Continuum model for nanocolumn growth during oblique angle deposition

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A continuum equation for the shadowing growth of individual nanostructures by oblique angle deposition is proposed and numerically integrated. The radius \( R \) of rotationally symmetric columns is calculated as a function of height \( z \). Before the radius \( R \) saturates at its final value \( R_{\text{sat}} \), column shapes obey the power law \( R \sim z^p \) with the exponent value \( p \approx 0.37 \pm 0.02 \). The results are compared to those of an experimental study of Si columns grown on a template \( (p \approx 0.39 \pm 0.03) \), and on a flat surface \( (p \approx 0.32 \pm 0.01) \). The model additionally predicts that the saturated radius should depend on column separation \( d \) as \( R_{\text{sat}} \sim d^{1.20 \pm 0.01} \). This relation implies that the gap between the surfaces of adjacent columns can be optimized by altering the column separation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1687033]

I. INTRODUCTION

Recently, researchers have shown that it is possible to grow many three-dimensional nanostructures on a surface by an oblique angle deposition technique with substrate rotation, also known as glancing angle deposition.1–3 Understanding the growth of these nanostructured thin films is of great interest both practically and from a more fundamental scientific perspective. Physically, the shape of nanostructures could give insight into their growth mechanism, which may, in turn, allow the shapes and sizes of structures to be better engineered. It is, therefore, beneficial to determine just how the geometry of this deposition process produces and controls the shape of the nanostructures. Possible applications of nanostructured thin films include photonic crystals, biosensors, field emitters, nanoelectromechanical systems, and microelectronics.

Oblique angle deposition refers to the process of shooting particles at a rotating substrate at an angle \( \theta \) (measured from the substrate normal; see Fig. 1) close to 90°. Characteristic of this method of deposition is the phenomenon of shadowing: incident particles preferentially deposit on taller structures, leading to the formation of discrete structures. By rotating the substrate in various ways, these structures have been grown into various shapes, such as springs and vertical columns.1–3 While a substantial amount of simulation work has quantitatively described oblique angle deposition without substrate rotation,4–9 very little work has been reported, mostly qualitative in nature, for the case of oblique angle deposition with substrate rotation.10–16 The detailed mechanisms and parameters that affect the growth are not well understood.

The simplest nanostructures formed by oblique angle deposition with substrate rotation, and those to be modeled in this article, are columns. They may be allowed to grow from sites of random nucleation, or from a template, which provides initial “seeds” on the substrate where columns start to grow. Figure 2 shows a scanning electron micrograph (SEM) of nanocolumns grown atop a template.

In the present study, a continuum equation is proposed to describe the growth of isolated nanocolumns during oblique angle deposition with substrate rotation. The model allows for overhang, but requires that columns be rotationally symmetric. The resulting columnar shapes agree with experimentally obtained columns grown both from a template (which, in practice, fixes the lattice positions of the structures, as in Fig. 2) and from a flat surface. In addition, many applications call for well-separated columns. The simulations in this work provide insight into how to optimize the gap between the adjacent columns.

II. CONTINUUM EQUATION AND ASSUMPTIONS

We make the following simplifying assumptions in the model, and hope to yield insight into the basic physics at work. Columns are assumed to be rotationally symmetric, identical, and periodically spaced. In practice, circular symmetry cannot be present exactly, especially with regard to the overall placement of columns on a substrate. We expect, however, that columns should be rotationally symmetric on average, because the substrate is rotated during deposition. Periodic separation may be intentionally obtained in experiment by growing columns on a template although, for growth on a flat surface, a characteristic separation has been demonstrated to exist.17 Finally, we assume that the flux of incoming material is continuous and even.

The above assumptions allow us to model column radius as a continuous single-valued function of height. As shown in Fig. 3(a), we set the \( z \) axis as the column height, which is an independent variable, and the \( x \) axis as the column radius, a dependent variable. Figure 3(b) shows the three-dimensional interpretation of this curve. The continuum equation governing the growth is

\[
\frac{\partial R}{\partial t} = F \cdot g \cdot \sqrt{1 + (\nabla R)^2} + \eta(z,t),
\]
where \( F \) is the flux of material (in units of length/number of iterations), \( R \) is the column radius (as a function of column height, \( z \), and time, \( t \)), and the noise term \( \eta(z, t) \) ensures that the resulting column shape is not an artifact of perfect functional form. \( g \) is a shadowing function, equals 0 at positions along the column that are shadowed from the flux of incoming particles, and 1 elsewhere, according to

\[
g = 0 \quad \text{if} \quad \frac{d - R(z') - R(z)}{z' - z} \leq \tan \theta
\]

or

\[
R(z') - R(z) \geq \frac{\tan \theta}{z' - z}.
\]

Here, \( \theta \) is the angle of incidence of the beam, measured from the surface normal (see Fig. 1) and \( d \) is the column-to-column separation. The value of \( g \) is computed for each \( z \) value by scanning the entire column to see whether the desired surface point falls in the geometric shadow of any other point \( z' \) on the same column, or a neighboring (identical) column. The form of Eq. (2) is purely geometric. In addition to growing outward according to Eq. (1), each column grows taller at a rate \( dz_{\text{max}}/dt = F \), where \( z_{\text{max}} \) represents the height of the column at time \( t \).

The square-root term in Eq. (1) provides for growth normal to the local surface (see the discussion in Ref. 3). For rotationally symmetric columns, the gradient term has the same magnitude, \( |\nabla R| = \partial R/\partial z \), whether in \((1+1)\) or \((2+1)\) dimensions. With this rotational symmetry, the \((1+1)\)-dimensional equation therefore describes a \((2+1)\)-dimensional growth of columns. Although other recent continuum models\(^{18,19}\) have been used to describe the shadowing effect that occurs during conventional deposition techniques, such as sputter deposition and chemical vapor deposition (not oblique angle deposition), the present model differs because it, allows for overhang in height values. Our model defines column radius as a function of height, allowing multiple height points to have the same radius, which can result in the overhang structure. Therefore, columns may be wider at the top than the bottom, as seen experimentally. However, in previous models, height is a function of lateral position, and can only take on single values.

### III. Numerical Calculations and Analysis

To obtain \( R(z, t) \), a code numerically integrates Eq. (1) and simultaneously increases the height of the column according to \( dz_{\text{max}}/dt = F \). Input parameters include an initial seed shape of the column, the column separation \( d \), flux term \( F \), incident angle \( \theta \), and number of iterations.

We find that numerical solutions resemble columns only under large \( \theta \) and small \( d \). This makes sense physically because the shadowing has the greatest effect under these conditions. Figure 4 shows how simulated columns grow in time. The “growth front” (defined in Fig. 4) is the only actively growing part of the column; all other surfaces are
shadowed. Since growth occurs normal to the local surface, the shape of the growth front is determined at short times by the shape of the initial seed. The sharp corner between the growth front and the outer surface is perhaps unphysical, and may be explained by the absence of any smoothening forces in this model. In general, the width increases rapidly before “saturating” at some final radius \( R_{\text{sat}} \) (saturation is not shown in Fig. 4). The exact value of \( R_{\text{sat}} \) depends not only on the parameters \( d, \theta \), and \( F \), but also on an internal parameter of the code: The spacing \( \Delta z \) of height points used to define the function \( R(z) \).

First, the effect of the noise term \( \eta \) [from Eq. (1)] may be examined. Our code implements the noise term as \( \eta = F_1 \cdot \text{rand}(z,t) \), where the function \text{rand} generates a random number in the interval \((-0.5,0.5)\) at each different \( z \) and \( t \). Varying the noise strength \( F_1 \) causes no change to the overall shape of the column, although increasing \( F_1 \) increases the surface roughness of column sides. This only holds, however, for \( F_1 \) below a critical value that depends on the column separation, initial seed shape, and the flux term \( F \); above this value, recognizable columns do not grow.

In the following sections, we examine the shape of the numerically generated columns, and the way it changes with column separation. First, we shall examine the region of the column where the radius increases rapidly, according to a power law. Next, the dependence of \( R_{\text{sat}} \) on \( d \) is analyzed, followed by a similar investigation into the width of the gap between columns. Finally, other factors that may affect the column shape, such as the initial seed shape, will be mentioned.

**A. Growth exponent \( p \) for column radius**

One way to characterize the shape of the structures is to assume that, initially (i.e., before saturation), the radius obeys the power-law function

\[
R = k z^p, \quad (3)
\]

where \( k \) is constant and \( p \) is the growth exponent. The reason for this choice, besides the visual quality of the fit, is the scaling prediction\(^50\) that the radius of columns grown from a flat surface will obey \( R \sim z^p \). However, the whole curve does not obey this functional form; the region of the numerical solution to be fit to Eq. (3) is determined as follows. First, \( R \) as a function of \( z \) is plotted in log–log scale so that we can extract the exponent \( p \) from the measured slope. The lower bound is taken as close as possible to the height of the initial seed (we do not include the crossover regime close to the initial seed height which has an undefined \( p \) value). Since solutions with different \( \Delta z \) saturate at different \( R_{\text{sat}} \), it follows that they must diverge above some value of \( z \). This value is taken as the upper bound. Within these limits, we obtain \( p \) from the slope of \( R(z) \) in the log–log plot.

Figure 5 shows column profiles grown from a spherical seed of radius 20 units with different column separations. The initial growth regions (indicated by the arrows) are fit to Eq. (3). When the column separations are very small, columns quickly saturate and the measurement of \( p \) becomes irrelevant (e.g., \( d = 50 \) plot in Fig. 5). Figure 6 plots the growth exponent \( p \) versus column separation \( d \) for columns grown as in Fig. 5. For column separations greater than 250, the numerical solutions did not resemble columns. In these cases, the gaps between columns quickly appeared to fill completely with material; one might say that the columns “grew together.” As can be realized in Fig. 6, \( p \) does not change significantly with \( d \). By averaging the measured \( p \) values in Fig. 6, we obtain an approximate growth exponent value \( p \sim 0.37 \pm 0.02 \).

**B. Saturation radius**

The model may also be used to determine the dependence of the column radius at saturation \( R_{\text{sat}} \) on column separation, \( d \). Figure 7 plots \( R_{\text{sat}} \) versus \( d \) on a logarithmic scale.
scale. Each data point represents a separate numerical solution; all parameters besides $d$ were held constant. The plot shows that 

$$R_{\text{sat}} = b \cdot d^q,$$

where $q = 1.20 \pm 0.01$ (valid for $\theta = 85^\circ$), and the constant $b$ is determined by $\Delta z$, $\theta$, and $F$. Although $R_{\text{sat}}$ depends on the internal parameter $\Delta z$, the spacing of points used to define the function $R(z)$, changing $\Delta z$ causes $R_{\text{sat}}$ to shift only by a multiplicative constant; the exponent $q$ remains unchanged.

It is clearly impossible for this relation to hold up to an arbitrarily large $d$, because the radius is physically limited by the column separation itself, i.e., $R_{\text{sat}} < d/2$. Figure 7 spans the entire range of $d$ for which our model produced recognizable columns, and the power law appears to hold for these values.

C. Gap between adjacent column surfaces

One implication of Eq. (4) is that the gap between adjacent column surfaces at saturation, represented as $S$ (see Fig. 1), may be maximized with respect to $d$. Figure 8 plots the values of $S$ from numerical solutions with different $d$ and shows that indeed a maximum $S$ exists. If the surface–surface gap between columns is defined as $S = d - 2R_{\text{sat}}$, then, the optimal $d$ value can be found by setting the derivative $\partial S/\partial d = 0$ and solving for $d$. The single solution $d_o = (2bq)^{1/q}$ does, however, require the knowledge of the constant $b$, which needs to be determined from experiment.

The gap between columns may be an important parameter when engineering nanostructured thin films. For some applications, such as biosensors, the efficacy of the film could depend on whether certain molecules may fit between adjacent nanocolumns. The magnitude of the gap $S$ varies by only about 8 units for a range of column separations up to 300 units in the numerical solutions here. This would scale to a variation in $S$ of about 30 nm in experiments where the templated column separation may have values up to 1000 nm. It is likely, however, that the value of $b$ in experiments would be quite different from simulations, so we can say very little about how advantageous it might be to maximize $S$ by varying $d$ in experimental situations.

D. Initial seed shape

The initial seed shape determines the shape of the growth front at later times through normal surface growth, while the geometry of the growth front and column separation determines precisely where neighboring columns are shadowed. As a rule of thumb, the flatter the growth front of the initial seed, the wider the column. Figure 9 shows the profiles of columns grown from various initial shapes (cone, paraboloid, sphere, and cylinder), at a single column separation of $d = 200$ units. Although the final size of columns is
different for different seed shapes, the value of \( p \) remains within the range of roughly \( p \approx 0.34-0.40 \), an average value of \( p \approx 0.37 \).

**IV. EXPERIMENTAL OF NANOCOLUMNS GROWTH BY OBLIQUE ANGLE DEPOSITION**

The setup of our oblique angle deposition system was described in Ref. 20 and is briefly mentioned here. The deposition chamber was evacuated to a high vacuum level (\(<2 \times 10^{-3} \) Pa) by a diffusion pump. The vapor source was positioned \( \sim 32 \) cm away from the substrate such that the gradient of incident flux could be ignored across the whole substrate. The silicon (99.9995%, from Alfa Aesar) inside a graphite crucible was evaporated by electron-beam bombardment method. The deposition vapor flux was incident onto the rotating substrate tilted at an angle \( \theta=85^\circ \). The substrate was a tungsten plug of a square symmetry template with a characterization of \( p \) within the range of roughly \( p \approx 0.34-0.40 \), an average value of \( p \approx 0.37 \).

A comparison of numerical calculations with experimentally grown columns shows that our numerical solutions display, at least qualitatively, the same behavior as actual nanocolumns (see Fig. 2) grown with oblique angle deposition. We attempt to make a more quantitative comparison between column shape and numerical solution, by comparing the exponent \( p \) for two cases, a patterned substrate and a flat substrate.

Because it is assumed that column separation \( d \) remains constant in time, the model employed here seems best to apply to structures grown from a template, which serves to fix the lattice positions of the columns. SEM images of Si nanocolumns grown on templates with four different column separations \( d = 550, 600, 700, \) and 1000 nm were examined, and the radius as a function of height was recorded for approximately six columns per sample. The resulting data were plotted in log–log scale, and by using the method described in Sec. III A, we attempted to obtain \( p \) from the measured slope values. However, except for the largest column separation \( d=1000 \) nm, columns grown on smaller \( d \) quickly reached the saturation point. This resulted in limited data points of power-law regime and, therefore, undefined \( p \) values. For columns grown at \( d=1000 \) nm (see Fig. 10 for an example column radius plot), we measured the experimental exponent \( p \approx 0.39 \pm 0.02 \), which is close to the simulated value of \( \sim 0.37 \pm 0.02 \).

The geometry of growth from a flat surface differs from columns grown from a template, as the flat surface lacks the well-defined column separation. In the growth from a flat surface, nucleation occurs randomly, so that there is a spread of column separations present at any time. However, since the exponent \( p \) should not depend on column separation (as predicted from Fig. 6), we can compare our simulation results to the experimental columns grown on flat surfaces. Previously, Karabacak et al.20 examined the shape of nanocolumns of various materials (Si, Co, Cu, and W) grown by oblique angle deposition on a flat surface, and found that the diameter obeys \( W \sim z^p \), with \( p \approx 0.28-0.34 \), where \( W = 2R \). For silicon, they obtained \( p = 0.32 \pm 0.01 \). The experimental results are slightly lower than the predicted exponent value of \( \sim 0.37 \pm 0.02 \) from simulations.

**V. CONCLUSION**

Numerical solutions of the continuum growth Eq. (1) for shadowing growth by oblique angle deposition have been presented. The solutions are rotationally symmetric columns that grow with radius \( R \sim z^p \) before saturating at some final \( R_{sat} \sim d^\delta \), and appear qualitatively similar to experimentally grown nanocolumns. Numerical value of \( p \approx 0.37 \pm 0.02 \) agree well with the experimental value \( p \approx 0.39 \pm 0.03 \) obtained for templated Si nanocolumns.

The agreement between numerical solutions of Eq. (1) and the shape of columns grown by oblique angle deposition indicate that, to a good approximation, a material can be treated as continuous with the growth local to the normal surface. Furthermore, the model presented here predicts that there is a maximum gap that may be achieved between adjacent column surfaces; this spacing does not continue to...
grow as the column separation is increased. If experimentally verified, this prediction could allow us to optimize the separation between the surfaces of adjacent columns, simply by changing $d$. The power-law behavior of Eq. (4) may also be used to easily estimate film properties, such as surface area and density. Similarly, the model may be used to relate $R_{\text{sat}}$ to other parameters such as $\theta$ and $F$.

Artifacts in the shape of the simulated columns, such as the sharp corner between the growth front and the outer surface seen in Fig. 4 that are not seen experimentally, indicate, however, that other non-negligible forces must be at work. These may include, for example, surface diffusion, marked departures from the symmetry of this model, an angular spread in incident flux, or an incident atom sticking probability not equal to 1.

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1 For a review, see for example, M. Malac, R. Egerton, and M. Brett, Vac. Technol. Coat. 2, 48 (2001).