The columnar growth angle in obliquely evaporated thin films

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Herrn Professor Karl Heinz Kloos aus Anlaß seines 65. Geburtstages zugeeignet

Vapor-deposited thin films grown under conditions of oblique incidence commonly develop a microstructure of columns, inclined at an angle β relative to the substrate normal, which differs from the angle of incidence α. Here it is shown that the functional relation $\beta(\alpha)$ is universally linked to the dependence of the film density ϱ on the angle of incidence, through the equation $\tan\beta = \tan\alpha + \varrho^{-1}(d\varrho/d\alpha)$. The theory is supported by an analysis of published numerical data obtained from simulations of ballistic deposition of disks and spheres.

Die Orientierung der Säulen in der Mikrostruktur schräg aufgedampfter dünner Schichten

Schräg aufgedampfte dünne Schichten entwickeln gewöhnlich eine Mikrostruktur aus Säulen, deren Wachstumswinkel relativ zur Substratnormalen, β, nicht mit dem Einfallswinkel α übereinstimmt. Hier wird gezeigt, daß der funktionale Zusammenhang $\beta(\alpha)$ durch die Gleichung $\tan\beta = \tan\alpha + \varrho^{-1}(d\varrho/\delta\alpha)$ in universeller Weise mit der Winkelabhängigkeit der Schichtdichte ϱ verknüpft ist. Ein Vergleich mit numerischen Daten aus Simulationen der ballistischen Abscheidung von Scheiben und Kugeln bestätigt die Theorie.

1 Introduction

Many of the unique mechanical, optical and electromagnetic properties of vapor-deposited thin films originate in their columnar microstructure [1, 2]. The large amount of porosity associated with the void network surrounding the columns is detrimental to the stability and adhesion of coatings. On the other hand, certain applications purposively exploit the anisotropy of magnetic [3] and optical [2, 4] film properties induced by the microstructure. As a representative example, the use of angular selective surface coatings in the development of energy efficient windows may be mentioned [5].

The columnar microstructure can be enhanced and, to some extent, controlled by carrying out the deposition process under conditions of oblique incidence, such that the deposition flux forms a nonzero angle $\alpha > 0$ with the substrate normal *(Fig. 1)*. The resulting column orientation lies in the deposition plane, formed by the flux direction and its projection onto the substrate, but the growth angle β enclosed by the columns and the substrate normal is typically less than the deposition angle α. Nieuwenhuizen and Haanstra [6], who first observed this phenomenon using electron microfractography, found that their data for aluminum films evaporated at angles $30° < \alpha \leq 80°$ were well described by the tangent rule

$$\tan\beta = \frac{1}{2}\tan\alpha. \qquad (1)$$

This relationship has been widely used to interpret both experimental data, and the results of computer simulations modeling the deposition process [1]. It has been recognized for some time, however, that the tangent rule is not universally (or even generally) valid. Experimental studies have established that the columnar growth angle β depends on temperature [7, 8] and film composition [9] as well as on the deposition angle α; large scale computer simulations also suggest relations between α and β that differ from equation (1) [10] (see Section 3 below).

An understanding of the factors that determine the columnar growth angle is of vital importance for thin film applications, because the column orientation defines one of the principal axes for all anisotropic film properties (the other being defined by the deposition plane) [2]. A number of theoretical approaches have therefore been aimed at replacing the empirical rule (1) by a more well-founded relation [11–13]. It should be emphasized, however, that the theoretical problem is formidable: The column orientation arises from collective self-shadowing, involving the long-ranged interaction of many columns, with an important stochastic component due to the randomness of the

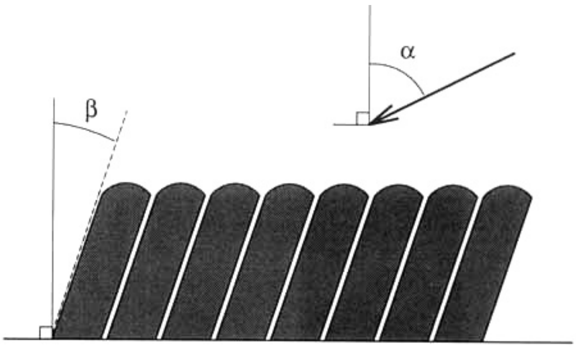

Fig. 1. Schematic of the columnar microstructure. The figure represents a cut along the deposition plane, which is spanned by the incidence direction and its horizontal projection.

Abb. 1. Schematische Darstellung der säulenförmigen Mikrostruktur. Das Bild zeigt einen Schnitt entlang der Einfallsebene, die von der Einfallsrichtung und ihrer horizontalen Projektion aufgespannt wird.

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deposition flux [14]. An analytic solution seems to be out of reach even for strongly simplified "ballistic deposition" models [10, 14] (see Section 3).

Consequently, the goal of the present contribution is more modest. It will be shown that, while the functional relation between α and β is not itself universal, it is nevertheless universally linked to the angular dependence of a second fundamental film property, viz. the film density $\varrho(\alpha)$, through the equation

$$\tan \beta = \tan \alpha + \varrho'(\alpha)/\varrho(\alpha) \tag{2}$$

with $\varrho' = d\varrho/d\alpha$. This will be derived in Section 2, using a kinematic approach to the deposition process developed in joint work with *Paul Meakin* [14]. In Section 3 some consequences of equation (2) are explored in relation to computer simulations and experiments.

2 Kinematic theory

The starting point of the theory is an expression for the growth rate of the obliquely deposited film. Let J denote the deposition flux, defined as the number of atoms passing through a unit area perpendicular to the beam in unit time, and let ϱ be the film density, i.e. the number of atoms per unit volume of the film. At typical (low) deposition temperatures, redesorption of material from the film surface can be neglected. The growth rate, measured along the substrate normal, is then given by

$$V(\alpha) = J \cos \alpha/\varrho(\alpha). \tag{3}$$

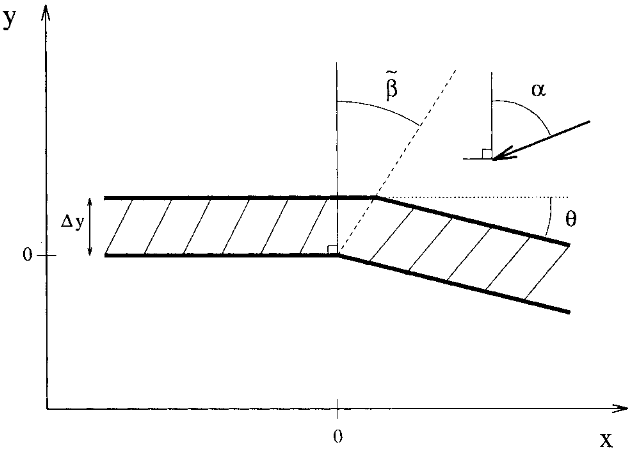

Fig. 2. Surface configuration and coordinate system used in the kinematic argument. The two bold lines show the surface at two subsequent times separated by an increment Δt. The thin tilted lines indicate the column orientation, which differs on the two surface segments. In the limit $\theta \to 0$ the corner angle $\tilde{\beta}$ converges to the columnar growth angle.

Abb. 2. Oberflächenkonfiguration und Koordinatensystem für die kinematische Ableitung von Gleichung (2). Die zwei starken Linien zeigen die Position der Oberfläche zu zwei Zeitpunkten, welche um ein kleines Inkrement Δt getrennt sind. Die schrägen dünnen Linien deuten die (auf den beiden Segmenten der Oberfläche unterschiedliche) Säulenorientierung an. Im Grenzfall $\theta \to 0$ konvergiert der vom Knickpunkt beschriebene Winkel $\tilde{\beta}$ gegen den Säulenwinkel β.

The geometric factor $\cos \alpha$ accounts for the fact that the incident flux per unit area of the film surface is only $J \cos \alpha$.

To extract the columnar growth angle from the expression (3), consider the situation depicted in *Fig. 2,* where a slightly inclined surface segment meets a flat segment at a sharp edge. The deposition angle on the inclined part of the surface is reduced by the inclination angle θ to $\alpha - \theta$, and consequently the column orientation differs from that on the flat surface. The strategy will be to observe the evolution of this surface configuration during a small time increment Δt, and to follow the position of the edge where the two surface segments meet.

We choose our coordinate system such that the initial position of the edge is at the horizontal coordinate $x = 0$, and the flat portion of the surface initially coincides with the x-axis, $y = 0$ for $x < 0$. The equation for the inclined piece is then $y = -x \tan \theta$, $x > 0$ (see Fig. 2). After a time Δt, the flat segment has moved vertically by an amount

$$\Delta y = V(\alpha)\Delta t, \tag{4}$$

while the new position of the inclined surface segment is described by the equation

$$y(x) = \frac{V(\alpha - \theta)}{\cos \theta} \Delta t - x \tan \theta. \tag{5}$$

The factor $1/\cos \theta$ in the first term on the right hand side arises because here the growth is measured along the y-axis, rather than along the surface normal. The new horizontal position Δx of the edge follows from setting (5) equal to (4), $y(\Delta x) = \Delta y$. The trajectory described by the edge position in the (x,y)-plane (marked by the dashed line in Fig. 2) forms an angle $\tilde{\beta}$ with the y-axis which is given by

$$\tan \tilde{\beta} = \frac{\Delta x}{\Delta y} = \frac{V(\alpha - \theta)/\cos \theta - V(\alpha)}{V(\alpha) \tan \theta}. \tag{6}$$

It is evident from Fig. 2 that $\tilde{\beta}$ converges to $\beta(\alpha)$ in the limit $\theta \to 0$, when the edge disappears and we are left with a flat surface grown at a unique deposition angle α. Taking the limit $\theta \to 0$ in equation (6) yields

$$\tan \beta = - V'(\alpha)/V(\alpha), \tag{7}$$

from which the main result (2) follows by using the expression (3) for the growth rate.

3 Discussion

It is well established experimentally that the density of vapor-deposited films is a decreasing function of the deposition angle [5, 15]. The reason is quite obvious: Increasing the deposition angle increases the range of shadowing from surface protrusions, which in turn leads to a larger porosity. An immediate consequence of the general relation (2) is then that, because $\varrho' < 0$, the growth angle β is always less than the deposition angle α; the columns are tilted towards the substrate normal, as is universally observed in the experiments.

However, the available experimental information on the angular dependence of the film density $\varrho(\alpha)$ is not sufficiently detailed to allow for a quantitative test of equation (2). For this purpose we now turn to computer simulations of thin film deposition. In the most basic ballistic deposition model [1, 10, 16, 17], devised to describe deposition under conditions of low temperature and negligible adatom mobility, disk-shaped (in two dimensions) or spherical (in three dimensions) particles are deposited sequentially along straight-line trajectories of fixed slope and randomly chosen starting points. The particles are permanently and irreversibly incorporated into the growing film at the point of first contact with the deposit. While the lack of post-deposition relaxation in this model leads to unrealistically low densities, the simplicity of the deposition algorithm allows very large, semi-macroscopic structures, consisting of more than 10^8 particles, to be generated. An example of the kind of structures generated by the deposition of disks in two dimensions is shown in *Fig. 3.*

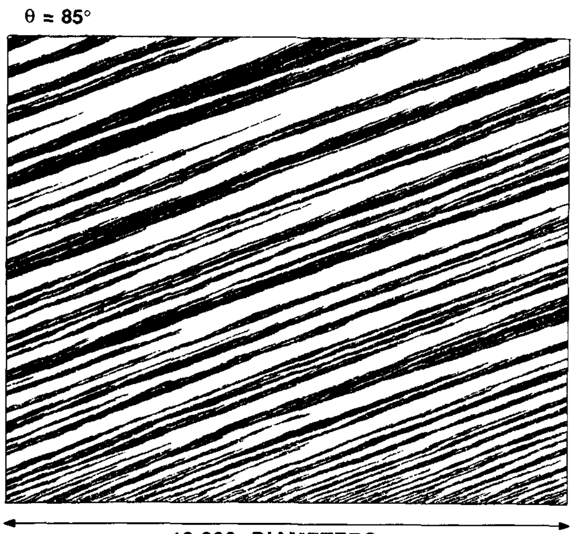

Fig. 3. Part of a large two-dimensional deposit grown by ballistic deposition of disks, at an angle of incidence $\alpha = 85°$. The horizontal extent corresponds to 10 000 disk diameters. Note the well-defined common columnar growth angle, and the wide distribution of column sizes (see [14]). By courtesy of P. Meakin.

Abb. 3. Teil einer durch ballistische Abscheidung von Scheiben erzeugten, zweidimensionalen Schicht. Der Einfallswinkel beträgt 85°, die horizontale Ausdehnung des gezeigten Ausschnittes entspricht 10 000 Scheibendurchmessern. Man beachte die wohldefinierte Orientierung der Säulen, und die breite Verteilung ihrer Größen (s. auch [14]). Mit freundlicher Genehmigung von P. Meakin.

In his extensive study of ballistic deposition at oblique incidence, Meakin [10] observed that the relationship between the angle of growth and the angle of deposition is well described by a linear equation

$$\beta = c\alpha, \tag{8}$$

where the constant $c \approx 0.78$ in the case of disks (two dimensions) and $c \approx 0.73$ in the case of spheres (three dimensions). The linear relationship (8) has also been found in some experiments [4], and in other cases it seems to provide at least a reasonable first approximation to the experimental results [7]. Meakin's numerical data are shown in *Fig. 4.*

Assuming that the relation (8) is valid, equation (2) may be used as a differential equation determining the angular dependence of the film density $\varrho(\alpha)$. The general solution is

$$\varrho(\alpha) = \varrho(0) \cos\alpha \exp\left[\int_0^\alpha d\phi \tan\beta(\phi)\right], \tag{9}$$

and specializing to the linear relation (8) yields

$$\varrho(\alpha) = \varrho(0) \frac{\cos\alpha}{(\cos c\alpha)^{1/c}} . \tag{10}$$

Simple limiting cases of this expression are $c = 0$, corresponding to growth in the direction of the surface normal ($\beta = 0$, $\varrho = \varrho(0)\cos\alpha$), and $c = 1$, corresponding to growth in the direction of the deposition beam ($\beta = \alpha$). In the latter case $\varrho(\alpha) \equiv \varrho(0)$, and there is no self-shadowing. It should also be noted that the tangent rule (1), inserted into the general solution (9), gives the relation

$$\varrho(\alpha) = \varrho(0) \sqrt{\cos\alpha} \tag{11}$$

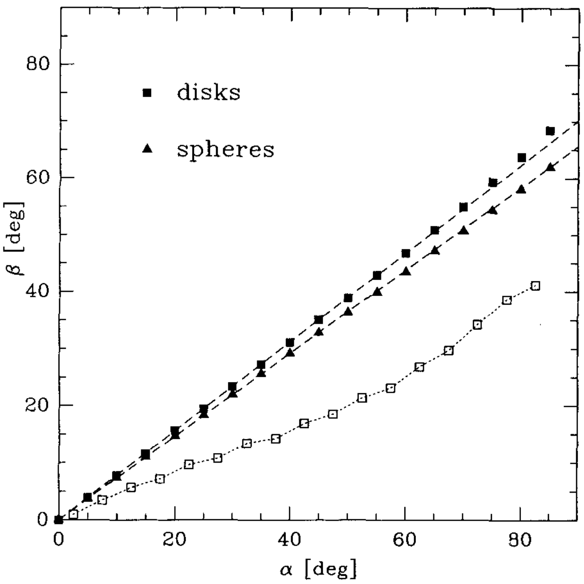

Fig. 4. Numerical estimates of the columnar growth angle obtained from ballistic deposition simulations. Full symbols show Meakin's [10] results for the deposition of disks (squares) and spheres (triangles). The dashed lines are fits to the linear relation (8). The open squares show the columnar growth angle for a two-dimensional ballistic deposition model with limited post-deposition mobility, calculated from equation (2) using the density estimates of Meakin and Jullien [16].

Abb. 4. Numerische Ergebnisse für den Wachstumswinkel aus Simulationen der ballistischen Abscheidung. Die gefüllten Symbole zeigen Meakin's [10] Daten für die Abscheidung von Scheiben (Quadrate) und Kugeln (Dreiecke). Die gestrichelten Linien sind Ausgleichsgeraden, der linearen Beziehung (8) entsprechend. Die offenen Quadrate zeigen den Wachstumswinkel für zweidimensionale ballistische Abscheidung mit begrenzter Beweglichkeit der aufgedampften Teilchen. Diese Daten wurden mit Hilfe der Beziehung (2) aus der numerisch bestimmten Schichtdichte [16] berechnet.

for the density. This is fundamentally different from equation (10), in that it approaches zero with an infinite, rather than a finite derivative at grazing incidence, $\alpha = 90°$.

In *Fig. 5* equation (10) is compared to the numerical estimates for the angular dependence of the film density obtained by *Meakin* and *Jullien* [16, 17]. Here the density is defined as the volume fraction filled by the particles. The functional form (10), with the parameter c determined from the independent measurement of the columnar growth angle, is seen to provide an excellent description of the data both in two and three dimensions, thus lending strong support to the validity of equation (2).

Meakin and Jullien [16] also explored a modification of the basic two-dimensional ballistic deposition model, which includes a limited amount of post-deposition mobility. In this model the deposited disk moves along the surface of the deposit until it finds a "pocket" where it can attach to two adjacent disks. The modification dramatically increases the density at normal incidence, from 0.3568 to 0.7229 (the largest density that can be achieved in two dimensions is that of a hexagonal crystal, $\varrho = \pi/(2\sqrt{3}) \approx 0.9069$). Numerical data for the growth angle are not available for this model, however the angular dependence of the density is known to sufficiently high accuracy [16] to allow for the calculation of the growth angle from equation (2). The result is represented by the open squares in Fig. 4. It shows that (i) the dependence of β on α in not well represented by the linear relation (8) in this case, and (ii) the growth angle is considerably smaller (that is, the columns grow closer to the substrate normal) than in the absence of relaxation. It remains to be seen whether any general conclusions, regarding for example the temperature dependence of β in real films, can be drawn from this observation.

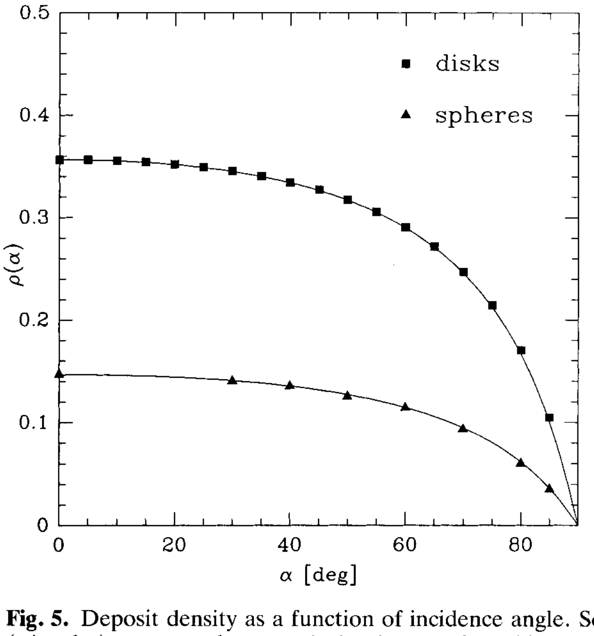

Fig. 5. Deposit density as a function of incidence angle. Squares (triangles) represent the numerical estimates of Meakin and Jullien [16, 17] for the ballistic deposition of disks (spheres). The full lines show the angular dependence predicted by equation (10), with $c = 0.78$ for the case of disks, and $c = 0.73$ for the spheres.

Abb. 5. Dichte der aufgedampften Schicht als Funktion des Einfallswinkels. Die Quadrate (Dreiecke) zeigen die numerischen Daten von Meakin und Jullien [16, 17] für die ballistische Abscheidung von Scheiben (Kugeln). Die durchgezogenen Linien stellen die Winkelabhängigkeit (10) dar, mit c = 0,78 (Scheiben) bzw. c = 0,73 (Kugeln).

4 Conclusion

In this paper a simple theory of oblique incidence ballistic deposition has been proposed, which relates the dependence of the columnar growth angle on the deposition angle to that of the deposit density. The result, equation (2), compares favorably with data taken from computer simulations of ballistic deposition. Since both the columnar growth angle and the film density are routinely measured as part of the characterization of vapor deposited thin films, it should be straightforward in principle to subject equation (2) to an experimental test. This would be useful in clarifying to what extent the kinematic picture of thin film evolution used in the derivation in Section 2 is valid in reality.

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