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The effects of cluster size-dependent aggregation on thin film formation

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The early stages of thin film formation by thermal atom deposition are modeled by a system of kinetic rate equations which describe atomic clustering phenomena. Specifically, a set of discrete kinetic rate equations, used to model small atomic clusters, is coupled to a set of kinetic moment equations which model large atomic clusters with a continuum description. Cluster growth and dissociation processes are assumed to occur via single-atom transitions. Growth behavior is investigated as a function of cluster size, x, with an aggregation parameter $w(x) = w_0 x^r$ *for* $0 \leqslant r < 1$*. Results from this statistical approach illustrate how size-dependent aggregation influences the cluster size distribution during the early stages of nucleation and growth.*

1. Introduction

In several theoretical studies of thin film formation, a kinetic formulation of hierarchical discrete rate equations has been used to describe cluster sizes[1–8]. These rate equations are coupled, non-linear, and extremely complex. Thus, they are difficult to solve unless some simplifying physical assumptions are introduced. From a computational standpoint, these approaches must solve a large system of equations to obtain specific clustering details since the number of atoms in the largest cluster dictates the number of discrete equations that must be solved.

We have recently outlined an atomic clustering model which includes many processes that occur during thin film formation by energetic atom deposition[9]. Our benchmark studied the early stages of a deposition process (i.e. substrate coverage $\leqslant 10\%$) for the first atomic monolayer with the assumptions that thermal, single atoms were deposited at a constant rate, cluster growth and decay resulted only from mobile single atoms, only single atoms could evaporate off the substrate, and aggregation and dissociation rate constants did not depend on cluster size. Following Zinsmeister's approach[7], these assumptions enabled us to model atomic clustering phenomena with a series of discrete kinetic rate equations for clusters containing up to $X_{\max}$ atoms[9]. To avoid solving $X_{\max}$ discrete equations, a continuum equation was derived for $3 \leqslant x \leqslant X_{\max}$, where x denotes the number of atoms in an x-atom cluster. A transition cluster size, X_c, was defined as the smallest cluster size described by the continuum. Thus, we modeled atomic clustering with a set of discrete kinetic equations for $1 \leqslant x \leqslant (x_c - 1)$ and with a continuum equation for $X_c \leqslant x \leqslant X_{\max}$[9].

Inherent in our earlier work and Zinsmeister's theory[7] is the assumption that mobile single atoms diffuse over the substrate and aggregate with large, stationary clusters at a constant rate. Physical intuition would lead one to believe that larger clusters present a bigger target for single atoms to diffuse into; however, the overall aggregation rate also depends on the population of large-size clusters residing on the substrate. The purpose of this work is to study the influence of a size-dependent aggregation parameter on the early stages of atomic clustering. Theoretical results will demonstrate how cluster geometry influences the cluster size distribution.

2. Kinetic clustering equations with size-dependent aggregation

Developing the system of kinetic clustering equations with a size-dependent aggregation parameter follows the same approach used previously[9]. The variable of interest is the cluster density distribution function, $C(x, t)$, which represents the number of clusters per unit substrate area found on the substrate at time t; x is the number of atoms in the cluster. Five basic processes govern the behavior of $C(x, t)$ during the early stages of atomic clustering. These processes include the deposition rate, direct impingement of the depositing species onto growing clusters, cluster evaporation, cluster aggregation, and dissociation. Focusing on the early stages of a deposition process allows one to neglect direct impingement phenomena because only a small portion of the substrate is assumed to be covered ($\leqslant 10\%$). Cluster dissociation will also be negligible in a thermal atom deposition process, especially if the growing nuclei form stable clusters. For a single-atom deposition process in which only single atoms can evaporate off the substrate and cluster growth is due to single-atom transitions, the following rate equation describes the population of single atoms on the substrate at time t:

$$\frac{\partial C(1, t)}{\partial t} = q - \nu_a C(1, t) - \left[\sum_{x=1}^{X_c - 1} \nu_{\text{agg}}(x, t) C(x, t)\right] - \langle \nu_{\text{agg}}(x, t) \rangle C_{\text{tot}}(t). \qquad (1)$$

The successive terms on the right-hand side of (1) represent the deposition rate of single atoms on the substrate (q), the evaporation of single atoms off the substrate, the aggregation of single atoms with discrete clusters (i.e. $1 \leqslant x \leqslant X_c - 1$), and the aggregation of single atoms with clusters in the continuum distribution.The frequencies ν_a and $\nu_{\text{agg}}(x, t)$ describe the respective rates at which single atoms evaporate off the substrate and aggregate with x-atom clusters. The frequency $\langle \nu_{\text{agg}}(x, t) \rangle$ represents an aggregation rate which has been appropriately averaged over the continuum cluster distribution; $C_{\text{tot}}(t)$ denotes the total density of clusters in the continuum.

Clusters containing two atoms are produced when two single atoms aggregate together, but are destroyed when a single atom aggregates with a two-atom cluster to form a three-atom entity.

The appropriate kinetic equation is

$$\frac{\partial C(2,t)}{\partial t} = \tfrac{1}{2} v_{\mathrm{agg}}(1,t)C(1,t) - v_{\mathrm{agg}}(2,t)C(2,t). \qquad (2)$$

The remaining discrete clusters, for $3 \leqslant x \leqslant (X_c - 1)$, are governed by

$$\frac{\partial C(x,t)}{\partial t} = v_{\mathrm{agg}}(x-1,t)C(x-1,t) - v_{\mathrm{agg}}(x,t)C(x,t). \qquad (3)$$

Clusters containing X_c or more atoms are described by a continuum distribution function, $C_{\mathrm{con}}(x,t)$, which depends on the following three characteristics of the distribution: $C_{\mathrm{tot}}(t)$, the total density of clusters in the continuum; $\langle x\rangle(t)$, the average size of the continuum clusters; and $M_2(t)$, the second central moment or variance of the continuum distribution. By taking the zeroth, first, and second moments of our continuity equation[9], the following kinetic moment equations can be derived for size-dependent aggregation phenomena:

$$\frac{\partial C_{\mathrm{tot}}(t)}{\partial t} = J(X_c,t) \qquad (4)$$

$$\frac{\partial \langle x\rangle(t)}{\partial t} = \langle v_{\mathrm{agg}}(x,t)\rangle + \frac{[X_c - \langle x\rangle(t)]J(X_c,t) + (1/2)v_{\mathrm{agg}}(X_c,t)C(X_c,t)}{C_{\mathrm{tot}}(t)} \qquad (5)$$

$$\frac{\partial M_2(t)}{\partial t} = \langle v_{\mathrm{agg}}(x,t)\rangle + 2\langle v_{\mathrm{agg}}(x,t)[x - \langle x\rangle(t)]\rangle + \frac{\{[X_c - \langle x\rangle(t)]^2 - M_2(t)\}J(X_c,t) + [X_c - \langle x\rangle(t)]v_{\mathrm{agg}}(X_c,t)C(X_c,t)}{C_{\mathrm{tot}}(t)} \qquad (6)$$

The transition cluster size, X_c, defines the smallest cluster size in the continuum. $J(X_c,t)$ represents the nucleation current going into the continuum from the discrete clusters, given by

$$J(X_c,t) = v_{\mathrm{agg}}(X_c - 1,t)C(X_c - 1,t). \qquad (7)$$

The $\langle\rangle$ symbols are used to denote quantities which have been appropriately averaged over the continuum and evaluated at $x = \langle x\rangle(t)$. Since the continuum construction is based on using second order moments, a convenient procedure is to assume that the continuum cluster distribution function is Gaussian, i.e. for $x \geqslant X_c$

$$C_{\mathrm{con}}(x,t) = \frac{C_{\mathrm{tot}}(t)}{\sqrt{2\pi M_2(t)}} \exp\left[-\frac{[x - \langle x\rangle(t)]^2}{2M_2(t)}\right] \qquad (8)$$

thus allowing us to approximate

$$C(X_c,t) = C_{\mathrm{con}}(X_c,t). \qquad (9)$$

To determine the averages $\langle v_{\mathrm{agg}}(x,t)\rangle$ and $\langle v_{\mathrm{agg}}(x,t)[x - \langle x\rangle(t)]\rangle$, the aggregation frequency is chosen to be

$$v_{\mathrm{agg}}(x,t) = w(x)C(1,t) \qquad (10)$$

where $w(x)$ is the aggregation parameter describing how mobile single atoms aggregate with stationary x-atom clusters. Selecting

$$w(x) = w_0 x^r \qquad (11)$$

and utilizing the Gaussian nature of the continuum leads to

$$\langle v_{\mathrm{agg}}(x,t)\rangle = v_{\mathrm{agg}}(\langle x\rangle(t),t)\left[1 + \frac{r(r-1)M_2(t)}{2\langle x\rangle^2(t)}\right] \qquad (12)$$

and

$$\langle v_{\mathrm{agg}}(x,t)[x - \langle x\rangle(t)]\rangle = v_{\mathrm{agg}}(\langle x\rangle(t),t)\left[\frac{rM_2(t)}{\langle x\rangle(t)}\right] \qquad (13)$$

where r is the growth exponent, defined over $0 \leqslant r < 1$. A specific value for r would indicate the cluster geometry. For example, atomic diffusion to 2-D discs can be described by $r = 1/2$, while that to 3D spheres by $r = 1/3$.

It should be mentioned that the factor x^r used in (11) is equivalent to the "capture number", σ, previously discussed in the literature[10,11,12,13,14]. A capture number describes the diffusional flow of single atoms to critical (σ_i) or stable (σ_x) nuclei present on a substrate. Since single-atom diffusion is assumed to occur over a two-dimensional surface, analytical solutions for the capture numbers emerge as expressions involving Bessel functions. Particular solutions depend somewhat on the regime of condensation involved and on the amount of substrate coverage.

In the complete condensation regime, where an atom experiences no difficulty in attaching itself to a growing stable cluster, Venables[14] has shown that two types of approximate expressions can be derived for σ_x that represent upper and lower bounds to the true value. The "lattice approximation"[15] determines the upper bound for σ_x by placing all the stable clusters on a lattice and evaluating cluster growth rates. The "uniform depletion approximation"[16] calculates the lower bound by randomly distributing the stable clusters over the substrate and determining cluster growth rates, accounting for capture events which compete with re-evaporation in the process. These two approximations determine σ_x to within a factor of about two, independent of the amount of surface coverage[14].

In the incomplete condensation regime, correlations between single atoms and stable clusters do not extend to the next cluster because the concentration of stable and subcritical nuclei is very small. For low substrate coverages, both σ_x and σ_i can be expressed with much more certainty than in the complete condensation regime.

Despite their relatively complex form, these capture numbers are not strong functions of the cluster size and do not depend strongly on other parameters involved. As shown by Stowell[15] and Venables[14], σ_x is in the range 5–10 and σ_i in the range 2–4 in many situations encountered in practice[10].

Venables and Price[12] mention several nucleation studies that have performed calculations with capture numbers which are proportional to cluster diameter and an "attachment coefficient", μ. They state that such a treatment is only true if $\mu \ll 1$, and in order to evaluate μ, one must know the details of the attachment mechanism. Our "capture number", x^r, is proportional to the diameter of the capturing species. By overlooking attachment mechanisms, this simple factor introduces size-dependent aggregation into the kinetic rate equations and allows us to study the effects of cluster geometry on the early stages of nucleation and growth. Theoretical comparisons with experimental measurements will be required in order to determine if this assumption applies in reality.

The solution of equations (1)–(13) enables one to study the influence of a size-dependent aggregation parameter, $w(x) = w_0 x^r$, on the early stages of thin film formation by thermal atom deposition, under the assumptions that cluster dissociation and direct impingement effects are negligible. To solve these equations, the parameters q, v_a, w_0, r, and X_c must be specified.

3. Results and discussion

To study the influence of size-dependent aggregation, (1)–(13) were solved for the case where $q = 10^{13}$ atoms cm^{-2} sec^{-1}, $\nu_a = 2.74 \times 10^5$ sec^{-1}, $w_0 = 1.50 \times 10^{-5}$ cm^2 sec^{-1}, and $r = 0$, 1/3, and 1/2. X_c was selected to be five; previous studies[9] indicate that X_c does not influence the clustering phenomena when cluster dissociation is neglected.

Since dissociation is not considered, continuous clustering occurs which promotes an increase in the values of $\langle x\rangle(t)$, $M_2(t)$, and $C_{tot}(t)$ with time. This is evident in our assumptions. Calculations also indicate that $\partial\langle x\rangle(t)/\partial t$ and $\partial M_2(t)/\partial t$ both increase with r over all deposition times. Consequently, at a specific time, 2D clusters will not only be larger than 3D clusters, but they will be growing larger at a much faster rate. Additionally, at the same time, the 2D cluster distribution function will have a broader range of cluster sizes than the 3D cluster distribution, as well as dispersing at a much faster rate. All of these results can be attributed to enhanced aggregation which is characteristic of a larger growth exponent.

Calculations also demonstrate that the total density of clusters first increases rapidly up to $t = 0.04$ sec. It is shown that if 2D discs grow, this results in a saturation in the total cluster density for $t \geqslant 0.04$ sec. The rapid growth of these discs nearly terminates further nucleation for $t \geqslant 0.04$ sec. On the other hand, nucleation is continuous for 3D clusters.

Figures 1 and 2 show how the continuum cluster distribution function varies over time for $r = 0$, 1/3, and 1/2. Since $X_c = 5$, all curves begin with five atoms in the smallest continuum cluster. Notice that for a specific r, the total density, average size, and the second moment (i.e. the area, mean, and width of the distribution) all increase as time progresses from $t = 0.05$ to 0.08 sec. This is due to the continuous nucleation phenomena previously discussed. At a specific time though, Figures 1 and 2 both indicate that a larger growth exponent promotes a larger average size and a more disperse distribution, in accordance with our $\langle x\rangle(t)$ and $M_2(t)$ results. Enhanced aggregation thus promotes a shift and a broadening in the calculated size distributions.

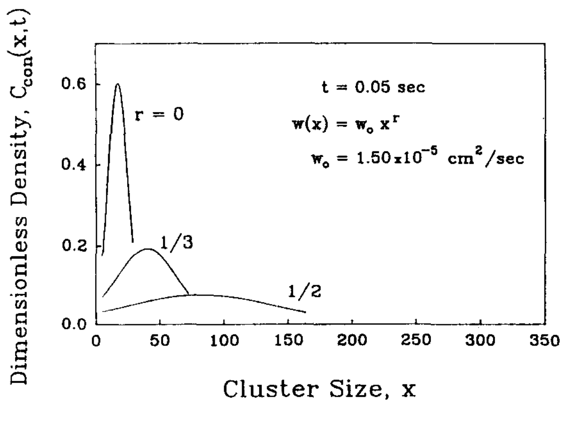

Figure 1. Continuum cluster distribution at $t = 0.05$ sec for various values of the growth exponent, r.

4. Conclusions

The influence of a size-dependent aggregation parameter on the early stages of thin film formation by thermal atom deposition has been investigated with a hybrid model that couples a set of discrete kinetic rate equations to a Gaussian continuum. Cluster aggregation rates increase with the growth exponent, promoting cluster distributions with larger average sizes and wider dispersions. Since extended aggregation eventually leads to coalescence, total cluster densities saturate at smaller equilibrium values when larger growth exponents are used. Such efforts are not noticeably obvious if constant capture numbers are employed. Theoretical comparisons with experimentally measured cluster size distributions are thus needed to determine if the form of the aggregation parameter, $w(x) = w_0 x^r$, is a realistic assumption.

Since the growth exponent is indicative of cluster geometry, the following remarks can be made. Since 3D clusters have a smaller surface-to-volume ratio and a higher self-binding than 2D clusters, they appear as more compact atomic arrangements than 2D entities. As a result, continuous nucleation and slow growth processes will be indicative of clusters which possess a high self-binding and exhibit compact atomic packing.

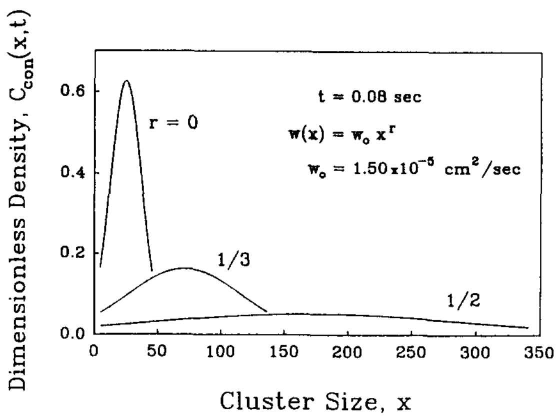

Figure 2. Continuum cluster distribution at $t = 0.08$ sec for various values of the growth exponent, r.

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