LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR--88-2451

DE88 014396

TITLE: THE EFFECT OF VAPOR INCIDENCE ANGLE UPON THIN FILM COLUMNAR GROWTH

AUTHOR(S): A. Mazor
B. G. Bukiet
D. J. Srolovitz*

SUBMITTED TO: J. Vac. Sci. Tech. A

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Permanent Address: Department of Materials Science and Engineering
University of Michigan
Ann Arbor, Michigan 48109

By acceptance of this article the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

THE EFFECT OF VAPOR INCIDENCE ANGLE UPON THIN FILM COLUMNAR GROWTH

A. Mazor, B. G. Bukiet and D. J. Srolovitz*

Los Alamos National Laboratory
Theoretical Division
Los Alamos, New Mexico 87545

*Department of Materials Science and Engineering
University of Michigan
Ann Arbor, Michigan 48109

Abstract

We present a generalized theory for the growth of columnar microstructure in vapor deposited thin films under the joint influence of a constant uniform deposition flux coming down with arbitrarily chosen incidence angle, and surface diffusion. The dependences of the Zone I to Zone II transition temperature, and the characteristic length scales associated with the unstable modes on the deposition angle are predicted. The surface morphology is obtained as a function of vapor incidence angle. For a specific deposition angle, there is a one-parameter family of steady-state surface profiles which corresponds to a range of possible columnar orientation angles, among which only one angle is associated with the tangent rule. These results agree with experimental observations.

I. Introduction

Over the last two decades, considerable effort has been expended in classifying thin film morphologies.¹⁻³ The technological importance of such studies arises from the relationship between the physical structure of the films and their properties. Microstructures are recognized as playing a major role in determining magnetic, optical, electronic and plastic properties of films. The microstructure and morphology of physical vapor-deposited films are known to be sensitive to deposition conditions, among which temperature T is of particular importance. Movchan and Demchishin,¹ in their experimental studies of metal and oxide films deposited at high rates, were the first to identify distinct microstructural zones and the temperature ranges in which they occur.

For high deposition rates (typically 10 to 500 nm/sec)² the following three temperature zones have been identified.¹ For $0 < T < T_1$ (where $T_1 \sim 0.3 T_m$ for metals, $T_1 \sim 0.24 T_m$ for oxides, and T_m is the melting point of the film), the microstructure is porous and consists of tapered crystallites separated by voided regions (the thickness of which is of order tens of nanometers). For $T_1 < T < T_2$ (where $T_2 \sim 0.45 T_m$), the film is made up of columnar grains separated by metallurgical grain boundaries (i.e. there is no porosity and the width of the grain boundaries is of order 0.5 nm). Finally, for $T > T_2$, the structure consists of equiaxed grains, and depends on both the type of material and deposition rate.⁴ These three microstructural regimes are known as Zone I, Zone II, and Zone III, respectively. The morphology of the surface associated with these zones is correlated with the underlying microstructure.

In previous papers^{5,6} we presented a theory for the development of columnar microstructures in vapor-deposited thin films. We proposed a nonlinear partial differential equation for the space-time evolution of Zone II microstructures, under the joint influence of constant uniform normal deposition rate and surface diffusion. The Zone I to Zone II transition temperature, the characteristic length scale associated with the unstable modes, the surface morphology, the columnar grain structure, and the film thickness dependence of the columnar grain size were all accounted for, in good agreement with experimental

results.

The microstructure of films deposited under Zone I conditions shows a strong dependence on the deposition angle. In particular, the tangent of the angle the microcolumns or crystallites make with the substrate normal in Zone I films is approximately equal to one half the tangent of the deposition angle (see Fig. 1). This result is based on experimental observations, numerical simulations (ballistic aggregation models) and theoretical analysis. The purpose of this paper is to investigate the effects of deposition angle under Zone II conditions by extending our previous theoretical results on columnar growth. In Section II we propose a generalized nonlinear growth equation. Section III presents the results of the linearized analysis of this equation: the width of the band of unstable perturbation modes is found as a function of the deposition angle θ . The minimal wavelength associated with an unstable mode $\lambda_0(T, \theta)$ and the wavelength of the most unstable mode $\lambda_m(T, \theta)$ are two important characteristic wavelengths, and they are both deposition angle dependent. The analysis also predicts the dependence of the Zone I to Zone II transition temperature on the vapor incidence angle. In Section IV, the steady state film profile is discussed.

II. Generalized Surface Evolution Equation

In previous papers^{5,6} we proposed a one-dimensional partial differential equation, which describes the evolution of an arbitrary initial surface profile $h(x, 0)$ under the joint influence of a constant uniform deposition rate J of finite-size atoms (of radius δ) incident normal to the substrate and surface diffusion. We now generalize this equation by incorporating the effect of a nonzero vapor incidence angle (measured relative to the substrate normal). The deposition geometry employed is indicated in Fig. 1. The rate of increase of the surface height over an infinitesimal interval dx of the substrate is given by

$$h_t dx = JA, \quad (1)$$

where JA is the amount of flux crossing the area A transverse to the deposition direction per unit time. (A is a length for the one dimensional substrate considered herein). The

subscript t indicates differentiation with respect to time. The area A is calculated as follows: we take two arbitrary points (x_1, y_1) and (x_2, y_2) lying respectively on the left and right deposition lines which intersect the boundaries of A (see Fig. 1). Then we minimize the distance between these points with respect to $(x_1 - x_2) \equiv \Delta$, i.e.,

$$A = \text{Min} \left\{ [(sx_1 + b_1) - (sx_2 + b_2)]^2 + (x_1 - x_2)^2 \right\}^{1/2}, \quad (2)$$

where $s = \cot \theta$, and θ is the incidence angle measured relative to the substrate normal. The minimization procedure yields

$$\Delta = -s(b_1 - b_2)/(s^2 + 1). \quad (3)$$

Using (2) and (3) A becomes

$$A = (b_1 - b_2)(s^2 + 1)^{-1/2}. \quad (4)$$

Note that $(b_1 - b_2) > 0$ by construction and, thus, A is well defined. To complete the calculation of A we need to know $(b_1 - b_2)$. At this point we remind the reader⁵⁻⁷ that due to the finite-size of the deposit atoms, the deposition does not take place on the actual surface $h(x, t)$, but on an imaginary surface displaced by $\delta \vec{n}(x)$ from $h(x, t)$ (i.e. the deposition surface is an atom radius 'above' the real surface), where $\vec{n}(x)$ is a unit vector normal to $h(x, t)$, i.e.,

$$\vec{n}(x) = [-h_x(x)\hat{i} + \hat{j}] [1 + h_x^2(x)]^{-1/2}. \quad (5)$$

$\hat{i}$ and $\hat{j}$ are unit vectors directed along the x and y axes and the subscript x designates differentiation. Thus, the points $[x, h(x, t)]$ and $[x + dx, h(x + dx, t)]$ are mapped to new points on the imaginary surface, and each one of them lies, respectively, on the left and right deposition lines intersecting the boundaries of A (see Fig. 1), i.e.,

$$h(x) + \frac{\delta}{\sqrt{1 + h_x^2(x)}} = s \left[x - \frac{\delta h_x(x)}{\sqrt{1 + h_x^2(x)}} \right] + b_1, \quad (6a)$$

$$h(x+dx) + \frac{\delta}{\sqrt{1+h_x^2(x+dx)}} = s \left[x+dx - \frac{\delta h_x(x+dx)}{\sqrt{1+h_x^2(x+dx)}} \right] + b_2. \quad (6b)$$

Subtracting (6a) from (6b) and expanding around x to leading order in dx , we finally obtain

$$(b_1 - b_2) = [1 + \delta\kappa(x)][s - h_x(x)]dx, \quad (7)$$

where $\kappa(x)$ is the local surface curvature

$$\kappa(x) = -h_{xx} (1 + h_x^2)^{-3/2}. \quad (8)$$

Combining Eqs. (1), (4), (7) and (8) yields the following contribution to the surface evolution equation due to the deposition of finite-size atoms with an incidence angle $\theta \neq 0$, i.e.,

$$\begin{aligned} h_i^{\text{deposit}} = & J \cos \theta - J \sin \theta h_x - \delta J \cos \theta [h_x (1 + h_x^2)^{-1/2}]_x \\ & + \delta J \sin \theta h_x [h_x (1 + h_x^2)^{-1/2}]_x. \end{aligned} \quad (9)$$

The contribution to the surface evolution equation due to surface diffusion is the same as reported in Refs. [5,6,8], i.e.,

$$h_i^{\text{diffusion}} = -D_e \left\{ (1 + h_x^2)^{-1/2} [h_{xx} (1 + h_x^2)^{3/2}]_x \right\}_x, \quad (10)$$

where $D_e = D_s \sigma_s \Omega^2 \epsilon / K_B T$ is the effective diffusivity, σ_s is the isotropic surface energy density, Ω is the atomic volume, ϵ is the number of atoms per unit area, $K_B T$ is the thermal energy, and D_s is the surface diffusivity.

The complete evolution equation of the film surface under the combined action of surface diffusion and a constant deposition rate of finite-size atoms deposited with an incidence angle $\theta \neq 0$ is

$$h_t = h_i^{\text{deposit}} + h_i^{\text{diffusion}}. \quad (11)$$

Equation (9) holds both for positive and negative values of θ , where the signature of θ is defined arbitrarily. The first term on the right-hand side (r.h.s.) of (9) is just a

uniform growth rate which depends on the incidence angle θ and does not disappear in the continuum limit $\delta \rightarrow 0$. The second term on the r.h.s. of (9) describes a uniform translational motion along the substrate (see Section IV). The last two terms on the r.h.s. of (9) are corrections to the uniform growth rate due to the discrete nature of the deposited atoms. The third term on the r.h.s. of (9) is of the form $\delta J \cos \theta \kappa(x)$, and it implies that an element of the surface $h(x, t)$ receives a net flux of atoms either greater (for positive curvature $\kappa > 0$) or smaller (for $\kappa < 0$) than $J \cos \theta$. The reason for this kind of behavior is that deposition takes place on an imaginary surface displaced by δ from $h(x, t)$. Depending on the surface curvature κ , the projected length of an element of this imaginary surface on the substrate is either greater (for $\kappa > 0$) or smaller (for $\kappa < 0$) than the projected length of the corresponding element of $h(x, t)$ (see Fig. 1 and references [6-8]). The fact that the third term is even under $\theta \rightarrow -\theta$ implies that neither the right half nor the left half of a concave (or a convex) portion of the surface profile is favored by the deposition flux. The fourth term on the r.h.s. of (9) is of the form $[-\delta J \sin \theta h_x \kappa(x)]$. The form of the dependence on h_x and $\kappa(x)$ means that this term favors growth towards the direction of the deposition flux. In other words, there is a symmetry breaking in the sense that the side of a hump facing the deposition direction grows faster than the side of the hump facing the other way.

Extracting the constant drift of the surface, and using the following dimensionless variables, i.e.,

$$H = \left(\frac{\delta J}{2D_s} \right)^{1/2} (h - J \cos \theta t) \quad x = \left(\frac{\delta J}{2D_s} \right)^{1/2} x \quad \tau = \frac{\delta^2 J^2}{4D_s} t, \quad (12)$$

where $\int H dx = 0$ and the integration is over the length of the system, Eq. (11) is rewritten as

$$H_\tau = -V(\theta)H_x - 2\cos\theta \left(\frac{H_x}{\sqrt{1+H_x^2}} \right)_x + 2\sin\theta H_x \left(\frac{H_x}{\sqrt{1+H_x^2}} \right)_x - \left[\frac{1}{\sqrt{1+H_x^2}} \left(\frac{H_x}{\sqrt{1+H_x^2}} \right)_{xx} \right], \quad (13)$$

where

$$V(\theta) = \frac{2 \sin \theta}{\delta} \left(\frac{2D_e}{\delta J} \right)^{1/2}. \quad (14)$$

In terms of $g = H_x(1 + H_x^2)^{-1/2}$, Eq. (13) may be written as:

$$\begin{aligned} g_\tau = & -V(\theta)g_x - 2 \cos \theta g_{xx}(1 - g^2)^{3/2} \\ & + 2 \sin \theta g_x^2 + 2 \sin \theta g(1 - g^2)g_{xx} \\ & - (1 - g^2)^{3/2} [(1 - g^2)^{1/2} g_{xx}]_{xx} \end{aligned} \quad (15)$$

III. Linearized Perturbation Analysis

In the small slope limit Eq. (13) reduces to

$$H_\tau = -V(\theta)H_x - 2 \cos \theta H_{xx} - H_{xxxx}. \quad (16)$$

Substituting an initial trial sinusoidal perturbation, $\sin(kx)$, in (16) we find it to behave for short times according to

$$e^{(W_r - iW_i)t} \quad (17a)$$

where

$$\begin{aligned} W_r &= 2 \cos \theta k^2 - k^4 \\ W_i &= V(\theta)k. \end{aligned} \quad (17b)$$

Thus, the perturbation grows (for $W_r > 0$) or decays (for $W_r < 0$) exponentially in time, and this behavior is superimposed on an oscillatory component. The pure oscillatory time-dependence originates from the first term on the r.h.s. of (16). This term describes a uniform translational motion along the horizontal axis and it is irrelevant to the onset of structural instability. A band of unstable modes exists with wavelengths $\lambda = \frac{2\pi}{k} > \lambda_0(\theta) = (4\pi^2 D_e / \delta J \cos \theta)^{1/2}$, and with the most unstable mode at $\lambda = \lambda_m = \sqrt{2} \lambda_0$ (see Fig. 2). These results imply that perturbations of wavelengths smaller than the diffusion length

$\lambda_0(T, \theta)$ are smoothed by the surface diffusion, whereas long wavelength perturbations grow without bound. Note that when $\theta \rightarrow \frac{\pi}{2}$, the band of unstable modes shrinks to zero. This is a natural outcome of the fact that the vertical deposition component vanishes and there is nothing to compete with the relaxational effect of the surface diffusion. However, the present analysis is inapplicable in this limit.

In Refs. 5-6 we claimed that due to the discrete nature of the atoms in the film, surface diffusion is ineffective when the diffusion length λ_0 is smaller than a few δ . For normal deposition, equating $\lambda_0(T, \theta = 0)$ with the minimum physically meaningful diffusion length $\eta\delta$ (where η is a constant of order 1 to 10) yielded a critical temperature below which surface diffusion plays essentially no role in the microstructural evolution. This critical temperature turned out to be^{5,6} $T = T_c \approx 0.23 T_m$ for the choice of $\sigma_s = 10^3$ dyne/cm, $\Omega = 2 \cdot 10^{-23}$ cm³, $\delta = 4 \cdot 10^{-8}$ cm, $J = 2 \cdot 10^{-5}$ cm/sec, and $\eta = 2$. Since D_s is proportional to D , which depends exponentially on temperature⁹ (i.e., $D_s = D_0 \exp(-Q/K_B T)$ where $Q = (5 + 20T/3T_m)K_B T_m$, T_c is relatively insensitive to variations around 2δ . Coming back to the case $\theta \neq 0$, the above type of arguments are still valid as long as the deposition angle $\theta \ll \pi/2$. For relatively small θ values, the factor $\sqrt{\cos \theta}$ in $\lambda_0(T, \theta)$ is of order unity and, thus, T_c will only vary slightly. With increasing deposition angle at constant J the rate of film growth is decreased and consequently, the diffusion length λ_0 is increased. Therefore, T_c must decrease with increasing θ . Since Zone I corresponds to microstructures formed under zero diffusion conditions (as seen in ballistic aggregation studies¹⁰) and T_c corresponds to the temperature below which surface diffusion is negligible, we equate T_c to the Zone I/Zone II transition temperature T_1 . This equality is further justified in Refs.[5,6].

IV. Steady-State Solutions of the Growth Equation

While the linear analysis presented above is capable of predicting the type of unstable modes, it is incapable of describing the steady-state columnar structure of Zone II. The nonlinear terms are the ones that saturate the long wavelength instability into a relatively

small amplitude surface profile (see below). The steady-state columnar structures for a nonzero vapor incidence angle θ are obtained in a moving reference frame which moves along the x-axis with a velocity $V(\theta)$ relative to the stationary Laboratory frame. The transformation to this moving frame is defined as follows:

$$\tilde{\tau} = \tau \quad (18a)$$

$$\tilde{z} = z - V(\theta)\tau \quad (18b)$$

where $V(\theta)$ is given by Eq. (14). The operators $\partial/\partial\tau$ and $\partial/\partial z$ become

$$\frac{\partial}{\partial\tau} = \frac{\partial}{\partial\tilde{\tau}} - V(\theta) \frac{\partial}{\partial\tilde{z}} \quad (19a)$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial\tilde{z}}. \quad (19b)$$

Using (18) and (19), and renaming again $\tilde{z}$ and $\tilde{\tau}$ as z and τ for simplicity of notation, the growth equation in the moving reference frame is:

$$\begin{aligned} H_\tau = & -2 \cos \theta \left(\frac{H_s}{\sqrt{1+H_s^2}} \right)_s - 2 \sin \theta \left(\frac{1}{\sqrt{1+H_s^2}} \right)_s \\ & - \left[\frac{1}{\sqrt{1+H_s^2}} \left(\frac{H_s}{\sqrt{1+H_s^2}} \right)_{ss} \right]_s \end{aligned} \quad (20)$$

Equation (20) is valid in the moving reference frame and from now on our analysis and results pertain to this moving frame. In terms of $g = H_s (1 + H_s^2)^{-1/2}$, Eq. (20) becomes

$$\begin{aligned} g_\tau = & -2 \cos \theta g_{ss} (1 - g^2)^{3/2} + 2 \sin \theta g_s^2 \\ & + 2 \sin \theta g (1 - g^2) g_{ss} \\ & - (1 - g^2)^{3/2} [(1 - g^2)^{1/2} g_{ss}]_{ss}. \end{aligned} \quad (21)$$

The reason we mention Eq. (21) is mostly numerical since it is easier, in principle, to integrate (21) forward in time keeping g always bounded between -1 and +1, and then apply one further spatial integration to get $H(z, \tau)$.

Assuming we have already extracted out all possible translational motions along the substrate, i.e., there are no travelling waves in the moving references frame, the stationary states of Eq. (20) are obtained by demanding that the right hand side of (20) vanish (i.e., $H_\tau = 0$). Putting (20) to zero and integrating once yields

$$0 = 2 \cos \theta \frac{H_s}{\sqrt{1 + H_s^2}} + 2 \sin \theta \left(\frac{1}{\sqrt{1 + H_s^2}} - 1 \right) + \frac{1}{\sqrt{1 + H_s^2}} \left(\frac{H_s}{\sqrt{1 + H_s^2}} \right)_{ss}. \quad (22)$$

The constant of integration in (22) is chosen to be $(-2 \sin \theta)$. The reason for this choice is that $H_s = 0$ is a possible stationary state (and definitely is the asymptotic state at $x = \pm \infty$), and this can be only if $(-2 \sin \theta)$ is the constant of integration. Multiplying (22) by $H_{ss}(1 + H_s^2)^{-1}$ and integrating once again we obtain

$$\frac{1}{2} \frac{H_{ss}^2}{(1 + H_s^2)^3} = 2 \cos \theta (1 + H_s^2)^{-1/2} + 2 \sin \theta \arctan(H_s) - 2 \sin \theta H_s (1 + H_s^2)^{-1/2} + C, \quad (23)$$

where $C, -2 \cos \theta \leq C \leq \infty$, is an integration constant. Let

$$H_s = \tan f. \quad (24)$$

Then Eq. (23) is rewritten as follows:

$$f_s^2 = \frac{4 \cos(\theta + f) + 4 f \sin \theta + 2C}{\cos^2 f}. \quad (25)$$

For a chosen vapor incidence angle θ , Eq. (25) defines a one-parameter family of steady-state profiles $H_s(x; C)$. The numerical analysis of the phase portrait (f, f_s) as a function of C (for a chosen θ), and the corresponding thin film morphology and microstructure are reported in the next section. The value of C is determined by the maximally unstable mode (assuming small-amplitude initial condition). It is worth noticing that for $\theta = 0$, Eq. (25) reduces to Eq. (B8) in Ref. 6. This means that Eq. (25) captures the correct steady-state surface profiles for the normal deposition case, as already reported in Refs. 5-6.

Figure 3 presents the steady-state phase-portrait profiles on the plane (f, f_s) for selected values of C , as obtained from Eq. (25) with $\theta = 0$. These profiles are symmetric both under $f \rightarrow -f$ and $f_s \rightarrow -f_s$. For $C > 0$ the $f_s(f)$ profiles are open curves approaching the values $f = \pm \frac{\pi}{2}$ asymptotically (i.e., when $f_s \rightarrow \pm \infty$). This class of open curves corresponds to oscillatory and periodic steady-state thin film surface profiles which consist of very nearly circular arcs connected by vertical lines (see Fig. 3 of Ref. 6). It is also known from that same reference that these steady states (with $C > 0$) are stable with respect to small perturbations and can be reached from typical initial conditions (e.g., sinusoidal and random initial conditions).

Putting $\theta = 0$ in (15), integrating it forward in time under periodic boundary conditions (for further details about the integration procedure, see Ref. 6), and transforming from $g(x, \tau)$ to $H(x, \tau)$ (via the relation $H_s = g(1 - g^2)^{-1/2}$), we have found typical initial conditions to evolve rapidly to profiles of the type discussed above with either a single characteristic wavenumber $k = k_m = 1$ or with a few wavenumbers around $k_m = 1$ (k_m is the most unstable mode in the linear perturbation analysis). As shown in Figs. 5 and 6 of Ref. 6, once infinite slope regimes are formed, there is very little additional evolution of the surface profile. We now make the observation that the wavenumbers associated with the true steady-state surface profiles (with $C > 0$) are bigger than the wavenumbers of the profiles obtained from the initial value problem, i.e., Eq. (15). This can be attributed to the rapid formation of the straight, vertical sections of the surface profile which greatly retards further evolution of the profile. Straight sections of the surface profile are of uniform zero curvature and hence there is no driving force for surface diffusion in these areas (see Eq. 10). While the numerics is thus incapable of reaching the steady-state wavelengths, it accurately reproduces the predicted surface morphology.

Figure 4 presents the phase portrait $f_s(f)$ for the choice $\theta = -30^\circ$ and selected C values. Since the $f_s(f)$ curves are only symmetric under $f_s \rightarrow -f_s$ this lowered symmetry relative to the $\theta = 0$ case indicates that the columns of the thin film are not symmetric around their extrema. Three classes of curves $f_s(f)$ are observed. The first one is a class

of closed curves for negative C values (i.e., $C \lesssim -0.6$) which cut the f -axis asymmetrically around $f = 0$, i.e., at values $f = f_R < \frac{\pi}{2}$ and $f = f_L > -\frac{\pi}{2}$ (where $f_L \neq f_R$, see Fig. 4). We neglect this class of solutions since it does not yield the observed steady-state surface morphology in the limit $\theta \rightarrow 0$. The second class of $f_s(f)$ curves is of open curves for positive C values, i.e., $C > 0.5$. The associated $H_s(z; C)$ morphologies are oscillatory surface profiles which consist of asymmetric caps connected by vertical segments. This type of steady-state solution is also neglected since it is inconsistent with the tilted surface morphology expected on the basis of the scaling of the translational velocity described by Eq. (18).

The third class of $f_s(f)$ curves is of semiclosed curves for positive and negative C values around zero, i.e., $-0.6 < C < 0.5$ (see Fig. 4). These curves are characterized by vertical lines which intersect the positive f axis in the range $f_R^* < f = f_R(C) < \frac{\pi}{2}$, where f_R^* is θ -dependent and for $\theta = -30^\circ$, $f_R^* \simeq 63^\circ$. These curves also approach $f = -\frac{\pi}{2}$ asymptotically as $f_s \rightarrow \pm \infty$. The corresponding $H_s(z; C)$ surface profiles show the shape of tilted columns (like Fig. 5), where the orientation angle ψ of the columns (measured relative to the substrate normal) is C -dependent and varies over a finite range of values (for the case $\theta = -30^\circ$, $0 < \psi < 27^\circ$). (The length of the straight segments of the surface profile shown in Fig. 10 were chosen to satisfy periodic boundary conditions.) Unfortunately, our calculations do not yield a unique profile orientation angle but a range of such angles. In other words, for a chosen deposition angle, there is a one parameter family of steady-state surface profiles $H_s(z; C)$, all having the proper morphology but with different profile orientation angles.

Figure 6 shows the predicted range of tilting angle ψ as a function of the deposition angle θ for Zone II films. In addition, Fig. 6 also presents the experimentally determined dependence of the tilting angle on the angle of deposition for Zone I films. In Zone I, this dependence has been described by the following "tangent rule" (see Ref. 10 and references therein).

$$\tan \psi / \tan \theta \cong \frac{1}{2}. \quad (26)$$

The tangent rule prediction, appropriate for Zone I films, falls within the range of tilting angles we predict for Zone II films. While the above analysis does not identify a unique tilting angle for Zone II films, we expect that tilting angles in Zone II will be smaller than in Zone I. Non-zero tilting angles are strictly a consequence of atomic shadowing during deposition. We base the above expectation on the fact that in the relatively high temperature Zone II regime, the enhanced surface diffusion decreases the effect of shadowing.

V. Conclusion

The effect of vapor incidence angle upon Zone II film growth has been presented. Primarily, the model yields a tilted columnar microstructure. For each deposition angle there is a one-parameter family of steady-state surface profiles of the above type, which corresponds to a range of possible profile orientation angles. The range of predicted orientation angles includes those observed in Zone I film growth. We expect that tilting angles in Zone II will be smaller than in Zone I due to increased influence of surface diffusion in Zone II. The dependencies of the Zone I to Zone II transition temperature and the characteristic length scales associated with the unstable modes on the deposition angle are also accounted for. These results are in reasonable agreement with experiment.

References

1. B. A. Movchan and A. V. Demchishin, *Phys. Met. Metallogr.* **28**, 83 (1969).
2. J. A. Thornton, *Ann. Rev. Mater. Sci.* **7**, 239 (1977).
3. R. Messier, A. P. Giri, and R. A. Roy, *J. Vac. Sci. Tech.* **A2**, 500 (1984).
4. C. R. M. Grovenor, H. T. G. Hentsell, and D. A. Smith, *Acta Metall.* **32**, 773 (1984).
5. A. Mazor, D. J. Srolovitz, P. S. Hagan, and B. G. Bukiet, *Phys. Rev. Lett.* **60**, 424 (1988).
6. D. J. Srolovitz, A. Mazor, and B. G. Bukiet, *J. Vac. Sci. Tech.* **A6**, 2371 (1988).
7. H. J. Leamy, G. H. Gilmer, and A. G. Dirks in "Current Topics in Materials Science," edited by E. Kaldis (North Holland, Amsterdam, 1980), Vol. 6, p. 309.
8. W. W. Mullins, *J. Appl. Phys.* **28**, 333 (1957).
9. K. H. Müller, *J. Appl. Phys.* **58**, 2573 (1985).
10. P. Meakin, P. Ramanlal, L. M. Sander, and R. C. Ball, *Phys. Rev.* **A34**, 5091 (1986).

Figure Captions

Figure 1. The deposition geometry. θ is the vapor incidence angle and $s = \cot \theta$. A is the area normal to the deposition flux which is deposited over an interval dx of the substrate. κ is the surface curvature and δ is the atomic radius. Note that the projected length of the surface displaced by δ from $h(x,t)$ is greater (less) than that of the actual surface when $\kappa > 0$ ($\kappa < 0$). See text.

Figure 2. The dimensionless dispersion relations for the perturbation modes of wave-number k , and various values of the deposition angle θ . Curves 1, 2, and 3 correspond to $\theta = 15^\circ, 30^\circ$, and 45° , respectively. $k_0(\theta)$ and $k_m(\theta)$ are associated with the shortest unstable wavelength and maximally unstable modes, respectively.

Figure 3. The upper half plane of the steady-state phase portrait $f_s(f)$ for C -values ranging from $C = -1.75$ (the inner closed curve) to $C = 1.25$ (the upper open curve) in increments of 0.5. This phase diagram corresponds to the normal deposition case $\theta = 0$. f is the angle of the local slope of the corresponding steady-state surface profile $H_s(x; C)$.

Figure 4. The steady-state phase portrait $f_s(f)$ around the origin, for C -values ranging from $C = -1.2$ (the inner closed curve) to $C = 0.6$ (the outer open curve) in increments of $\Delta C = 0.2$. The deposition angle is $\theta = -30^\circ$ (see text).

Figure 5. A characteristic steady-state surface profile which belongs to the class of semiclosed $f_s(f)$ curves ($C = -0.5$ and $\theta = -30^\circ$). The tilted surface morphology is shown with orientational angle $\psi \simeq 25^\circ$ (measured relative to the substrate normal).

Figure 6. The ranges of possible tilting angles (vertical bars) for various deposition angles θ predicted for Zone II. Also shown (solid line) is the tangent rule prediction (Eq. 26) appropriate for Zone I films.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6