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LETTER TO THE EDITOR

The multi-nuclei growth equation for a vacuum-deposited thin film

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Abstract. We study the early stage behaviour of nucleus growth in a vacuum-deposited thin film. Solving a stationary diffusion equation with boundary conditions on each nuclei periphery, we derive for the first time the multi-nuclei growth equation. This equation is found to express the cooperative interactions among nuclei via the diffusion field. We also examine a linear stability of a growing nucleus for many nuclei systems.

Recently nucleus growth processes on substrates have attracted much attention in many areas of condensed matter physics [1]. Such phenomena are widely seen in nature, i.e. vapour-deposited thin films [2], wetting [3], breath figures [4], and two-dimensional Ostwald ripening [5].

In the present letter we discuss the early stage behaviour of nucleus growth in a vacuum-deposited thin film. Sigsbee has studied this growth process on the basis of the surface diffusion theory of adsorbed deposit atoms (called adatoms) [6]. However, he has ignored the cooperative effects among nuclei via the diffusion field. Subsequent authors have discussed such effects phenomenologically. Here we derive the multi-nuclei growth equation which may be a starting equation for studying the cooperative effects systematically.

In the following discussions it is assumed [6] that:

(i) a stable nucleus is immobile and has the shape of a spherical cap, i.e. portion of a sphere, as is shown in figure 1;
(ii) a contact angle θ is constant during growth process;
(iii) the effects of direct impingement of incident atoms to a nucleus is negligible, since we have considered the small cap-shaped nuclei in the early stage, and thus the growth rate is controlled by the rate of diffusive adatoms transported along the periphery of the nucleus;
(iv) at each nucleus periphery, the assumption of local equilibrium is maintained;
(v) the mean distance between nuclei is much larger than their radii.

We consider an ensemble of N nuclei with projected radii R_j centred at $\boldsymbol{X}_j$ ($1 \leq j \leq N$), as is shown in figure 1. Under the above assumptions the growth rate of the jth nucleus volume V_j is given in terms of adatom concentration $n(\boldsymbol{r}, t)$ at position $\boldsymbol{r}$ on the substrate and time t by

$$(\mathrm{d}/\mathrm{d}t)\, V_j = 2\pi v D B(j) \tag{1}$$

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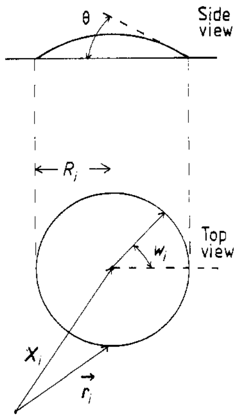

Figure 1. Geometry of the ith cap-shaped nucleus growing on a substrate.

with

$$V_j = (4\pi/3) f(\theta) \sin^{-3}\theta R_j^3 \tag{2}$$

$$B(j) = (R_j/2\pi D) \oint \mathrm{d}w_j\, \boldsymbol{n}(w_j) \cdot D\boldsymbol{\nabla}_j n(\boldsymbol{r}_j, t) \tag{3}$$

where D is the adatom surface diffusion constant, v the atomic volume of an adatom, $\boldsymbol{r}_j$ and w_j are, respectively, the position vector and corresponding angle variable on the periphery of the jth nucleus, $\boldsymbol{n}(w_j)$ the outward unit vector normal to the jth periphery, and $f(\theta)$ the geometric correction term for the cap-shaped nucleus volume given by $f(\theta) = 2(2\text{–}3\cos\theta + \cos^3\theta)/3$. Here $\boldsymbol{\nabla}_j n(\boldsymbol{r}_j, t)$ denotes $\boldsymbol{\nabla} n(\boldsymbol{r}, t)$ evaluated at $\boldsymbol{r} = \boldsymbol{r}_j$, and $\oint \mathrm{d}w_j$ denotes $\int_0^{2\pi} \mathrm{d}w_j$. The adatom concentration $n(\boldsymbol{r}, t)$ can be found from a solution of the continuity equation in the cylindrical coordinate [6]

$$(\partial/\partial t)\, n(\boldsymbol{r}, t) = D\nabla^2 n(\boldsymbol{r}, t) + \bar{n}/\tau - n(\boldsymbol{r}, t)/\tau \tag{4}$$

with boundary conditions

$$n(\boldsymbol{r}_j, t) \equiv n_{\mathrm{e}}(R_j) \equiv n_{\mathrm{eq}} S^z \tag{5}$$

$$n(\boldsymbol{r}, t) \to \bar{n} \qquad \text{for} \qquad |\boldsymbol{r}| \to \infty \tag{6}$$

with

$$n_{\mathrm{eq}} \equiv n_{\mathrm{e}}(\infty) \qquad S \equiv \bar{n}/n_{\mathrm{eq}} \qquad z \equiv R_{\mathrm{c}}/R_j$$

where τ is the mean absorption time of an adatom, $n_{\mathrm{e}}(R_j)$ the local equilibrium concentration at $\boldsymbol{r} = \boldsymbol{r}_j$, $\bar{n}$ the average concentration, and R_{c} the projected radius of critical nucleus. Here the second term in the right-hand side of (4) represents the impingement of atoms on the substrate, while the last term represents the re-evaporation of adatoms.

Now let us solve (4) with boundary conditions (5) and (6). In order to take into account the effects of the presence of many nuclei, we add a fictitious sink term $T(\boldsymbol{r}, t)$ to (4), which is defined by [7, 8]

$$T(\boldsymbol{r}, t) = -n_{\mathrm{eq}} \sum_j \oint \mathrm{d}w_j \delta(\boldsymbol{r} - \boldsymbol{r}_j) c_j(w_j) \tag{7}$$

where c_j denotes the strength of the fictitious source located on the nucleus periphery. We later determine c_j to satisfy the boundary conditions. The formal solution of (4) with (7) under the quasi-static approximation $\partial n/\partial t = 0$ is given by

$$n(\boldsymbol{r}) = \bar{n} + \sum_j \oint \mathrm{d}w_j\, G(\boldsymbol{r} - \boldsymbol{r}_j) c_j(w_j) \tag{8}$$

where the two-dimensional Green function with $D(\nabla^2 - L^{-2})G(\boldsymbol{r}) = -\delta(\boldsymbol{r})$ is given by

$$G(\boldsymbol{r}) = (1/2\pi D)K_0(|\boldsymbol{r}|/L) \tag{9}$$

where K_0 is the modified Bessel function and $L^2 \equiv D\tau$.

Here we consider the relation between $B(j)$ and c_j. Substituting (8) into (3) and using the equation for $G(\boldsymbol{r})$ and $L \gg R_j$, we have [8, 9]

$$B(j) = -\frac{1}{2\pi D}\oint \mathrm{d}w_j c_j(w_j). \tag{10}$$

Thus we need to obtain the equation for c_j. For this end we introduce here $K_j(w_j, w_j')$ which is defined on the periphery of the jth nucleus and is the reciprocal of $G_j(w_j, w_j') \equiv G(\boldsymbol{r}_j - \boldsymbol{r}_j')$. That is

$$\oint \mathrm{d}w_j'' K_j(w_j, w_j'')G_j(w_j'', w_j') = \delta(w_j - w_j'). \tag{11}$$

Then from (8) with $\boldsymbol{r} = \boldsymbol{r}_j$ and using (5) and (11) we obtain the following equation for c_j:

$$c_j(w_j) = \frac{D}{I_0(R_j/L)K_0(R_j/L)}\left([n_e(R_j) - \bar{n}] - \sum_{i\neq j} G(\boldsymbol{X}_j - \boldsymbol{X}_i)\oint \mathrm{d}w_i\, c_i(w_i)\right) \tag{12}$$

where we have replaced $G(\boldsymbol{r}_i - \boldsymbol{r}_j)$ by $G(\boldsymbol{X}_i - \boldsymbol{X}_j)$ because $|\boldsymbol{r}_i - \boldsymbol{r}_j| \simeq |\boldsymbol{X}_i - \boldsymbol{X}_j|$, and have also used

$$\oint K_j(w_j, w_j')\,\mathrm{d}w_j = \frac{D}{I_0(R_j/L)K_0(R_j/L)}. \tag{13}$$

Relation (13) arises as a consequence of the following expansion of G_j and K_j in the normalised circular harmonics $Y_n(w) = (2\pi)^{-1/2}\exp(\mathrm{i}nw)$:

$$G_j(w_j, w_j') = \sum_n A_n Y_n(w_j)Y_n^*(w_j') \tag{14}$$

$$K_j(w_j, w_j') = \sum_n A_n^{-1} Y_n(w_j)Y_n^*(w_j') \tag{15}$$

with

$$A_n = I_n(R_j/L)K_n(R_j/L)/D. \tag{16}$$

As a result we obtain the nucleus growth equation for R_j

$$(\mathrm{d}/\mathrm{d}t)\,R_j = [vD\sin^3\theta/2f(\theta)]R_j^{-2}B(j) \tag{17}$$

$$B(j) = \frac{1}{I_0(R_j/L)K_0(R_j/L)}\left(\bar{n} - n_e(R_j) - \sum_{i\neq j} K_0(|\boldsymbol{X}_i - \boldsymbol{X}_j|/L)B(i)\right). \tag{18}$$

This equation is a starting equation in studying the nuclear growth process for multi-nuclei system. Equation (18) is found to consist of three terms. The first two terms are the mean field terms which are similar to those of Sigsbee, since for small x

$$[I_0(x)K_0(x)]^{-1} \simeq xK_1(x)/K_0(x) \tag{19}$$

can be used. The last term in (18) represents the spatial interaction between nuclei, which was not studied by any of the previous authors.

Finally we examine the linear stability of the shape deformation $\rho_j(w_j)$ of a growing nucleus. We expand $\rho_j(w_j)$ as

$$\rho_j(w_j) = R_j + \sum_{n\geq 1} a_n(j)Y_n(w_j). \tag{20}$$

Substituting (20) into (17) we have up to first order in $a_n(j)$

$$\frac{\mathrm{d}}{\mathrm{d}t} a_n(j) + \frac{n}{\pi R_j} \sum_{i \neq j} \sum_{m \geq 1} R_i I_{nm}(ji) \frac{\mathrm{d}}{\mathrm{d}t} a_m(i) = \Omega_n(j) a_n(j) + 2\pi R_j^2 \sum_{i \neq j} F_n(ji) \frac{\mathrm{d}}{\mathrm{d}t} R_i \tag{21}$$

with

$$\Omega_n(j) = (n-1) R_j^{-1} \frac{\mathrm{d}}{\mathrm{d}t} R_j - n(n^2-1) D n_{\mathrm{eq}} R_j^{-3} \tag{22}$$

$$I_{nm}(ji) = \frac{1}{2\pi} \oint \mathrm{d}w_i \oint \mathrm{d}w_j \exp(\mathrm{i}nw_j + \mathrm{i}mw_i) K_0(|\boldsymbol{r}_i - \boldsymbol{r}_j|/L) \tag{23}$$

$$F_n(ji) = -2R_j R_i I_{n0}(ji) - 2 \sum_{m \geq 1} R_j a_m(i)(1+m) I_{nm}(ji) - 2 \sum_{m \geq 1} R_i a_n(j)(1+n+m) I_{n+m,0}(ji). \tag{24}$$

The first term in the right-hand side of (21) gives the Mullins–Sekerka type instability [10]. Many-body effects enter through $(\mathrm{d}/\mathrm{d}t)\, R_i$ in the right-hand side of (21). These results are similar to those for two- and three-dimensional Ostwald ripening [8, 11].

To summarise, we have derived the nucleus growth equation in a vacuum-deposited thin film. This equation expresses the early stage behaviour of a growth process in the presence of many nuclei. We have also examined the linear stability of a growing nucleus. These results seem to suggest that the cooperative effects among nuclei play an important role on growth processes. The detailed derivation of formulae and further analyses of (17) and (21) will be given elsewhere.

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