Revision of single atom local density and capture number varying with coverage in uniform depletion approximation and its effect on coalescence and number of stable clusters*

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In vapour deposition, single atoms (adatoms) on the substrate surface are the main source of growth. The change in its density plays a decisive role in the growth of thin films and quantum size islands. In the nucleation and cluster coalescence stages of vapour deposition, the growth of stable clusters occurs on the substrate surface covered by stable clusters. Nucleation occurs in the non-covered part, while the total area covered by stable clusters on the substrate surface will gradually increase. Carefully taking into account the coverage effect, a revised single atom density rate equation is given for the famous and widely used thin-film rate equation theory, but the work of solving the revised equation has not been done. In this paper, we solve the equation and obtain the single-atom density and capture number by using a uniform depletion approximation. We determine that the single atom density is much lower than that evaluated from the single atom density rate equation in the traditional rate equation theory when the stable cluster coverage fraction is large, and it goes down very fast with an increase in the coverage fraction. The revised equation gives a higher value for the 'average' capture number than the present equation. It also increases with increasing coverage. That makes the preparation of single crystalline thin film materials difficult and the size control of quantum size islands complicated. We also discuss the effect of the revision on coalescence and the number of stable clusters in vapour deposition.

Keywords: single atom density, coverage, uniform depletion approximation, coalescence

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1. Introduction

The precise control of thin film growth in vapour deposition and thus the precise control of the structure and relevant properties become possible only after a variety of competitive mechanisms are understood. High quality thin film preparation, single crystalline material hetero epitaxial growth, and quantum size island vapour deposition depend on the physical processes of nucleation and cluster coalescence in the early stage of growth. For a growing material, its structure and orientation relative to the substrate are dependent on the nucleus structure and orientation.[1,2] Thin film rate equation theory gives a clear physical picture of the various processes involved in nucleation and growth, and it allows the prediction of average quantities with rather good accuracy. Nevertheless, the traditional rate theory yields reliable results only in small total coverage and cannot describe coalescence very accurately.[3,4] It cannot give the results in agreement with experimental data or kinetic Monte Carlo (KMC) simulation data.[5,6] In building up the thin film rate equation theory,[7−15] nucleation has always attracted the attention of many researchers, but cluster coalescence has not received enough. This may be because the rate equation theory that was built up early on was based mainly on the metal thin film vapour growth experiments. No matter whether the prepared metal thin films are single crystalline or poly crystalline, there are small differences in their electrical, thermal, and mechanical properties. This may be the reason why the process of cluster coalescence, which is in close relation to intercrystalline growth, has not been studied further.

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The process of cluster coalescence mainly happens in the case of a larger coverage fraction of stable clusters. The larger the coverage fraction, the more important the role that it takes in growth in the coalescence process. So the coverage has a greater effect on the growth in the coalescence stage than in the nucleation stage. For semiconductors, the quality of thin films strongly depends on their crystalline structure and they are clearly different between single crystals and poly crystals. Electrons, photons, and phonons transmitted in crystals will be reflected from the crystalline boundaries. Hence the crystalline boundaries in thin films will intensely affect the electrical, thermal, and optical properties of thin films. The crystal lattice completeness of thin films synthesized from vapour is related mainly to the coalescence process of stable clusters. Similarly, the size and stability of quantum size islands grown from vapour are also related mainly to the coalescence process in growth, and the density of single atoms as the principal growth source in this process. In conclusion, it is particularly important to investigate the effect of the stable cluster coverage on the coalescence process and the single atom density in the process. Carefully taking into account the coverage effect, a revised single atom density rate equation is given for the widely used rate equation theory,[16] but the work of solving the revised equation has not been done. We solve the equation and obtain the single-atom density and capture number by using a uniform depletion approximation.

2. Thin film growth process and coverage

Thin film growth from single atoms (adatoms), which may be admolecules or precursors in some cases, deposited from the gas phase, is intrinsically a non-equilibrium phenomenon governed by irreversible competition between kinetics and thermodynamics on the substrate surface. The formation processes of the surface new phase in the initial growth stage, which determine thin film structure, quality, and properties, include the processes of adsorption, accommodation, desorption, diffusion, collection, and mutual meeting of adatoms, unstable cluster formation, adatom attachment to and detachment from clusters, cluster mobility, and aggregation, nucleation, nucleus growth, and coalescence.

According to atomic views of nucleation and growth, the processes in the initial stage of thin film growth can be described as adsorption, desorption, and diffusion of atoms on a substrate surface. Initially, single atoms from the vapour source impinge on the substrate surface at a rate R (the number of single atoms per second per unit area). On the substrate surface containing N_0 (per unit area) sites of equal adsorption energy E_a, adsorption and desorption of the atoms occur with the re-evaporation rate characterized by an average staying time τ_a. The atoms with surface density $n_1(t)$ may diffuse on the substrate surface at a diffusivity D and an activation energy E_d for diffusion. Surface diffusion leads to the formation and growth of 2D or 3D clusters. Small clusters containing j atoms with surface density $n_j(t)$ may grow or decay. Growth becomes more probable than decay when the cluster size exceeds a certain critical size i. All clusters larger than the critical cluster can be considered stable and may form nuclei even if some atoms leave during subsequent growth. From the single atom density equation in the previous theory of thin films,[8] it can be seen that the single atom density n_1 is defined as the number of single atoms per unit area on the substrate surface. However, when stable clusters appear, they will capture single atoms, which leads to the growth of stable clusters. Hence, the single atom density would be zero on a substrate surface covered by stable clusters. We can see that the single atom density n_1 used in traditional thin film theory is the average density of the covered and uncovered areas of the substrate surface. In fact, on the area of substrate surface uncovered by stable clusters, the single atom density is defined as $n_{\mathrm{u}1}$, that is, m_1 in Refs. [16]–[19] should be different from n_1. The $n_{\mathrm{u}1}$ is an objective real density and it is a local density. The n_1 is an artificially introduced quantity in the early establishment of the rate equation theory. Then, at any point (x, y) of the substrate surface uncovered by stable clusters, $n_{\mathrm{u}1}$ can be expressed as $n_{\mathrm{u}1} = n_1/(1–Z)$ for the presence of stable clusters, which cover a fraction Z of the substrate. Therefore, the uncovered parts of the substrate surface should be discussed. The related density of single atoms is $n_{\mathrm{u}1}$, but the stable cluster density is still expressed as n_j $(j > i)$. Previously, carefully considering the coverage effect, a revised single atom density rate equation was given for the widely used rate equation theory,[16] but the work of solving the revised equation has not been done.

In this paper, we solve the equation and obtain the single atom density and capture number by using a uniform depletion approximation. According to the

obtained single atom density and capture number, it is shown that the stable cluster coverage on a substrate surface causes a large variation in single atom density, and affects the growth of thin films, quantum size islands, and nanostructure materials in vapour deposition. In Section 3, we discuss the single atom local density, the capture number, and the effect of short-distance correlation between single atoms and stable clusters in the case of incomplete condensation. In Section 4, we study the single atom local density, the capture number and the correlation effect by taking the coverage of the new phase into account in rate equations quantitatively in the uniform depletion approximation. The changes and trends in the single atom local density and capture number with the coverage of the new phase increasing are analysed.

3. Single atom local density, capture number and effect of the short-distance correlation between single atoms and stable clusters

We study the case of incomplete condensation, where the correlation between single atoms and stable clusters does not yet extend into the next cluster, and the densities of both stable and subcritical clusters are very small. For the local density $n_1(\boldsymbol{r},t)$ around a stable cluster of size k, with corresponding radius r_k and the area of the substrate that is covered by the stable clusters, a_k, the diffusion equation takes the form[20]

$$\frac{\partial n_1(\boldsymbol{r},t)}{\partial t} = D\nabla^2 n_1(\boldsymbol{r},t) - \frac{n_1(\boldsymbol{r},t)}{\tau_{\rm a}} + R \qquad (1)$$

with the boundary conditions, $n_1(\boldsymbol{r},t)=0$ for $t>0$ at the periphery of the stable clusters and $n_1(\boldsymbol{r},t)=R\tau_{\rm a}$ at large distances away. This leads to a transient result for $t<\tau_{\rm a}$, but for $t>\tau_{\rm a}$ the steady-state solution is

$$n_1(\boldsymbol{r}) = R\tau_{\rm a}\left[1-\frac{{\rm K}_0(\sqrt{r^2/D\tau_{\rm a}})}{K_0(\sqrt{r_k^2/D\tau_{\rm a}})}\right], \qquad (2)$$

where R is the rate at which atoms arrive from the vapour; D is the diffusion coefficient of single atoms; $\tau_{\rm a}$ is the mean stay time of single atoms before re-evaporation; and ${\rm K}_0$ is the Bessel function. Viewed from a diffusion standpoint, the density of single atoms, e.g., $n_1(\boldsymbol{r},t)$ for a stable cluster at the origin, varies locally around each stable cluster.[21] The $n_1(\boldsymbol{r},t)$ is just $n_{\rm u1}(\boldsymbol{r},t)$, which is defined by us in the above section.

We focus on the substrate surface region with area S, including a cluster at the origin. Suppose that only one stable cluster is in the region, and the periphery of the region is far from other clusters. In fact, equation (1) holds true only on an uncovered surface outside the stable cluster. We have

$$\frac{\partial n_{\rm u1}(\boldsymbol{r},t)}{\partial t} = D\nabla^2 n_{\rm u1}(\boldsymbol{r},t) - \frac{n_{\rm u1}(\boldsymbol{r},t)}{\tau_{\rm a}} + R, \qquad (3)$$

where we use $n_{\rm u1}(\boldsymbol{r},t)$ instead of $n_1(\boldsymbol{r},t)$. The term on the left-hand side of Eq. (3) is the number of single atoms increasing per second on the surface uncovered by the stable cluster. The second and third terms on the right-hand side of Eq. (3) are the desorption number and impinging number of single atoms per unit area per second on the surface uncovered by the stable clusters, respectively.

The boundary condition: $n_{\rm u1}(\boldsymbol{r},t)=0$ for $t>0$ at the periphery of the stable cluster and $n_{\rm u1}(\boldsymbol{r},t)=R\tau_{\rm a}$ at large distances away. For $t>\tau_{\rm a}$ the steady–state solution is

$$n_{\rm u1}(\boldsymbol{r}) = R\tau_{\rm a}\left[1-\frac{{\rm K}_0(\sqrt{r^2/D\tau_{\rm a}})}{{\rm K}_0(\sqrt{r_k^2/D\tau_{\rm a}})}\right]. \qquad (4)$$

From Eq. (2), in the previous model, the solved single atom local density $n_1(\boldsymbol{r})$ is clearly independent of the coverage of the new phase. And according to expression (4), the single atom local density $n_{\rm u1}(\boldsymbol{r})$ is also clearly independent of the coverage of the new phase.

Now we come to consider the capture number, σ_k, of a k-sized stable cluster. In the rate equations (Eqs. (9), (10), and (12) in Ref. [21]) or mean-filed rate equations (Eqs. (5) and (6) in Ref. [22]), the loss number of single atoms by diffusion to a k-cluster (in an 'average' environment) is given by $\sigma_k n_{\rm u1} D$. The 'average' of all σ_k is σ_x. Viewed from a diffusion standpoint, the density of single atoms must vary locally around each stable cluster, e.g., it is $n_{\rm u1}(\boldsymbol{r},t)$ for a stable cluster at the origin, and this diffusive loss is just $2\pi r_k D\left(\partial n_{\rm u1}(\boldsymbol{r},t)/\partial r\right)_{r_k}$. Thus, in order to evaluate the capture number σ_k, we need a model to reveal how $n_{\rm u1}(\boldsymbol{r},t)$ varies in the neighbourhood of a stable k-sized cluster, and the definition of the capture number is given as follows,[21] which follows from the equivalence of these two viewpoints,

$$\sigma_k = \left(\frac{2\pi r_k}{n_{\rm u1}}\right)\left(\frac{\partial n_{\rm u1}(\boldsymbol{r},t)}{\partial r}\right)_{r_k}. \qquad (5)$$

In Eq. (5), $n_{\rm u1}(\boldsymbol{r})$ is approximately taken to be a large distance from the stable cluster, that is, $R\tau_{\rm a}$.

To find the diffusive flux of single atoms into the stable cluster, the corresponding expression for σ_k is obtained by differentiating Eq. (4) and substituting the result into Eq. (5), as

$$\sigma_k = \left[\frac{2\pi r_k}{\sqrt{D\tau_{\rm a}}}\right]\left[\frac{{\rm K}_1(\sqrt{r_k^2/D\tau_{\rm a}})}{{\rm K}_0(\sqrt{r_k^2/D\tau_{\rm a}})}\right], \tag{6}$$

where $\rm K_0$ and $\rm K_1$ are the Bessel functions. Being the same as the theoretical value in the previous model,[21] the capture number obviously does not rely on the coverage of the new phase.

There are two interesting limits of the Bessel functions $\rm K_1$ and $\rm K_0$. For very high temperatures (small $\tau_{\rm a}$) and large clusters, the arguments are large and ${\rm K}_1 = {\rm K}_0$. In this case, the contribution of diffusion to the growth of k-sized stable clusters, $\sigma_x D n_{\rm u1}$, is just $2\pi r_k R\sqrt{D\tau_{\rm a}}$. The clusters therefore grow as if absorbing all the atoms that fall on an area $[a_k + 2\pi r_k\sqrt{D\tau_{\rm a}}]$. Since $a_k = \pi r_k^2$, the details of the contribution of diffusion are not of great significance when $r_k \gg \sqrt{D\tau_{\rm a}}$. Then direct impingement is a most important mechanism for the growth of these clusters.

At lower temperatures and for smaller clusters, still within the incomplete condensation regime, the situation can be reversed. The σ_k term becomes dominant and the arguments of the Bessel function are small. In this case, the asymptotic behaviours of $\rm K_1$ and $\rm K_0$ give

$$\sigma_k = \frac{2\pi}{\ln\left[\sqrt{D\tau_{\rm a}/r_k^2}\right]}. \tag{7}$$

In this case, the loss term clearly varies more slowly, though it still increases with increasing cluster size.

In order to use Eq. (6), an average of σ_k is taken over all values of size k. However, since σ_k is a slowly varying function of k, it will usually be sufficient to evaluate σ_k by using Eq. (6) for the average cluster radius r_x. Correction terms may be required if the size distribution is very pronounced.

4. Uniform depletion approximation

For the nucleation theory to be useful generally, we need expressions for σ_i and σ_k (and hence σ_x) in the general case. Although no exact solutions have been obtained, two approaches have been developed.

Lewis[23,24] has developed a computational scheme, in which the clusters are randomly distributed and the capture process is also taken into account, which competes with re-evaporation. This approximation is called the 'uniform depletion approximation'. Stowell and Hutchinson,[25] Stowell[26] and Sigsbee[27] have evaluated cluster growth rates by placing all the clusters on a lattice. This model is called the 'lattice approximation'. Stowell[26] and Venables[21] obtained the values for σ_x, σ_i, and σ_k in the approximations called the "lattice approximation" and the "uniform depletion approximation", respectively. We use the real single-atom density $n_{\rm u1}(\boldsymbol{r}, t)$, that is, the single atom density in a region uncovered by the stable clusters, to replace the single-atom average density $n_1(\boldsymbol{r}, t)$ on the surfaces covered and uncovered by stable clusters in the traditional rate equation theory, which will be applied to uniform depletion approximation, and give the corresponding results. The real problem consists in evaluating the loss of single atoms to stable clusters by solving the single atom diffusion equation, similar to expression (4), where the local density $n_{\rm u1}(\boldsymbol{r}, t)$ is zero at the boundary of each stable cluster. This is clearly an impossible problem to solve, since we do not know where the clusters are or how large they are. The 'uniform depletion approximation' consists in singling out a stable k-sized cluster and the value of $n_1(\boldsymbol{r}, t)$ around this cluster at $\boldsymbol{r} = 0$ is then given by the solution of[21]

$$\frac{\partial n_1(\boldsymbol{r}, t)}{\partial t} = D\nabla^2 n_1(\boldsymbol{r}, t) - n_1(\boldsymbol{r}, t)(\tau_{\rm a}^{-1} + \sigma_x D n_x) + R(1 - Z). \tag{8}$$

The boundary conditions are $n_1(\boldsymbol{r}, t) = 0$ at $r = r_k$ and $\nabla^2 n_1(\boldsymbol{r}, t) = 0$ as $r \to \infty$; e.g., for large $\boldsymbol{r}$, $n_1(\boldsymbol{r}, t)$ equals the density of single atoms given by the rate equation (Eq. (9) in Ref. [20]). Equation (8) is in exactly the same form as that of Eq. (1), if we define τ and R_1 as follows,

$$\begin{cases} \tau^{-1} = \tau_{\rm a}^{-1} + \sigma_x D n_x, \\ R_1 = R(1 - Z). \end{cases} \tag{9}$$

Consequently, this equation has a similar solution: for $t > \tau$, this solution (far from the stable clusters) is $n_1 = R_1\tau$, with τ and R_1 given by Eq. (9). The corresponding expression for single atom density $n_1(\boldsymbol{r}, t)$ around stable clusters is in the same form as that of Eq. (2), with τ instead of $\tau_{\rm a}$ and R_1 instead of R. Therefore, it is

$$\sigma_k = 2\pi X_k {\rm K}_1(X_k)/{\rm K}_0(X_k), \quad X_k = \sqrt{(r_k^2/D\tau)}, \tag{10}$$

and

$$n_1(\boldsymbol{r},t) = R_1\tau\left[1-\frac{\mathrm{K}_0(\sqrt{r^2/D\tau})}{\mathrm{K}_0(\sqrt{r_k^2/D\tau})}\right]. \quad (11)$$

In a way similar to the above consideration, we focus on the substrate surface region with area S, including a cluster at the origin and n_xS clusters in the region. In fact, equation (8) holds true only for the real density of single atoms, $n_{\mathrm{u}1}(\boldsymbol{r},t)$, defined on uncovered surface outside stable clusters. If considering only the region where single atom density is $n_{\mathrm{u}1}(\boldsymbol{r},t)$, that is, the region uncovered by stable clusters, with $n_{\mathrm{u}1}(\boldsymbol{r},t)$ replacing $n_1(\boldsymbol{r},t)$ and R replacing $R(1-Z)$ in equation (8), we have

$$\frac{\partial n_{\mathrm{u}1}(\boldsymbol{r},t)}{\partial t} = D\nabla^2 n_{\mathrm{u}1}(\boldsymbol{r},t) - \left[n_{\mathrm{u}1}(\boldsymbol{r},t)\tau_{\mathrm{a}}^{-1} + n_{\mathrm{u}1}\sigma_x D n_x\right] + R. \quad (12)$$

The term on the left-hand side of Eq. (12) is the number of single atoms increased per second on the surface uncovered by the stable clusters. The second and fourth terms on the right-hand side of Eq. (12) are the desorption number and impinging number of single atoms per unit area per second on the surface uncovered by stable clusters, respectively. The first term on the right-hand side is the loss number of single atoms per unit area per second on the surface uncovered by stable clusters captured by the cluster at the origin, that is the number of single atoms arriving at this stable cluster at the origin. The third right term is the loss number of single atoms per unit area per second on the surface uncovered by stable clusters captured by the $[(n_x-1)S \approx n_xS]$ stable clusters outside the origin, that is the number of single atoms arriving at these stable clusters outside the origin. The total number of the stable clusters outside the origin per unit area, in the total surface region, covered and uncovered by stable clusters, is approximately n_x, and the corresponding surface area uncovered by stable clusters is $(1-Z)$, so viewing from the surface region uncovered by stable clusters, the corresponding total number of stable clusters outside the origin per unit surface area uncovered by stable clusters is $n_x/(1-Z)$. Therefore, the third term on the right-hand side of Eq. (12) should be replaced by $n_{\mathrm{u}1}\sigma_x D n_x/(1-Z)$, and a more detailed proof can be found in Ref. [16]. We rewrite this revised equation (12) as

$$\frac{\partial n_{\mathrm{u}1}(\boldsymbol{r},t)}{\partial t} = D\nabla^2 n_{\mathrm{u}1}(\boldsymbol{r},t) - n_{\mathrm{u}1}(\boldsymbol{r},t)\left(\tau_{\mathrm{a}}^{-1} + \frac{\sigma_x D n_x}{1-Z}\right) + R. \quad (13)$$

The boundary conditions are $n_{\mathrm{u}1}(\boldsymbol{r},t) = 0$ at $r = r_k$ and $\nabla^2 n_{\mathrm{u}1}(\boldsymbol{r},t) = 0$ as $r \to \infty$.

Equation (13) is in exactly the same form as that of Eq. (3), if we define τ_1, such that

$$\tau_1^{-1} = \tau_{\mathrm{a}}^{-1} + \frac{\sigma_x D n_x}{1-Z}. \quad (14)$$

Consequently, this equation has a similar solution: for $t > \tau_1$, the solution (far from the clusters) is $n_{\mathrm{u}1}(\boldsymbol{r},t) = R\tau_1$, with τ_1 given by Eq. (14), that is, $n_{\mathrm{u}1}(\boldsymbol{r},t) = R\tau_{\mathrm{a}}[1+\tau_{\mathrm{a}}\sigma_x D n_x/(1-Z)]^{-1}$. The corresponding expression for $n_{\mathrm{u}1}(\boldsymbol{r},t)$ around the cluster is the same form as that of Eq. (4) with τ_1 replacing τ_{a}. Hence, one can write

$$n_{\mathrm{u}1}(\boldsymbol{r}) = R\tau_1\left[1-\frac{\mathrm{K}_0(\sqrt{r^2/D\tau_1})}{\mathrm{K}_0(\sqrt{r_k^2/D\tau_1})}\right], \quad (15)$$

and

$$\sigma_k = \left[\frac{2\pi r_k}{\sqrt{D\tau_1}}\right]\left[\frac{\mathrm{K}_1(\sqrt{r^2/D\tau_1})}{\mathrm{K}_0(\sqrt{r_k^2/D\tau_1})}\right]. \quad (16)$$

In the previous model of uniform depletion approximation, the correlation between single atoms and stable clusters is not an explicit function of the coverage of the new phase, so neither corresponding single atom density $n_{\mathrm{u}1}(\boldsymbol{r},t)$ nor capture number is an explicit function of the coverage. However, from the revised Eqs. (13), (15), and (16) in which the coverage of stable clusters is quantitatively taken into account, it can be seen that the effect of correlation between single atoms and stable clusters is clearly an explicit function of coverage and becomes strong with coverage increasing. So the corresponding single atom density $n_{\mathrm{u}1}(\boldsymbol{r},t)$ and capture number are also a clearly explicit function of the coverage each, and decrease and increase with coverage increasing, respectively. When the coverage is close to unity, the single atom density $n_{\mathrm{u}1}(\boldsymbol{r},t)$ approaches zero.

In the rate equations (8) and (9), and (13) and (14), losses of single atoms by diffusion to a k-sized cluster (in an 'average' environment) are given by $\sigma_k n_1 D$ and $\sigma_k n_{\mathrm{u}1} D$, respectively: the 'average' of all σ_ks is σ_x. The approximation used before, namely $\sigma_x = \sigma_k$ for $r_k = r_x$, enables one to calculate σ_x self-consistently using Eq. (10). Once σ_x is calculated and hence τ via Eq. (9), the individual σ_k can be calculated using Eq. (10). The variation in capture number σ_x with coverage Z is shown in Fig. 1, in the complete condensation case, for the uniform depletion approximation from the present equation (8) (□) and the revised equation (13) (◯), respectively. The data (□)

of σ_x are directly cited from Fig. 2(a) in Ref. [21]. The data (◯) of σ_x for the revised equation (13) are calculated by us, which are similar to the data (□) of σ_x. The revised equation (13) gives higher values of σ_x than the present equation (8), it also increases with Z increasing. When $Z = 1/3$, the values of capture number σ_x for the present equation (8) (□) and the revised equation (13) (◯) are equal to 9.3 and 12.1, respectively. When Z increases from 0 to 1/3, figure 1 shows the percentage difference in capture number between the revised equation (13) and the present equation (8) ranges from 0% to 30.1%.

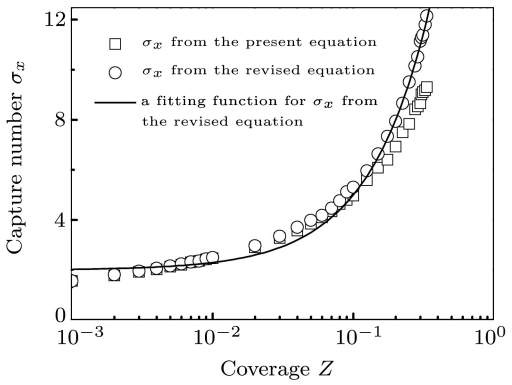


Fig. 1. Variation in capture number σ_x with coverage Z, for the present equation (8) (□) and the revised equation (13) (◯), respectively.

To further investigate the differences in single atom densities n_1 and n_{u1} between the present equation (8) and the revised equation (13), we calculate the single atom densities $n_1/(R/Dn_x)$ and $n_{u1}/(R/Dn_x)$ with varying distance $r/(D\tau)^{1/2}$ between the point and the origin, for $Z_k = Z$, $Z = 0.01$, 0.1, and 0.3, obtained from the present equation solution (11) and the revised equation solution (15), respectively. Single atom densities n_1 and n_{u1} are displayed in Fig. 2(a), showing that the present equation solution (11) is fully consistent with the revised equation solution (15) at low coverage $Z = 0.01$, for the long range of $r/(D\tau)^{1/2}$ from 0 to 3.5. However, the single atom density n_1 is inconsistent with the single atom density n_{u1} at coverage $Z = 0.1$ and 0.3, for $r/(D\tau)^{1/2} < 1.5$ or $\tau/(D\tau)^{1/2} > 3.0$. The inconsistency becomes greater with the increase in coverage Z. For $Z_k = Z$, $Z = 0.3$, and $r/(D\tau)^{1/2} < 1.05$, $n_1/(R/Dn_x)$ is over 10 times as great as $n_{u1}/(R/Dn_x)$ (see Fig. 2(b)). As the coverage increases, the average distance becomes closer between the origin (stable nucleus) and single atoms in the uncovered substrate area, the single atom density near the origin plays a major role, the difference between $n_{u1}/(R/Dn_x)$ and $n_1/(R/Dn_x)$ becomes larger.

If considering only the region where single atom density is $n_{u1}(\boldsymbol{r}, t)$, that is, the region uncovered by stable clusters, with $n_{u1}(\boldsymbol{r}, t)$ replacing $n_1(\boldsymbol{r}, t)$ and R replacing $R(1 - Z)$ in Eq. (8), we have

$$\frac{\partial n_{u1}(\boldsymbol{r}, t)}{\partial t} = D\nabla^2 n_{u1}(\boldsymbol{r}, t) - n_{u1}(\boldsymbol{r}, t)(\tau_a^{-1} + \sigma_x D n_x) + R. \quad (17)$$

The solution is as follows:

$$n_{u1} = R\tau \left[1 - \frac{K_0(\sqrt{r^2/D\tau})}{K_0(\sqrt{r_k^2/D\tau})}\right], \quad (18)$$

with

$$\tau^{-1} = \tau_a^{-1} + \sigma_x D n_x,$$

and

$$\sigma_k = \left[\frac{2\pi r_k}{\sqrt{D\tau}}\right]\left[\frac{K_1(\sqrt{r^2/D\tau})}{K_0(\sqrt{r_k^2/D\tau})}\right]. \quad (19)$$

The single atom density $n_{u1}(\boldsymbol{r}, t)$ and the capture number obtained are not explicit functions of coverage either.

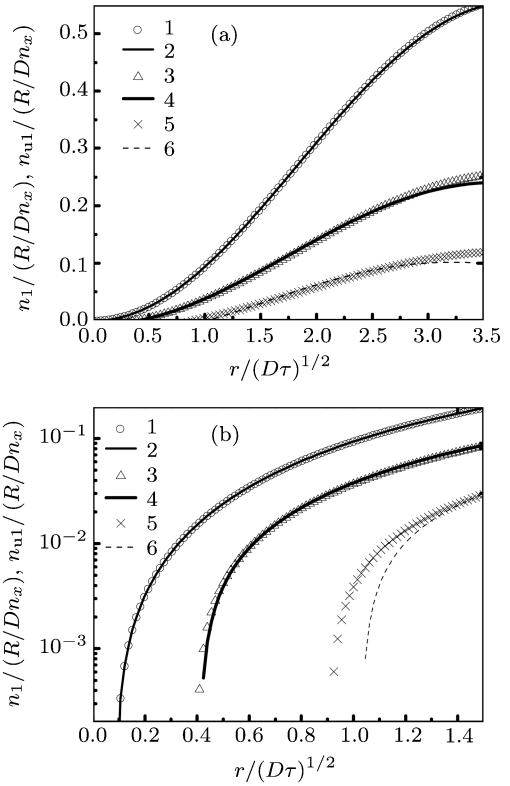


Fig. 2. Single atom densities n_1 and n_{u1} versus distance between the point and the origin, obtained from the present equation solution (11) and the revised equation solution (15), respectively, for the parameters shown in the figure. 1: $n_1/(R/Dn_x)$ for $Z_k = Z$, $Z = 0.01$; 2: $n_{u1}/(R/Dn_x)$ for $Z_k = Z$, $Z = 0.01$; 3: $n_1/(R/Dn_x)$ for $Z_k = Z$, $Z = 0.1$; 4: $n_{u1}/(R/Dn_x)$ for $Z_k = Z$, $Z = 0.1$; 5: $n_1/(R/Dn_x)$ for $Z_k = Z$, $Z = 0.3$; 6: $n_{u1}/(R/Dn_x)$ for $Z_k = Z$, $Z = 0.3$.

In Fig. 3, we compare the variations in $n_1/(R/Dn_x)$ and $n_{u1}/(R/Dn_x)$ with coverage Z ($Z < 0.35$) for $r/(D\tau)^{1/2} = 1.05$ and $Z_k = Z$. The comparison in Fig. 3 shows that the single atom density n_1 obtained from the present equation (8) is fully consistent with the single atom density n_{u1} obtained from the revised equation (13) at low coverage Z ($Z < 0.20$). However, the single atom density n_1 begins to deviate significantly from the single atom density n_{u1} for $Z > 0.25$. The inconsistency becomes greater with the increase in coverage Z. For $Z_k = Z$, $Z = 0.3$ and $r/(D\tau)^{1/2} = 1.05$, $n_1/(R/Dn_x t)$ is more than five times as great as $n_{u1}/(R/Dn_x t)$ (see Fig. 3). In Fig. 3, when $Z > 0.306$, $n_{u1}/(R/Dn_x)$ is already zero.

Due to the consideration of the effect of coverage in Eq. (13), the diffusion contribution to the growth of k-clusters is lower than that in the previous model in the uniform depletion approximation. As the nucleation rate becomes smaller, the nucleation time interval of stable clusters is lengthened. In the case of the same growth rate, the size difference between the stable nuclei becomes larger, the distribution of nucleus sizes broadens, and there is also a corresponding reduction in the number of stable nuclei per unit size interval. The results will be helpful in reducing the difference between theory and experiment.[3,28]

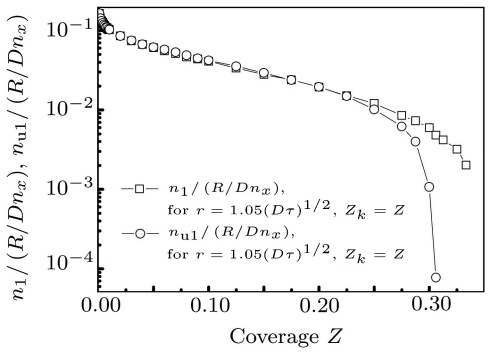


Fig. 3. Single atom densities n_1 and n_{u1} versus coverage Z, obtained from the present equation solution (11) (□) and the revised equation solution (15) (◯), respectively, for the parameters shown in the figure.

In Fig. 4, n_1/n_x and n_{u1}/n_x are calculated for $r/(D\tau)^{1/2} = 1.05$, $Z_k = Z$, $Z = 0.01$, 0.1, and 0.3, respectively, with varying D/F. The comparison in Fig. 4 shows that the revised equation solution (15) and the present equation solution (11) are consistent with each other within a small error margin of 0.25% for $Z = 0.01$, and of 3% for $Z = 0.1$. The single atom density n_1/n_x calculated from the present rate equation (8) is inconsistent with and about 3.71 times greater than the single atom density n_{u1}/n_x from the revised rate equation (13) for $Z = 0.3$. All the results have almost the same slopes.

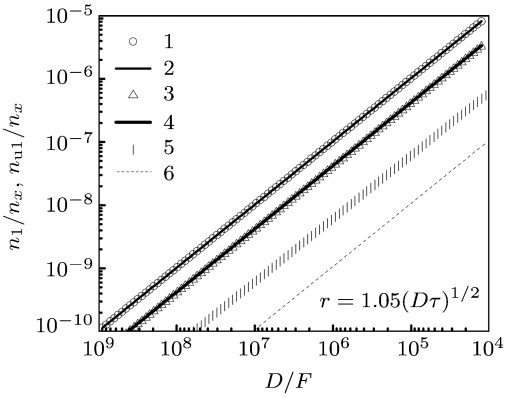


Fig. 4. Single atom densities n_1 and n_{u1} versus D/F, obtained from the present equation solution (11) and the revised equation solution (15), respectively, for the parameters shown in the figure. 1: n_1/n_x for $Z_k = Z$, $Z = 0.01$; 2: n_{u1}/n_x for $Z_k = Z$, $Z = 0.01$; 3: n_1/n_x for $Z_k = Z$, $Z = 0.1$; 4: n_{u1}/n_x for $Z_k = Z$, $Z = 0.1$; 5: n_1/n_x for $Z_k = Z$, $Z = 0.3$; 6: n_{u1}/n_x for $Z_k = Z$, $Z = 0.3$.

Similar to the approximation used before, namely $\sigma_x = \sigma_k$ for $r_k = r_x$, enables one to calculate σ_x self-consistently using Eq. (16). Once σ_x is calculated and hence τ_1 via Eq. (14), the individual σ_k can be calculated using Eq. (16).

5. Discussion

The development of a quantitative theory of thin film growth needs to address several differences that exist in the traditional rate equation theory and experiments.[3] The measured stable cluster density curves at the early stage were lower than the values from theory [on page 147 in Ref. [7], [29]–[31]]. Compared with the experimental results, the theory cannot be a very accurate description of the coalescence and island size distributions.[3] According to expression (15), the single atom density $n_{u1}(\boldsymbol{r}, t)$ decreases with coverage increasing, and the corresponding stable cluster density n_x will decline faster, which can reduce the difference between the present rate equation and experiments. As the nucleation rate is smaller, the nucleation time interval of stable clusters is lengthened. In the case of the same growth rate, the size difference between the stable nuclei becomes larger, the nucleus size distribution broadens, and there is also a corresponding reduction in the number of stable nuclei per unit size interval. Thus, compared with the result of the traditional rate equation, island size distribution

obtained in KMC simulations will be wider, the number of stable nuclei per unit size interval varies more slowly with size, and the number of stable nuclei per unit size interval near the maximum becomes smaller (see Fig. 4 in Ref. [28]). The results of this paper can improve the island size distribution.

For the case of metal epitaxy at low temperatures, e.g., dimmers stable and immobile, no re-evaporation (complete condensation) and 2D islands [see Eqs. (2), and (3) in Ref. [4], the rate equations for monomers and stable islands can be written as

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = F - 2\sigma_1 D n_1^2 - \sigma_x D n_1 n_x - k_x F(Ft - n_1) - 2k_1 F n_1, \quad (20)$$

$$\frac{\mathrm{d}n_x}{\mathrm{d}t} = \sigma_1 D n_1^2 + k_1 F n_1. \quad (21)$$

The terms on the right-hand side of Eq. (20) denote the increase in monomer density due to deposition with flux F, and it decreases due to the encounter of two diffusing atoms to create a dimer, accompanied by the disappearance of two atoms. Then the decrease occurs when a monomer is captured by a stable island. The last two terms denote the decrease in n_1 caused by direct impingement onto ($k_1 = k_x = 1$), or into the immediate vicinity of stable islands and monomers, expressed by k_1, $k_x > 1$. For typical values of k, these direct impingement terms are small with respect to the first three terms in Eq. (20). In Eq. (21), the terms on the right-hand side account for the increase in stable island density n_x due to the creation of dimers, first when two monomers meet each other by diffusion, and second when an atom direct deposition onto an adatom. Coalescence is neglected in Eq. (21); incorporation will lead to the addition of a further term of the form $-2n_x(F - \mathrm{d}n_1/\mathrm{d}t)$.[4] On the right-hand side of Eq. (20), we combine the first and the fourth, ignore the fifth term, and then the result becomes similar to Eq. (13), and equation (20) can be rewritten as Eq. (22). On the right-hand side of Eq. (21), we ignore the second term, add a further term of the form $-2n_x(F - \mathrm{d}n_1/\mathrm{d}t)$, and then the result becomes similar to the first term on the right-hand side of Eq. (27) in Ref. [18], and equations (13) and (21) can be rewritten as Eq. (23)

$$\frac{\mathrm{d}n_{\mathrm{u}1}}{\mathrm{d}\theta} = 1 - 2\sigma_1 \left(\frac{D}{F}\right) n_{\mathrm{u}1}^2 - \frac{\sigma_x \left(\frac{D}{F}\right) n_x}{1-\theta} n_{\mathrm{u}1}, \quad (22)$$

$$\frac{\mathrm{d}n_x}{\mathrm{d}\theta} = (1-\theta)\,\sigma_1 \left(\frac{D}{F}\right) n_{\mathrm{u}1}^2 - 2n_x \left[2\sigma_1 \left(\frac{D}{F}\right) n_{\mathrm{u}1}^2 + \frac{\sigma_x\,(D/F)\,n_x n_{\mathrm{u}1}}{(1-\theta)}\right], \quad (23)$$

where coverage $\theta = Ft$. Other than the very short time when the deposition starts, we generally have $n_x \gg n_{\mathrm{u}1}$, and can write approximately Eqs. (22) and (23) respectively as

$$\frac{\mathrm{d}n_{\mathrm{u}1}}{\mathrm{d}\theta} = 1 - \frac{\sigma_x (D/F) n_x}{1-\theta} n_{\mathrm{u}1}, \quad (24)$$

$$\frac{\mathrm{d}n_x}{\mathrm{d}\theta} = (1-\theta)\sigma_1 \left(\frac{D}{F}\right) n_{\mathrm{u}1}^2 - \left[\frac{2\sigma_x\,(D/F)\,n_{\mathrm{u}1}}{(1-\theta)}\right] n_x^2. \quad (25)$$

Based on the calculated values of σ_x (see Fig. 1) and σ_1, we use the corresponding fitting functions as follows,

$$\sigma_x = 30\theta + 2, \quad (26)$$

$$\sigma_1 = 3.64\theta + \frac{0.73}{1-\theta}. \quad (27)$$

We solve Eqs. (24)–(27) with the MATLAB code45 (Runge–Kutta method), considered the error in calculation, and corrected the calculation results. The obtained n_x is shown in Fig. 5.

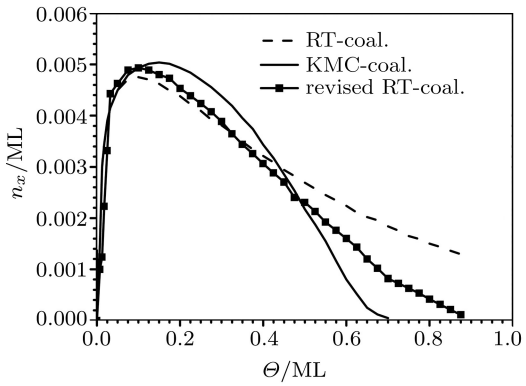


Fig. 5. Coalescence investigated for compact islands by the rate theory, our revised rate theory and KMC simulations on a square lattice performed for $D/F = 1 \times 10^5$. The rate theory and KMC simulation data are cited from the corresponding data of Fig. 9(a) in Ref. [4]. Coalescence begins to affect island densities at $\theta > 0.1$ ML. The coalescence term of mean-field theory overestimates coalescence effects at early times while it does not reduce n_x down to 0 at $\theta = 1$ ML. The results of the revised rate theory are between the rate theory and KMC simulation results. The coalescence term of the revised rate theory is closer to the KMC simulation at $\theta = 0.05$ ML–0.15 ML, closer to the rate theory at $\theta = 0.15$ ML–0.43 ML, and closer to the KMC simulation at $\theta = 0.43$ ML–1 ML, while it does reduce n_x down to 0 at $\theta = 0.9$ ML.

Density scaling for any fixed coverage below saturation can be obtained very easily within the mean-field nucleation theory.[4] Coalescence, however, is explained less well with the theory. The curves for compact islands in Fig. 5 show that adding the coalescence term in Eq. (21) yields island densities that are

too small at low coverage, whereas coalescence is underestimated at higher coverage.[4] Therefore, the island density does not reduce down to 0 even long after KMC has shown percolation. The failure of the nucleation theory in describing coalescence is well known. The rate theory and KMC simulation data in Fig. 5 are cited from the corresponding data of Fig. 9(a) in Ref. [4]. The results of revised rate theory are between the rate theory and KMC simulation results. The coalescence term of the revised rate theory is closer to the KMC simulation at $\theta = 0.05$ ML–0.15 ML, much closer to the rate theory at $\theta = 0.15$ ML–0.43 ML, and closer to the KMC simulation at $\theta = 0.43$ ML–1 ML, while it does reduce n_x down to 0 at $\theta = 0.9$ ML. The revised rate theory significantly improves the coalescence description in the rate theory. The error of the coalescence description in the revised rate theory may come from the approximation in Eqs. (24)–(27), the n_1 calculation error with the MATLAB software, and some other unknown reasons. In coalescence of isolated clusters, there has been much research work.[32,33] If these coalescences are included in the growth environment of the clusters, such as single atoms that are continuously injected and captured, then the coalescence research work will be more meaningful. The research on cluster size distribution in deposition process is still ongoing.[34]

In the derivation of the single atom rate equation,[16] Z and $n_{\rm u1}(\boldsymbol{r}, t)$ are the local values, different from the average value Z in the traditional rate equation. This revised single-atom rate equation can be used to describe the variation in single-atom local density with the local Z. Therefore, Z changes at different substrate positions, and $n_{\rm u1}(\boldsymbol{r}, t)$ will also change. Island edges facing wider island-free regions, that is, with smaller Z, typically capture more single atoms and have a higher growth rate. The environmental influence on the island growth can be seen in Fig. 1(b) in Ref. [35].

6. Conclusion

The revised single-atom density rate equation is solved. We solved the equation and obtained the single-atom density and capture number by using a uniform depletion approximation. We found that the single atom density is much lower than that evaluated from the single atom density rate equation in the traditional rate equation theory when the stable cluster coverage fraction is large. The coverage makes the density of the single atoms act as a main growth source that is lower in the vapour deposition process. The larger the coverage fraction, the lower the single atom density is. The decline in the single atom density prevents the stable clusters for coalescing in vapour deposition and the quantum size islands from further growing, which makes the preparation of single crystalline thin film materials difficult and the size control of quantum size islands complicated. The revised equation gives a higher value of σ_x than the present equation, and it increases also with increasing Z. We also discussed the revision effects on the coalescence and the number of stable clusters in vapour deposition.

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[3] Brune H 1998 *Sur. Sci. Rep.* **31** 121. In this paper, the sentences from the thirty-ninth to fourty-fourth line on page 137 reads: "The mean-field approach assumes that the mean density of monomers sufficiently far away from the island takes on a constant value, no matter what the local environment of the island looks like. The first consequence is that, although average island sizes are predicted correctly, as are island densities, the island size distributions are far from being realistic. As a second consequence, coalescence cannot be described very accurately." This implies that present rate theory yields reliable results only for $\Theta \leq \Theta_{\rm sat}$ and for average quantities (see the sentence of the first and second lines on page 138).

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