of incomplete condensation results in a dramatic decrease in  $n_x(R, T)$  at a temperature determined in addition by the adsorption energy ( $E_a$ ). Thus application of this model amounts to the simplest two parameter (or three parameter at high temperatures) fit to the experimental data  $N(R, T)$ , measured by microscopy.

Particular emphasis is given to the systems Ag/W(110),<sup>3</sup> Ag/Mo(100),<sup>4</sup> and Ag/Si(100) and

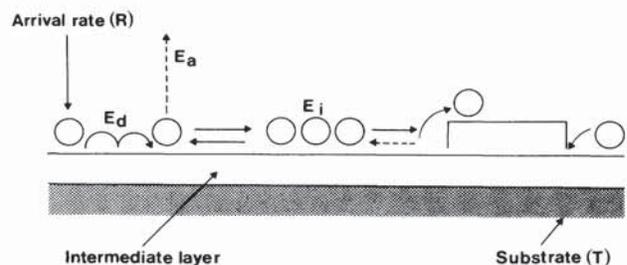


FIG. 1. Schematic illustration of the processes occurring in layer plus island, or Stranski-Krastanov growth. The independent variables are the arrival rate ( $R$ ) and substrate temperature ( $T$ ). Also indicated are the activation energies for adsorption ( $E_a$ ) and diffusion ( $E_d$ ), and the binding energy  $E_i$  of the critical cluster, which contains  $i$  atoms. Here and in Fig. 2, the dotted lines indicate the processes which are less important in this growth mode.

Ag/Si(111),<sup>5</sup> which have been studied by using UHV scanning electron microscopy (SEM) techniques. Comments are also made on rare-gas deposition systems, which were studied recently<sup>6</sup> and earlier<sup>7</sup> by low-temperature transmission electron microscopy (TEM) techniques.

The nucleation theory developed previously is described in Sec. II: this is extended to ensure consistency in the low supersaturation limit in Sec. III. Comparisons with experiment are made in Sec. IV: a discussion follows in Sec. V.

## II. NUCLEATION OF 2D CLUSTERS

### A. Rate equations and processes

The first nucleation theory for 2D clusters was given by Stowell and Hutchinson,<sup>8</sup> and a general equation for the maximum cluster density was first given by Stowell.<sup>9</sup> The nucleation theory needed can be derived within the rate equation framework described previously,<sup>10</sup> assuming single adatoms to be the only species which are effectively mobile on the surface. The equations for the density  $n_j$  of clusters of size  $j$  can be written as

$$dn_1/dt = R - n_1/\tau_a - d(n_x w_x)/dt, \quad (2.1)$$

$$dn_j/dt = 0 \quad (2 \leq j \leq i), \quad (2.2)$$

$$dn_x/dt = \sigma_i D n_1 n_i - 2n_x dZ/dt. \quad (2.3)$$

Here Eq. (2.1) expresses the change in single adatom population  $n_1$  due to arrival from the vapor at rate  $R$ , loss by evaporation with a stay time  $\tau_a$ , and by incorporation into existing clusters. Equation (2.2) expresses the (approximate) local thermodynamic equilibrium which exists between subcritical clusters of size  $j \leq i$ . The critical size  $i$  corresponds to the clusters with the lowest concentration, or highest free energy if equilibrium is assumed.

Equation (2.3) sums the supercritical (stable) clusters as  $n_x = \sum_{j=i+1}^{\infty} n_j$ , in terms of a nucleation rate ( $\sigma_i D n_1 n_i$ ) and a coalescence rate proportional to the rate of change of the substrate coverage by stable clusters ( $Z$ ).

The coupling of Eqs. (2.1) and (2.3) arises because of the interaction between nucleation and growth stages, as illustrated in Fig. 2.<sup>2</sup> The last term in (2.1) can be written as

$$d(n_x w_x)/dt = n_1/\tau_n + n_1/\tau_c + RZ. \quad (2.4)$$

The three terms represent incorporation of single atoms into stable clusters by nucleation, diffusion capture, and direct impingement, respectively. As shown earlier,<sup>1,10</sup> most nucleation occurs under steady-state conditions, with  $dn_1/dt = 0$  in Eq. (2.1). Under these conditions it is convenient to write (2.1) and (2.4) as

$$n_1 = R\tau(1-Z), \quad (2.5)$$

with  $\tau^{-1} = \tau_a^{-1} + \tau_n^{-1} + \tau_c^{-1}$ , where  $\tau_c^{-1} = \sigma_x D n_x$ . This expresses the competitive nature of reevaporation, which is dominant at high temperatures, and capture by stable

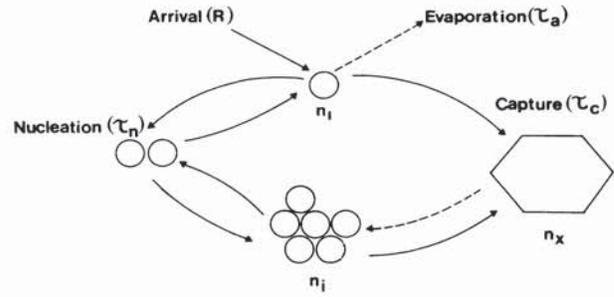


FIG. 2. Schematic illustration of the interaction between the nucleation and growth stages. The single adatom population ( $n_1$ ) determines the critical cluster population ( $n_i$ ); however,  $n_1$  is itself determined by the arrival rate  $R$ , and the characteristic times for evaporation ( $\tau_a$ ), nucleation ( $\tau_n$ ), and diffusion capture ( $\tau_c$ ) by  $n_x$  stable clusters. Only after these clusters cover a sizable fraction of the substrate ( $Z$ ) is direct impingement significant.

clusters which dominates at low temperatures under complete condensation conditions; the nucleation term is always unimportant numerically, and will be ignored subsequently. The capture number  $\sigma_x$  and the adatom diffusion coefficient  $D$  enter via solution of the relevant (2D) diffusion equation.<sup>10</sup>

Two other relations are needed to couple (2.1) and (2.3) analytically. There is first the relation between substrate coverage  $Z$  and atoms in stable clusters ( $n_x w_x = \sum_{j=i+1}^{\infty} n_j w_j$ ). Specializing to 2D clusters, this is simply

$$dZ/dt = N_a^{-1} d(n_x w_x)/dt, \quad (2.6)$$

where  $N_a$  is the density of atoms per unit area in the deposit. Clearly if the deposit is 1 ML thick,  $N_a^{-1} = \Omega^{2/3}$ , where  $\Omega$  is the atomic volume, but Eq. (2.6) allows for (constant thickness) multilayer nuclei.

The second relation needed is that between  $n_i$  and  $n_1$  in (local) thermodynamic equilibrium. This is the Walton relation, often written in the form

$$(n_i/N_0) = (n_1/N_0)^i \sum_m C_i(m) \exp[\beta E_i(m)], \quad (2.7)$$

where  $N_0$  = the substrate atomic density,  $\beta = (kT)^{-1}$ , and  $E_i(m)$  and  $C_i(m)$  are the energies and statistical weightings of  $i$ -sized clusters of configuration  $m$ . In simplified theories appropriate to relatively high supersaturation ( $S \gg 1$ ), Eq. (2.7) is limited to one configuration having the highest binding energy, so that we write  $C_i$  and  $E_i$  for a given  $i$ .

When these (2D) approximations have been made, Eq. (2.3) can be written as a function of the coverage  $Z$ , i.e.,

$$dn_x/dZ = J - 2n_x, \quad (2.8)$$

where the "nucleation rate" term is

$$J = (\sigma_i C_i D n_1^{i+1} \exp(\beta E_i) N_0^{1-i} N_a) / (\sigma_x D n_1 n_x + RZ)$$

and  $n_1$  is given by Eq. (2.5). The differential equation (2.8) for  $n_x(Z)$  therefore has solutions which depend on

the dominant contribution to  $n_1$ . However, Stowell<sup>9</sup> initially showed that the maximum cluster density, assumed to occur at a coverage  $Z_0$ , can be obtained simply from Eq. (2.8) as  $n_x = J/2$ . Rearranging this equation and setting in the explicit expressions for  $J$  and  $n_1$  leads eventually to

$$(n_x/N_0)(g+r)^i(Z_0+r) = f(Z_0, i)(R/N_0^2 D)^i \times \exp(\beta E_i)(\sigma_x D \tau_a N_0)^{i+1}, \quad (2.9)$$

where the ratio  $r = \tau_a/\tau_c = \sigma_x D \tau_a n_x$ . Equation (2.9) is of the same form as given previously (Ref. 1, Eq. 2.17), but the constants  $f$ ,  $g$ , and  $Z_0$  contained in Eq. (2.9) have been retained explicitly. This means that the three analytical regimes (denoted *complete*, *initially incomplete*, and *extreme incomplete*<sup>1</sup>) can be obtained exactly, depending on which terms are dominant on the left-hand side of Eq. (2.9). For complete condensation  $r \gg g$ , for initially incomplete condensation  $Z_0 < r < g$ , and for extreme incomplete condensation  $r \ll Z_0$ .

Equation (2.9) has been used to calculate  $n_x(R, T)$  in general, given particular forms for  $D$ ,  $\tau_a$ , and  $E_i$ . But for layer and Stranski-Krastanov growth, the special case of *complete condensation*, when reevaporation is negligible, is particularly important. In this case, Eq. (2.9) simplifies to

$$(n_x/N_0)^{i+2} = f(Z_0, i)(R/N_0^2 D)^i \exp(\beta E_i). \quad (2.10)$$

By taking the  $(i+2)$ th root of this equation we obtain an equation of the same form as derived previously<sup>1,3,5</sup> for  $(n_x/N_0)$ , with the correct constants. In order to reproduce this regime exactly we have  $f(Z_0, i) = \eta(Z_0, i) Q(i)$  with  $Q(i) = (\sigma_i C_i N_a/N_0)^{1/(i+2)}$ , and  $\eta(Z, i)$  as computed previously (Ref. 1, Fig. 6c or Ref. 3, Fig. 5). The factor  $g$  is given by  $g^i = \sigma_x^{i+1}$ . In Eq. (2.9), however, its exact value is unimportant as it is only used to interpolate between the low- and high-temperature regimes, so we have used  $\sigma_x = 5$ . A short physical argument explaining the form of Eq. (2.10) is given elsewhere.<sup>2</sup> It is also important to realize that  $(n_x/N_0)$  is very insensitive to the choice of  $Z_0$  since most nucleation occurs in the low-temperature limit  $Z \ll Z_0$ .

### B. Thermally activated processes and numerical solutions

The various processes: adsorption, adatom diffusion, cluster formation, and bulk evaporation and/or condensation are typically thermally activated processes with Arrhenius temperature dependences, and energies  $E_a$ ,  $E_d$ , and  $E_i$  indicated in Fig. 1. In particular, it is conventional to write the adatom stay time  $\tau_a$  as

$$\tau_a^{-1} = \nu_a \exp(-\beta E_a) \quad (2.11)$$

and the diffusion constant  $D$  as

$$D = \alpha \nu_d N_0^{-1} \exp(-\beta E_d), \quad (2.12)$$

where  $E_a, \nu_a$  and  $E_d, \nu_d$  are adsorption and diffusion energies and frequencies, respectively, and  $\alpha = 0.25$  for

diffusion in two dimensions.

Evaluation of the right-hand side of Eq. (2.9) or (2.10) requires a model for the critical cluster binding energy  $E_i$ . In fact only models in which all  $E_j$  can be evaluated can be solved. This is because these equations *assume* that  $i$  is the critical size, and correspondingly that local equilibrium is maintained [Eq. (2.7)] for all  $j \leq i$ . This only happens for small  $j$ , and the actual critical size  $i$  is that size for which  $n_x(j)$ , or equivalently the predicted nucleation rate  $J(j)$ , is a minimum.<sup>1</sup> Thus this paper is limited to a very specific pair binding model in which  $E_j = b_j E_b$ , and  $b_j$  is the number of nearest-neighbor bonds, of strength  $E_b$ , in a  $j$ -sized cluster. Furthermore, the explicit calculations have to assume a particular cluster geometry. Although any geometry is possible in principle, and is of course actually determined by the forces between the adatoms themselves and the substrate, we assume here close-packed clusters on a hexagonal lattice. For these, the  $b_j$  can be evaluated by simple counting, and some values are given in Appendix A.

With these values Eq. (2.10) can be solved directly. Equation (2.9) is solved by iteration, using Eq. (2.10) as the starting point. In this complete condensation limit, the  $n_x(R, T)$  predictions depend sensitively on  $E_d$  [via Eq. (2.12)] and  $E_b$ , and less on the frequency factor  $\nu_d$  and numerical constants. Such predictions have been published previously for Ag/W(110).<sup>11</sup> When reevaporation is allowed [Eq. (2.9)], the behavior at high temperatures is also influenced sensitively by  $E_a$ . Some calculations for Ag/Si(111) and (100) using Eq. (2.11) inserted into (2.9) have been published.<sup>5</sup> However, these high-temperature predictions need to be revised as discussed in the next section.

## III. NUCLEATION AT LOW SUPERSATURATION

### A. General considerations

It might seem an elementary requirement that a nucleation model predicts zero nucleation rate at the equilibrium sublimation pressure  $p_0$  of the deposit: however, this is not assured by the equations described as yet. There are several reasons for this. First, the adsorption energy  $E_a$  is a free parameter, which can be used to model adsorption on a substrate different from the deposit material. In this case, as discussed in general terms elsewhere,<sup>1</sup> the effective supersaturation ratio  $S = p/p_e$  or  $R/R_e$ , where the equilibrium pressure ( $p_e$ ), or rate of evaporation ( $R_e$ ), corresponds to a step in the adsorption isotherm, which for layer-growth systems occurs at  $p_e < p_0$ . For deposition of a material on itself we must have  $E_a$  and  $E_i$  related to the sublimation energy  $L$  by

$$L = E_a + \lim_{i \rightarrow \infty} (E_i/i). \quad (3.1)$$

For a special case of a lattice with nearest neighbor pair bonds this reduces to  $L = E_a + b_\infty E_b$ , and for the hexagonal lattice  $b_\infty = 3$ .

In this limit of large critical cluster size we can see that the transition to incomplete condensation will take place approximately when Eq. (2.10), for large  $i$ , corre-

sponds also to  $r = \sigma_x D \tau_a n_x \approx 1$ . By eliminating  $\sigma_x D n_x$  we find this condition to be

$$\tau_a^{-1} = v_a \exp(-\beta E_a) = (1-Z)(R/N_0) \exp(\beta E_i / i), \quad (3.2)$$

or rearranging using Eq. (3.1):

$$(R/N_0 v_a) = (1-Z)^{-1} \exp(-\beta L). \quad (3.3)$$

Equation (3.3) qualitatively follows the sublimation line with energy  $L$ , but quantitatively it almost certainly does not. In particular, a finite nucleation rate can still occur within the model at the experimental sublimation pressure, given particular choices of parameters, and Eq. (3.3) does not necessarily describe a line which occurs within the actual crystal-growth regime.

To overcome these problems at low supersaturation, generalizations to Eqs. (2.7) and (2.11) have been made which ensure consistency with the equilibrium sublimation pressure, within an Einstein model of the solid. This model has been used to fit the experimental sublimation pressure quite accurately for the cases of Ag and various rare gases, as described in Appendix B.

Similar arguments could be advanced to change the form of the diffusion constant  $D$  [Eq. (2.12)]. But because diffusion is only involved in the kinetics of crystal growth, not the thermodynamics, this has not been done here. In practice the form of the diffusion constant is rather uncertain, and comparison with experiments may have to average over the effects of anisotropic surface crystallography, steps and other defects. Thus we prefer to use  $E_d$  in (2.12) as a parameter to characterize the effective value of  $D$  which is appropriate to the experiments. This is discussed further in Sec. V.

#### B. An Einstein model of adsorption, cluster formation, and evaporation

The model considered can be visualized in terms of the vibrations of the entities indicated in Fig. 2. Adsorption of single adatoms is taken to be localized on  $N_0$  sites. In these sites the adatoms vibrate with frequency  $\nu_a$  perpendicular, and  $\nu_d$  parallel to the surface. The corresponding "Einstein" free energy can be expressed in terms of  $x_a = h \nu_a / kT$  and  $x_d$  using the function we designate as  $\mathcal{E}(x)$ :

$$\mathcal{E}(x) = 0.5x + \ln[1 - \exp(-x)],$$

as

$$E_a(T) = E_a(0) - kT[\mathcal{E}(x_a) + 2\mathcal{E}(x_d)], \quad (3.4)$$

where  $E_a(0)$  corresponds to the energy  $E_a$  used previously in Eq. (2.11).

Adsorption in this model follows the Langmuir isotherm for low adatom concentrations  $n_1$ , and the equilibrium evaporation rate  $R_e$  is given by<sup>12</sup>

$$R_e = p_e / (2\pi m kT)^{1/2} \\ = (2\pi m / h^3)(kT)^2 (n_1 / N_0) \exp[-\beta E_a(T)]. \quad (3.5)$$

The same model can give the evaporation rate of the bulk solid, with no vacancies, in the form

$$R_e = (2\pi m / h^3)(kT)^2 \exp[-\beta L(T)], \quad (3.6)$$

where  $L(T) = E_a(T) + b_\infty E_b(T)$  is the temperature-dependent sublimation energy corresponding to Eq. (3.1). For consistency, we need  $R_e = n_1 / \tau_a$ , so that

$$\tau_a^{-1} = (2\pi m / h^3 N_0)(kT)^2 \exp[-\beta E_a(T)] \quad (3.7)$$

is the expression to use instead of Eq. (2.11).

Within the nearest-neighbor model we assume that atoms within clusters on the surface retain the same  $\nu_a$  as isolated adatoms, but have  $\nu_b \neq \nu_d$  parallel to the surface. This is consistent with Eq. (3.6) provided that

$$E_b(T) = E_b(0) - (2/b_\infty) kT[\mathcal{E}(x_b) - \mathcal{E}(x_d)], \quad (3.8)$$

where  $E_b(0)$  is the  $E_b$  used previously. Under these conditions, the cluster free energy  $E_j = b_j E_b(T)$  in the simplified Walton expression for  $j = i$ :

$$(n_i / N_0) = C_i (n_1 / N_0)^i \exp[\beta E_i(T)]. \quad (3.9)$$

The above equations [(3.7)–(3.9)] are sufficient to ensure consistency within an Einstein model with the equilibrium vapor pressure of a solid bound by nearest-neighbor forces. Over a limited temperature range  $p_e$  (or  $R_e$ ) can be expressed as

$$p_e = p_0 \exp(-\beta L_0). \quad (3.10)$$

The values of the parameters  $L_0$  and the average frequency  $[(\nu_a + 2\nu_b)/3]$  needed to agree with the vapor pressure of bulk Ag and rare gases in the pressure range below  $10^{-3}$  Torr are given in Appendix B.

## IV. COMPARISON WITH EXPERIMENT

Recent experimental work at Sussex has involved nucleation and growth studies of Ag on W(110), Mo(100), and Si(100) and Si(111) substrates<sup>3–5</sup> by ultrahigh vacuum SEM. In addition, attempts have been made to grow Xe crystals on (xenon-plated) amorphous carbon substrates at low supersaturation<sup>6</sup> following earlier work at low temperatures and pressures,<sup>7</sup> using TEM techniques. The fit of these experiments to the equations of Secs. II and III are discussed here. The calculations were done and the figures produced on a laboratory based PDP11-23 system.<sup>13</sup>

### A. Silver deposits on metals and semiconductors

Figure 3 shows a comparison of the Ag/W(110)  $N(T)$  data<sup>3</sup> with the calculated  $n_x(T)$  based on the complete condensation equation (2.10). Two curves which fit the data tolerably well are shown, corresponding to different values of  $E_b$  around 0.3 eV and  $E_d$  around 0.1 eV. The larger value of  $E_d$  (0.15 eV) gives the steeper slope on the Arrhenius plot and vice versa, and corresponds to the smaller values of  $E_b$  (0.275 eV). Changes of  $E_d$  by around  $\pm 0.05$  eV coupled with changes in  $E_b$  by 0.025 eV are thus consistent with the data, but much larger changes would be inconsistent. In particular  $E_d \geq 0$ , so that we can bracket  $0 \leq E_d \leq 0.20$  eV, and consequently  $0.35 \geq E_b \geq 0.25$  eV.

Figure 4 shows a similar calculation compared with