Model for Columnar Microstructure of Thin Solid Films

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A theory for columnar microstructure is presented. Column orientation is predicted, and the tangent rule is shown to be an approximate special case of a more general relationship. Results also predict that columns occur only at low substrate temperature. All of these results agree with experimental data. In addition, a relationship is found between column width and mean square diffusion length. The theory substantiates the empirical suggestion that adatom mobility is an important parameter governing column development.

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Thin solid films are of active scientific interest,[1,2] as well as of great technological importance.[3] Electron microscopy reveals that thin films are often composed of an ordered array of thin columns.[4] This ubiquitous and interesting form, called columnar microstructure, is detrimental to the performance and structural integrity of the film.[5,6] More fundamentally, the formation of columnar microstructure is a basic problem of aggregation processes.[7-9]

At present there is no cogent theory of columnar growth. However, empirical results[10,11] strongly suggest that columnar microstructure is correlated with a certain level of adatom mobility. In this Letter we follow this suggestion to derive an equation for adatom motion of vapor-deposited thin films. The results agree with the observed features of the columns. For example, one fascinating observation is that column orientation, β, is not aligned with the trajectory of the incoming beam, α, i.e., $\alpha \neq \beta$, as shown schematically in Fig. 1. We show how this inequality arises naturally from a consideration of adatom mobility.

There is a great body of research done on diffusion-limited aggregation (DLA).[7,8,12,13] In this process, flux arrives at the surface by diffusion rather than following ballistic trajectories. Dendritic growth is due to the tips' being more effective at collecting newly arriving particles than interior points.[8] Though the physical process and mechanism presented in this Letter are different than in DLA, the outcome, once again, is that the tips are most effective in acquiring those particles which ultimately reside in the film.

For all but perhaps the thinnest films, column diameter is many times the lattice spacing. This disparity of length scales suggests a model of columnar growth based on macroscopic variables. The continuum approach, then, offers an alternative to molecular-dynamics simulation.

For small surface slopes, $\partial h/\partial x$, the rate of change of adatom concentration at a point (x,h) on the surface of the film is described by

$$\frac{\partial c}{\partial t} = J\rho\cos\alpha - J\rho\frac{\partial h}{\partial x}\sin\alpha + D\frac{\partial^2 c}{\partial x^2} - Ac, \qquad (1)$$

where t is time, c is concentration of mobile atoms per unit substrate area, D is the diffusion coefficient, ρ is the film density in atoms per unit volume, and A is defined below [in Eq. (3)]. The first two terms on the right-hand side describe the distribution of incoming flux on the surface,[3] where h is the surface height and J is the magnitude of the beam flux in volume per unit beam area per unit time. The third term on the right-hand side describes adatom diffusion. For simplicity, in this model we ignore particles which will reevaporate, and include in J only those particles which ultimately reside in the film.

A finite time after their arrival on the surface, the adatoms lose their mobility and "stick" at their final location. The rate at which adatoms augment the film thickness is given by the last term in Eq. (1). That is,

$$\rho\,\partial h/\partial t = Ac. \qquad (2)$$

The time scale controlling the residence time before an adatom is adsorbed is $1/A$, so that approximately

$$A = 2D/\langle x^2\rangle, \qquad (3)$$

where $\langle x^2\rangle$ is the mean square diffusion distance.

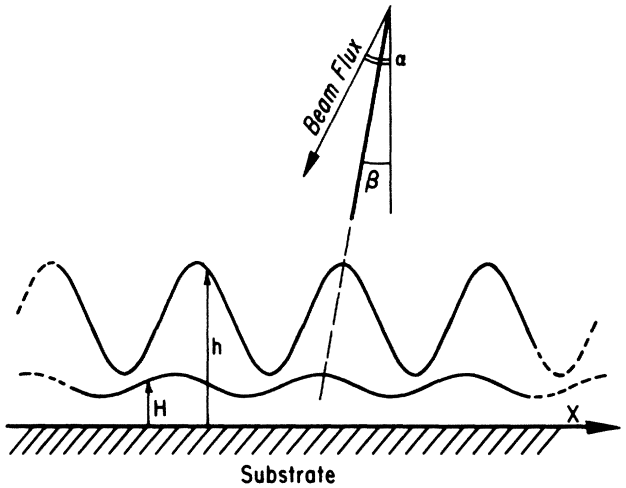

FIG. 1. Definition of notation.

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The quantity A may be expected to vary with the local conditions at the surface, e.g., local temperature perturbations and surface curvature. We assume, however, that variations in local conditions are small, and A, in this analysis, is taken to be constant.

Combining Eqs. (1) and (2), we find an equation describing film growth rate resulting from a flux of incident particles which are redistributed, before condensing, by diffusion;

$$\frac{\partial^2 h}{\partial t^2} + A\frac{\partial h}{\partial t} = JA\cos\alpha - JA\frac{\partial h}{\partial x}\sin\alpha + D\frac{\partial^3 h}{\partial x^2 \partial t}. \quad (4)$$

Note that ρ does not appear in Eq. (4). In fact, ρ need not have been introduced to the analysis, if we had chosen the dimensions of c, at the outset, as volume concentration per unit area. Equation (4) is subject to the initial condition

$$h = H(x) \text{ at } t = 0, \quad (5)$$

and the periodic boundary condition

$$h(x,t) = h(x+\lambda,t), \quad (6)$$

where λ is the column wavelength.

The set of equations (3)–(6) define the problem. We now choose the simplest relevant initial condition,

$$H(x) = H_0 + H_1 \sin kx,$$

where k is the column wave number, $k = 2\pi/\lambda$, and H_0 and H_1 are constants. The extension to more complicated, and perhaps more realistic, initial conditions is done easily as a result of the linearity of the problem. This particular initial condition and the associated boundary condition (6) assume that nascent columns with a fixed wavelength are present, and we wish to investigate their potential for growth. So we now look for solutions of the form

$$h = vt + h_1 e^{\sigma t}\sin[k(x-ut)],$$

where u and v are constants, and h_1 is a perturbation amplitude with growth rate σ. For σ we find

$$4\sigma^4 + 8\mathscr{D}\sigma^3 + 5\mathscr{D}^2\sigma^2 + \mathscr{D}^3\sigma = (AJk\sin\alpha)^2, \quad (7)$$

$$\mathscr{D} = DK^2 + A,$$

and the diffusion coefficient is given by[14] $D = (a^2\nu/2)\exp(-E/KT)$, where a is the lattice spacing, ν is the vibrational frequency, E is the diffusion activation energy, K is Boltzmann's constant, and T is the absolute temperature of the substrate. Some insight into Eq. (7) can be gained by consideration of limiting cases. If the adatoms never freeze onto the substrate, then $\langle x^2\rangle$ is large and $A \to 0$. With the right-hand side of (7) equal to zero, no solutions have positive growth rate. Similarly, if the arriving flux sticks immediately on arriving at the surface, then $A \to \infty$, and from Eq. (7) there is again no column growth. So finite A is a prerequisite for column growth. This consequence substantiates the suggestion, based on empirical results,[10,11] that "limited mobility" is necessary for column growth.

Growth rate as a function of wavelength is shown in Fig. 2. Note that for each curve of fixed E/KT and mean diffusion distance there is a most rapidly growing wavelength. This, of course, is the column size one is most likely to observe. For the parameters of Fig. 2, the most rapidly growing wavelength is close to the diameter measured by Nieuwenhuizen and Haanstra.[4] At high temperature, however, the growth rate is exponentially small, and so column growth will not be apparent above a certain substrate temperature. This is in accord with observation.[10] Physically, diffusivity tends to be large at high temperatures, and the adatoms spread uniformly over the surface.

For low substrate temperatures for which the time scale on which the adatoms freeze is short with respect to the time scale for column growth, the condition

$$\sigma/\mathscr{D} \ll 1 \quad (8)$$

can be used to linearize Eq. (7) in σ. Then solving for the maximum growth rate and use of Eq. (3) yield an approximate but very simple relationship for the most rapidly growing wavelength,

$$\lambda(\sigma_{\max}) = 2\pi(\langle x^2\rangle)^{1/2}.$$

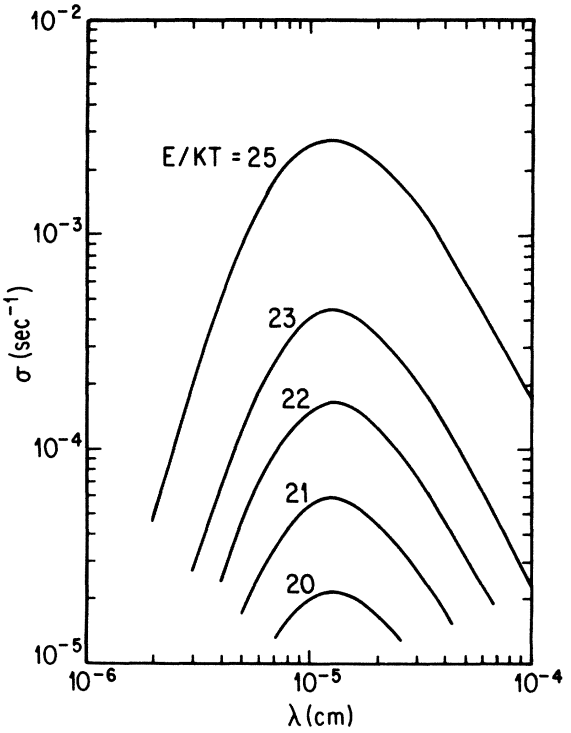

FIG. 2. Growth rate as a function of column wavelength. The curves are for $J = 10$ Å/sec, $\langle x^2\rangle = 4\times10^4$ Å^2, and $\alpha = 30°$, $a = 4.05$ Å, and $\nu = 10^{13}$/sec.

The mean square diffusion length can be expected to increase with temperature, and so λ will increase with temperature, as is observed.[4,10,15]

Column orientation, β, is defined by following a point of constant phase[3]; see Fig. 1. Figure 3 shows the theoretical results plotted with experimental data from several thin-film systems. Each set of points represents data for the material noted at a particular deposition rate and substrate temperature. As defined above, $\tan\beta$ is the ratio of the horizontal velocity, u, of a perturbation peak, to its vertical velocity, which is the sum of the mean growth rate of the layer, v, plus $h_1\sigma$, the velocity of the peak amplitude relative to the mean at $t=0$. In the general case, then, $\tan\beta = u/(v+h_1\sigma)$, and solving Eqs. (3)–(6) for u, v, and σ yields an equation for β which is algebraically complex.[19] However, with use of condition (8) to linearize (7), β is very accurately described by the simplified solution,

$$\tan\beta = \tfrac{2}{3}\tan\alpha/(1+\Phi\tan\alpha\sin\alpha), \quad (9)$$

$$\Phi = \tfrac{4}{27}h_1 J/D.$$

Over a wide range of values of D, J, and h_1 of practical interest ($D \geq 10^3$ Å^2/sec, $J \leq 100$ Å/sec, $h_1 \leq 250$ Å) Φ varies over the limited range

$$0 < \Phi \leq 3.7.$$

Within these values of Φ, Eq. (9) encompasses the data presented in Fig. 3.

The angles α and β are frequently correlated by the tangent rule[3,4,18]

$$\tan\beta = \tfrac{1}{2}\tan\alpha.$$

This relationship is approximated for deposition conditions corresponding to small but finite Φ.

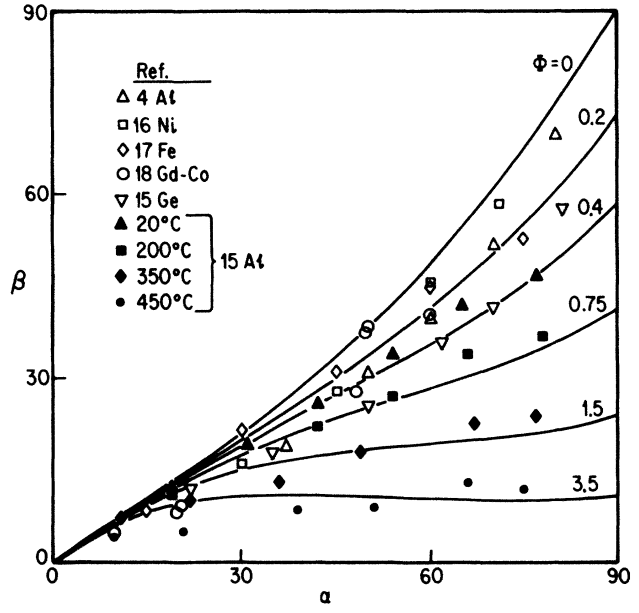

FIG. 3. Column orientation as a function of incident beam angle; data from Refs. 4 and 15–18. Four substrate temperatures are plotted for aluminum, from Ref. 15.

The theory presented above can be given a physical interpretation as follows. For any nonzero deposition angle α, the concentration of deposited adatoms is greatest at some location at a distance M from the location of peak amplitude (the "tip"). In the linear approximation, the location of the maximum deposition concentration is determined from the maximum (with respect to x) of the sum of the first two terms on the right-hand side of Eq. (1). This gives $M = \lambda/4$, independent of incident angle ($\alpha \neq 0$). For these adatoms to reach the peak they must migrate the distance M. So the most unstable time scale, $1/A$, is such that the adatoms can migrate the distance M before sticking, i.e., $A \simeq 2D/M^2$. Then the maximum growth rate should occur when $\lambda^2 \simeq 32D/A$. This order-of-magnitude calculation can be compared to the results from our linearized governing equations, $\lambda(\sigma_{max}) = 2\pi M$, and with use of Eq. (6), $\lambda^2(\sigma_{max}) = 8\pi^2 D/A$.

Monte Carlo simulations of finite-size particles arriving at the surface with ballistic trajectories and no surface diffusion also show columnlike structures.[3] However, unlike our model, these columns are a direct consequence of the use of finite-size particles and the columns scale with particle size. The ultimate location of an incoming particle is indeterminate, to within about one particle diameter, depending on the location of the previously deposited finite-size particles.[3] This small indeterminacy can be thought of as a surface "diffusivity" which is sufficient to produce the columns observed in the simulations. In the continuum limit (i.e., as particle size approaches 0) and with no surface diffusion, column growth is neutrally stable.[3,9]

Additionally, in these simulations, when surface diffusion is absent the columns are more "chainlike" or "tendril-like" than columnar. Several researchers[7,20,21] have, by allowing the incoming particle to "diffuse" away from its initial point of contact before sticking, produced more realistic columns. These observations helped motivate our approach in which particle-size effects are neglected and the effects of surface diffusion are treated directly; this treatment of diffusivity seems able to reproduce structures which are more columnar than tendril.

In conclusion, a model of columnar growth has been presented. The theory is developed from the experimental observation that adatom mobility is critical for determining columnar microstructure. The analysis is limited to small surface slopes. Calculation of the full nonlinear shape of a realistic column still awaits a complete analysis. Though extremely simple, the model accounts for most of the experimentally observed

features of columnar structure. The model predicts that columnar microstructure will not be observed at high substrate temperature. A relationship between column width and mean square diffusion length is found. Column orientation is predicted, and the tangent rule is shown not to be a universal correlation, but rather column orientation is dependent on the deposition conditions.

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