13.1 Introduction

Oblique angle deposition has been of interest to the thin film community for more than 100 years owing to enhancement of properties such as dichroism, birefringence, and anisotropic resistivity [1–4]. The film microstructure which produces these novel properties and
Glancing angle deposition (GLAD) is an extension to oblique angle deposition where the substrate position is manipulated during film deposition. Although some early experiments used mobile substrates [5], oblique depositions are typically performed with a fixed substrate. GLAD developed as researchers realized they could manipulate the columnar structure by actively managing substrate position during deposition. Structures produced by GLAD have steadily improved in sophistication and quality as seen in Figure 13.1; modern GLAD implementations require real-time feedback and computer control of substrate position. Applications already demonstrated and those under investigation include:

- active and passive optical devices using numerous materials, providing design flexibility and creating characteristics useful in retarding elements, circular polarizers and polarized light emitters, among others;
- sensor devices (pressure sensors, optical resonators, humidity sensors, nanomotors);
- energy devices (electrochemical supercapacitors, microbattery charge storage, fuel cells, solar energy conversion).

Although GLAD has seen some impressive developments over the past 15 years, there is an extremely large parameter space available and the true complexity is not yet well understood. Empirical studies are far ahead of theoretical ones, because the key advantage of GLAD films – simultaneous control of multiple size scales – makes theoretical studies of GLAD films a challenge. Today, the dominant applications reflect large-scale effects; for example, optical properties are well understood. Even mid-range effects, such as surface area and mechanical properties, can be addressed experimentally and rest on reasonably developed theoretical models. Nanoscale applications, on the other hand, have been constrained by current limits on
simulation size; as a better understanding of GLAD’s nanoscale physics develops, exciting new applications of GLAD films are anticipated.

Readers interested in the technique’s historical development are referred to the patents [6–8], reviews [9–12], and a book [13] which cover GLAD. This chapter focuses on experimental aspects of the GLAD technique – its methods and possibilities. Section 13.2 introduces the basic theory, and describes the canonical microstructures and apparatus required to produce GLAD films; Section 13.3 describes advanced GLAD techniques, covering procedures which occur before, during, and after a GLAD process; Section 13.4 discusses the properties of GLAD films at several length scales: single column properties, the properties of an ensemble of columns, and the ‘bulk’ properties of a GLAD film; and Section 13.5 reviews applications and devices made with GLAD films.

13.2 Theory, Structures and Apparatus

This section defines important terms that are used in the GLAD field to describe substrate position, geometric aspects of GLAD apparatus, film properties, and characteristic column morphologies. The first use and definition of such terms are indicated in italic. We note that some of the symbols used to represent the terms defined here are not used universally in the GLAD field, so some care must be exercised when examining the literature.

13.2.1 GLAD Theory

13.2.1.1 Incident Vapor Collimation

Ballistic shadowing is the foundation of GLAD-based thin film engineering. Such shadowing is only possible if the incoming vapor flux is well collimated. If there is a large angular spread in incoming vapor flux, shadows will be poorly defined. Two main approaches achieve collimated vapor flux: large distance between vapor source and substrate, and physical obstacles which select a subset of an uncollimated vapor plume. For a fixed substrate size, as distance from the source increases, incident vapor collimation improves. However, the number of collisions also increases the farther the vapor flux travels before reaching the substrate. To fabricate high-quality structures, the vapor mean free path should be larger than the source–substrate distance. This is easily achieved with electron-beam evaporation systems, widely used for GLAD depositions.

However, some materials are not suited to electron-beam or other evaporation methods. Techniques such as sputtering may be used, but at the cost of a wider angular distribution due to large target size and scattering from the working gas. In such cases, a physical screen which selects a subset of incident flux can restore collimation [14]. If even higher pressures must be used, alternative deposition techniques can maintain GLAD conditions. Sun et al. demonstrated reactive-pulsed-laser deposition of GLAD ZnO films at 0.1 torr, approximately
three orders of magnitude above typical electron beam pressures [15, 16]. GLAD was still possible at such high pressures owing to an extremely oblique vapor flux, and a laser focal spot of \( \sim 3 \text{ mm}^2 \) which produces a very small angular distribution.

### 13.2.1.2 Film Nucleation and Column Growth

The previous chapter detailed film nucleation, growth, and microstructure evolution. Here we discuss only aspects of film nucleation that are important for producing GLAD thin films. During oblique deposition at an angle \( \alpha \), defined in Figure 13.2(a), any surface topology is amplified by ballistic shadowing. A nominally planar substrate will roughen through Volmer–Weber mode growth; any defects in the substrate will accelerate roughening [17]. This initial stage of GLAD film growth is given schematically in Figure 13.2(a).

The arrival of vapor flux and formation of film nuclei is a random process. The nuclei grow into columns, seen in Figure 13.2(b), and develop shadows. The columns and shadows they cast will have a size distribution. As a result, some nuclei will screen neighboring nuclei from incoming vapor flux, suppressing their growth (Figure 13.2c). Given sufficient time, smaller nuclei and columns can become completely shadowed and stop growing. This process, referred to as column extinction and seen schematically in Figure 13.2(d), continues throughout the growth of a GLAD film.

![Figure 13.2: Schematic view of GLAD growth](image-url)

**Figure 13.2**: Schematic view of GLAD growth: (a) initial arrival of vapor flux at an angle \( \alpha \), producing a random distribution of nuclei on substrate surface; (b) nuclei grow, casting shadows across substrate; (c) columns develop, partially shadowing smaller neighbors and suppressing their growth; (d) columns grow at an inclined angle. Some columns have become extinct, fully shadowed by larger neighbors. Further growth is restricted to the top of columns.
As the nuclei grow, more incoming vapor flux will deposit on them. This self-reinforcing behavior develops isolated columns, provided that adatom surface mobility is low. Thus, GLAD principally occurs in zone I of Movchan and Demchishin’s structure zone model [18], where $T_{\text{substrate}} \lesssim 0.3T_{\text{melting}}$ limits surface diffusion, leading to the formation of columnar grains. Eventually, only the top of nuclei are able to grow, developing into columns tilted towards the vapor source. Column tilt angle is described by a single angle, $\beta$, shown in Figure 13.2(d). When a column is parallel with the substrate normal, $\beta = 0^\circ$, and would be $= 90^\circ$ for a column parallel with the substrate surface. For some of the GLAD structures described in Section 13.2.2, it is possible to exhibit multiple values for $\beta$. Section 13.2.1.3 gives a detailed discussion of the variables affecting column tilt angle.

### 13.2.1.3 Column Tilt Angle

It has long been known that column tilt angle in oblique depositions does not fully follow the incidence angle of vapor flux. Various rules have been proposed to describe this behavior, but the experimental data reveal a dependence that cannot be described by a single relationship. The growth of GLAD columns depends on shadowing between columns, deposition temperature, deposition rate, deposition pressure, vacuum composition, substrate type, substrate preparation, and preferred crystallinity of the deposited material. Under these conditions, the general relationships known as the tangent rule and Tait’s rule must be understood as guidelines only. For applications in which precise column tilt angle is important, these rules should be verified for any material system that has not been studied in the literature.

The tangent rule was one of the early attempts to describe the experimental data by Nieuwenhuizen and Haanstra [19], who proposed the relationship

$$\tan \alpha = 2 \tan \beta$$

(13.1)

Hodgkinson et al. generalized the tangent rule, adding a fitting parameter that could be used to describe differences in material tilt angles [20]. However, as the deposition angle becomes increasingly oblique, the tangent rule fails to describe experimental data. Using a ballistic model for columnar growth, Tait et al. derived the following relationship [21]:

$$\beta = \alpha - \arcsin \left( \frac{1 - \cos \alpha}{2} \right)$$

(13.2)

Although these rules can successfully provide a first order approximation of the expected behavior of $\beta$, the actual behavior of GLAD films can be perturbed from these relationships by several factors. Increased temperature has been shown to reduce $\beta$ [22, 23], although non-monotonic behavior has also been observed [24]. Increased deposition rate has been shown to increase $\beta$ for Fe thin films [25, 26], as has decreasing chamber pressure [25, 27]. Data from Lintymer et al. suggest that the effect of chamber pressure is more pronounced at
higher $\alpha$ [27]. Differences between materials are observed [20], and different crystalline phases of a single material can have a significant effect [26]. The interaction between substrate and deposited film can also have an impact, and must be determined on a case-by-case basis [24]. Finally, some advanced GLAD substrate motion control techniques can decrease $\beta$ in a controlled manner (see Section 13.3.2.1) and limited increases can be achieved through techniques such as ion-assisted GLAD (see Section 13.3.2.4).

13.2.1.4 Film Density

As part of Tait’s geometric model for column growth, an expression for GLAD film density was derived [21]. Density is expressed in terms of $\rho_0$, the density of a film deposited at $\alpha = 0^\circ$, and may be written as

$$\rho = \rho_0 \frac{2\cos\alpha}{1 + \cos\alpha}$$

(13.3)

Once again, this relationship can successfully provide a first order approximation of $\rho$, but the same caveats expressed in Section 13.2.1.3 about the tangent and Tait’s rule also apply here. Exceptions to this relationship are known to exist, and for applications sensitive to small variations in density this equation must be verified.

13.2.2 Basic GLAD Structures

Substrate orientation is described in terms of two angles, defined in Figure 13.3. The deposition angle, $\alpha$, defines the incidence angle of vapor flux: an $\alpha$ of $0^\circ$ occurs when the substrate normal is pointed directly at the source; an $\alpha$ of $90^\circ$ occurs when the substrate normal is perpendicular to a line between the center of the substrate and the center of the vapor source. The substrate rotation angle, $\phi$, defines the azimuthal substrate position relative to an arbitrary starting position. While $\phi$ is periodic, in practice tracking the absolute angular displacement of

![Figure 13.3: Schematic of the substrate coordinate system, showing the angle $\alpha$, $\phi$, and $\gamma$. The incident vapor vector and substrate normal define the deposition plane.](image)
a substrate is useful. In this chapter, substrate positions will be described using an ordered pair notation: \((\alpha, \phi)\). For some advanced techniques, it is useful to define an offset angle, \(\gamma\), describing a temporary deviation from \(\phi\). This angle will be recorded separately: \((\alpha, \phi + \gamma)\).

Analogous to optics, we define deposition plane, defined by the substrate normal and a line connecting the center of the substrate with the center of the vapor source. Shadowing occurs only in the direction parallel to the incident vapor flux. As a result, there is no mechanism for limiting column growth in the transverse direction, leading to column broadening. The columns can continue broadening until they merge with adjacent columns [28]. Some methods discussed in Section 13.3 are designed to minimize the effects of column extinction and broadening.

The basic GLAD structures are shown in Figure 13.4, categorized by the variation of \(\alpha\) and \(\phi\) during deposition. The behavior of both \(\alpha\) and \(\phi\) is broken into three categories: constant, discrete and continuous. A constant designation means that the substrate remains stationary at a given angle during a deposition. A discrete designation means that the substrate undergoes periodic changes in a given angle, but remains stationary otherwise. A continuous designation means the substrate is in motion continuously during a deposition for the specified angle. While most examples of discrete and continuously varying substrate positions are periodic, there is no requirement that periodicity be retained. There are nine possible combinations of \(\alpha\) and \(\beta\) motions, but only six are in common use. The six basic GLAD structures offer a wide selection of film morphologies, each of which is described below. Substrate angular velocities are described in terms of deposited film thickness (measured along substrate normal), and are denoted \(\alpha'\) or \(\phi'\).

**Slanted posts** occur when a substrate is held stationary \(((\alpha, \phi), \alpha' = \phi' = 0)\) during a deposition. For isolated posts, \(\alpha\) is typically above \(\approx 70^\circ\). **Chevrons** are produced by depositing a series of slanted posts. The substrate is held at \((\alpha, \phi)\) for one arm of the chevron, followed by deposition of an additional arm with the substrate held at \((\alpha, \phi + \pi)\). This sequence has been repeated twice for the film shown in Figure 13.4(b). **Square spirals** fall into the same category as chevrons, but with a \(\pi/2\) rotation at discrete intervals.

**Vertical posts** are produced by rotating the substrate at a constant rate during deposition \(((\alpha, \phi(t)), \alpha' = 0, \phi' = k)\). As seen in Figure 13.4(c), vertical posts can experience broadening during growth. The rate of rotation is an important parameter in controlling vertical post morphology [30]. **Helical** thin films can be produced using slower rotation rates.

A **slanted post stack** is produced with discrete changes in both \(\alpha\) and \(\phi\) during deposition, such that the substrate adopts the orientations: \((\alpha_1, \phi_1), (\alpha_2, \phi_2), \text{ etc.}\) For the case pictured in Figure 13.4(d), \(\phi = n\pi\), where \(n\) is layer number.

**High–low stacks** are produced with a continuous rotation in \(\phi\), and discrete changes in \(\alpha\). Such films are well suited for optical applications: the film in Figure 13.4(e) is a Bragg stack. To
produce a Bragg stack, the optical thickness of each layer should be $\lambda/4$. Substrate motion is defined by a repeating sequence: $(\alpha_1, \phi(t)), \phi' = k$; $(\alpha_2, \phi(t)), \phi' = k$.

Rugate filters are produced with a continuous rotation in both $\alpha$ and $\phi$. Substrate motion can be described approximately as $(\alpha(t), \phi(t)), \alpha \approx \text{asin}(t) + \alpha_0, \phi' = k$. The exact functional form of $\alpha$ must be chosen to produce a sinuisodal index profile. The required $\alpha$ profile depends on the optical properties of GLAD films, discussed in Section 13.4.3.1. Capping layers and graded density films are also members of this category.
Figure 13.5: Combination of several structures from Figure 13.4. From bottom to top, this structure is composed of a helix, a one-period chevron, a short vertical post, and finished with another helix. (Reproduced with permission from [31].)

The six basic structures shown in Figure 13.4 can be combined to make very sophisticated structures, as seen in Figure 13.5. From bottom to top, this film was produced by combining a helix, chevron, vertical post, and another helix. Additional modifications to the basic structures described here are the subject of Section 13.3.

### 13.2.3 GLAD Apparatus

A schematic of a GLAD-capable physical vapor deposition (PVD) system is shown in Figure 13.6(a). The deposition angle $\alpha$ is defined as the angle subtended between the substrate normal and the incident vapor. Azimuthal rotation about the substrate normal is measured by the angle $\phi$. In general, a line connecting the centers of the substrate and vapor source goes through the maximum of vapor flux plume.

Substrate rotation alters the location of the vapor source from the perspective of the growing columns. This changes the shadowing dynamics and the column growth will follow the source location. The manipulation of substrate orientation can therefore sculpt column growth, leading to the term sculptured thin film (STF), often used in the literature.

The requirements of a GLAD system vary with the required structures, since the necessary motions vary. A thorough description of a very capable system is given by Robbie et al. [11].
This section gives an overview of the requirements for a fully functional GLAD system capable of manufacturing the structures shown in Figure 13.4, and combinations thereof. In addition, system operating procedures specific to GLAD are discussed. It is worth noting that limited retrofits to existing deposition systems can make them GLAD capable.

### 13.2.3.1 Pressure Requirements

As discussed in Section 13.2.1.1, ballistic shadowing of incoming vapor flux is critical for GLAD. As a result, a flexible GLAD system should have a mean free path longer than the chamber dimensions. For typical systems with a source–substrate distance of $\approx 45$ cm, an operating pressure of $\approx \leq 10^{-3}$ torr is required. While these constraints vary with source type used, in general a lower operating pressure is preferred for production of high-quality structures.

### 13.2.3.2 Vapor Sources

Many vapor sources have been used for GLAD, including electron-beam evaporation, thermal evaporation, sputtering, several co-sputtering techniques, and pulsed-laser deposition. Table 13.1 summarizes materials and vapor sources used in GLAD.

### 13.2.3.3 Substrate Motion

To produce the structures shown in Figure 13.4, it is necessary for the substrate to be able to assume any orientation between $(0, 0)$ and $(\pi/2, \approx \infty)$. This may be accomplished using two
motors, as seen in Figure 13.6. We note that the ability to orient the substrate such that \( \alpha > \pi/2 \) is useful for shielding substrates from vapor flux during source conditioning, and that, in practice, \( \phi \) should be unbounded. It is also useful to be able to monitor the absolute angular displacement of a substrate.
13.2.3.4 Monitoring Requirements

Production of high-quality GLAD structures depends on in situ, real-time measurement of the vapor flux plume to monitor deposition rate. For GLAD, deposition rate is defined as the increase in film thickness per unit time at the center of a substrate with an orientation of \((0, 0)\). Monitoring deposition rate is typically accomplished with a crystal thickness monitor, and must be used to modify substrate motion to better satisfy the substrate motion algorithm. Optical in situ thickness monitoring methods are difficult in GLAD due to substrate motion, and have not yet been demonstrated.

13.2.3.5 Substrate Motion Algorithm

To take full advantage of deposition rate monitoring, substrate motion for a particular structure is defined as a series of ordered triplets. Each triplet defines a thickness \(h_n\) above the substrate, and a substrate orientation \((\alpha, \phi)\) that should be satisfied when \(h_n\) is reached. Linear interpolation may be used between defined positions in the algorithm by the computer controlling substrate motion. Table 13.2 gives sample algorithms. By defining a target height \(h_n\), rather than deposition time, substrate motion can be corrected to respond to changes in deposition rate, better matching the target structure.

The deposition rate is monitored by a crystal thickness monitor, and corrected for tooling to report deposition rate at the center of a substrate oriented at \((0, 0)\). However, this rate does not correctly describe the vapor flux rate for an oblique substrate. The deposition rate must be corrected to the substrate frame of reference to satisfy the substrate motion algorithm. The deposition ratio is a function of \(\alpha\), defined as the ratio of thicknesses between a film deposited

<table>
<thead>
<tr>
<th>Slanted post</th>
<th>Chevron</th>
<th>Slanted post stack</th>
<th>Bragg stack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height (nm)</td>
<td>((\alpha, \phi))</td>
<td>Height (nm)</td>
<td>((\alpha, \phi))</td>
</tr>
<tr>
<td>0</td>
<td>(80, 0)</td>
<td>0</td>
<td>(85, 0)</td>
</tr>
<tr>
<td>1000</td>
<td>(80, 0)</td>
<td>250</td>
<td>(85, 0)</td>
</tr>
<tr>
<td></td>
<td>(80, 0)</td>
<td>252</td>
<td>(80, 180)</td>
</tr>
<tr>
<td></td>
<td>(80, 180)</td>
<td>500</td>
<td>(80, 180)</td>
</tr>
<tr>
<td>Vertical post</td>
<td>Height (nm)</td>
<td>((\alpha, \phi))</td>
<td>Height (nm)</td>
</tr>
<tr>
<td>0</td>
<td>(80, 0)</td>
<td>502</td>
<td>(75, 0)</td>
</tr>
<tr>
<td>1000</td>
<td>(80, 0)</td>
<td>750</td>
<td>(75, 0)</td>
</tr>
<tr>
<td></td>
<td>(80, 180)</td>
<td>752</td>
<td>(65, 180)</td>
</tr>
<tr>
<td></td>
<td>(80, 180)</td>
<td>1000</td>
<td>(65, 180)</td>
</tr>
</tbody>
</table>

The algorithms listed here will produce a film 1 \(\mu\)m thick, and assume a deposition rate compatible with a substrate reorientation within 2 \(nm\) of growth.
at an orientation of \((\alpha, 0)\) and a film deposited at \((0, 0)\), assuming the same deposition rate and deposition time. Using the deposition ratio, it is possible to convert from the vapor deposition rate measured by the crystal thickness monitor to film height, as required.

As pointed out by Robbie et al., deposition ratios are not simply the expected \(\cos \alpha\) geometric scaling from rotating the substrate [11]. As the substrate is tilted at more oblique angles, the deposition ratio remains above the \(\cos \alpha\) dependence. This effect reflects the impact of shadowing combined with limited surface diffusion. To produce high-quality GLAD structures, a good understanding of a system’s deposition rate for a given material is required. Calibration of deposition ratio can be performed by a series of depositions at different angles. The resulting data can be fitted parametrically, or by equations such as those described by Poxson et al. [32]. Substrate temperature can also affect deposition ratio through surface diffusion rates. As a result, different deposition ratios may be observed for different layers of multilayered structures as the temperature rises during deposition. Finally, column tilt angle can vary in multilayered structures, as observed by Harris et al. [33]. Such changes produce a change in deposition ratio, which must be corrected for high-quality structures.

### 13.2.4 Demonstrated Materials

Table 13.1 gives a selection of the materials that have been successfully deposited by GLAD. Neither the list of materials nor references are exhaustive, serving only as a starting point for the reader.

### 13.3 Advanced GLAD Processes

This section describes perturbations to the basic GLAD process described in Section 13.2. This section is broken up into three subsections, describing advanced techniques that are applied before, during, and after GLAD depositions. As we have seen in Section 13.2.2, complex structures can be assembled using the basic canonical structures. Similarly, many of the following techniques can be used in parallel, as they offer orthogonal improvements to the basic GLAD process.

#### 13.3.1 Predeposition Treatment: Substrate Seeding

The ballistic shadowing process responsible for producing GLAD structures begins with the initial nucleation of deposited material. However, the nucleation process is random, and leads to a distribution in column size and random locations on the substrate surface [111, 112]. To produce a film ordered in the substrate plane, it is necessary to circumvent the randomness of nucleation. This may be achieved by introducing topography on the substrate surface, which act as ‘forced’ nucleation sites. While such topography need not be periodic, some of the most
Figure 13.7: (a) Top–down and (b) cross-section SEM images of a GLAD film deposited on a substrate with an untreated (left side of both images) and seeded (right side of both images) regions. With careful design of the seeds, forced nucleation can produce GLAD films that exhibit ordering in the substrate plane. The individual GLAD columns are more uniform in the seeded region due to reduction of competitive growth. (Reproduced with permission from [113], © 2005 IEEE.)

successful examples have been produced with periodic arrays. These features act as the initial nucleation seeds for column growth.

With correct design of the shape, size, and spacing of these seeds, a single GLAD column will grow at each lattice point. Consequently, column uniformity can be greatly improved by reducing competitive growth. Figure 13.7 illustrates the difference between columns deposited on a bare substrate and on an appropriate seed layer.

The first report of GLAD onto forced nucleation sites was by Malac et al., who used electron-beam lithography to write features in PMMA resist [114]. Since then, many other researchers have used several techniques to achieve forced nucleation, including electron-beam lithography [85, 115–119], embossing [67], optical lithography [120–122], laser-direct write lithography [113, 123], monolayers of colloidal crystals [124–137], and block co-polymers [138]. While not yet demonstrated, the use of metal dot arrays fabricated using a diffraction mask and laser ablation have also been proposed as seeds for GLAD deposition [139]. In the following subsections, three rules of thumb for seed design are given, followed by a description of a more rigorous simulation method for seed design. Finally, advantages of the different seeding techniques used to date are discussed.

13.3.1.1 Seeding Theory

The first objective of forcing nucleation is to control the location of GLAD columns. This requires that growth from forced nucleation sites dominates growth elsewhere. Thus, it is
desirable to maximize the incident vapor flux that deposits on the seeds, rather than allowing flux to freely impinge on the substrate and nucleate at random. This consideration produces the first rule of thumb for designing seeds. To prevent condensation between seeds for a given deposition angle $\alpha$, the following condition should be satisfied,

$$\Delta \lesssim h \tan \alpha + d$$

(13.4)

where $\Delta$ is the center-to-center seed spacing, $h$ is seed height, $\alpha$ is the deposition angle, and $d$ is seed width [113]. When this condition is exactly satisfied, a shadow cast from one seed will just touch the base of a nearest neighboring seed. When the deposition plane is not aligned with the seed array, shadowing will not be complete. In general, deposition on the sides of seeds is not desirable, so $\Delta$ should be slightly less than the right side of Eq. (13.4).

The second objective of forced nucleation is to minimize the extinction processes that arise from competitive growth. The dependence of density on $\alpha$ in a GLAD film was discussed in Section 13.2.1.4. Neglecting column broadening, the in-plane density will determine the bulk density. The bulk density is determined by the macroscopic geometry of the deposition, and a GLAD film can only be perturbed from this value for short periods. For circular seeds,

$$\frac{\pi d^2}{4 \Delta^2} \approx \frac{2 \cos \alpha}{1 + \cos \alpha}$$

(13.5)

where $\Delta$, $d$ and $\alpha$ are as defined in Eq. (13.4). The left-hand side of Eq. (13.5) is the fractional area covered by the seeds, and the right side is Eq. (13.3), Tait’s equation for GLAD thin film density. If the fractional area covered by the seeds does not approximately match the density determined by the deposition angle $\alpha$, the order initially imposed by forced nucleation will be lost as the GLAD film returns to its equilibrium density.

However, it is insufficient to simply match the expected density of the GLAD film with the fill fraction of the seeds. Equations (13.4) and (13.5) can be satisfied for any size of seed ($d$, $h$), simply by adjusting the interseed spacing $\Delta$. In the limit, small seeds are equivalent to substrate surface roughness and large seeds are equivalent to a smooth substrate. These effects give rise to the third rule of thumb for seed design: seeds must be approximately equal in size to the expected size of a single GLAD column. An example where this rule was violated is given in Figure 13.8, where the seed size is larger than a single GLAD column, resulting in the growth of multiple columns from each seed.

If requirements for column spacing and uniformity are severe, then the simple design rules outlined above may be insufficient. In such cases, Summers has shown that a more rigorous simulation can guide seed design and deposition conditions for demanding applications [110]. In this work, seed profiles were simulated using parametric equations which captured some
typical profiles found in electron-beam lithography. Seed diameter is given by

\[ D(s) = D_0 \left( \cos \frac{\pi s}{2} \right)^\kappa \]  

where \( D \) is seed diameter, \( s \) is a height parameter which varies between 0 and 1, \( D_0 \) is the seed diameter at the substrate, and \( \kappa \) is an exponent which controls seed curvature. By projecting the shadow of such a seed, it is possible to calculate the area exposed to incoming vapor flux, known as interstitial deposition. Summers and Brett have shown that the column broadening of seeded GLAD structures improves as interstitial deposition is decreased [140]. As a result, simulation of this quantity can be used as a proxy for GLAD column quality.

Summers simulated the interstitial deposition fraction as a function of offset angle, \( \gamma \), for several seed profiles, geometries, and deposition conditions [110]. This work was performed to optimize an advanced deposition method, called PhiSweep, for deposition of square spiral structures. Further details of the PhiSweep and related methods are given in Section 13.3.2.1. Some results for a square lattice of seeds, with seed parameters determined empirically from the work reported in [140], are presented in Figure 13.9. The expected decrease in interstitial deposition with increasing deposition angle and increasing fractional area coverage is observed. Moreover, the optimum offset angle is revealed by these simulations, and matches the experimental result determined by Summers and Brett [140]. Such modeling efforts can be extended to any seed profile or geometry, and used to determine the optimum deposition conditions.
Figure 13.9: Interstitial deposition fraction as a function of (a) deposition angle and offset angle ($d = 0.49a$, $h = 0.166a$, $\kappa = 0.6$), and (b) seed diameter and offset angle ($\alpha = 85^\circ$, $h = 0.166a$, $\kappa = 0.6$). The solid dots are experimental values from [140], and seed parameters were estimated empirically from the same source. (Adapted from [110].)

13.3.1.2 Seeding Methods

One additional constraint on seed design is production method. Examples from the literature are given in Figure 13.10. The previous design discussion has implicitly assumed that full control of seeds is possible. In principle, this is true of the electron-beam lithography [85, 115–119], laser direct-write lithography [113, 123], and optical lithography methods [120–122], within the resolution limits of the respective techniques. The drawback to these approaches is the long time required to produce a patterned substrate. While extremely flexible, scaling to large substrate areas may not be possible. One method that may scale to large substrate areas is embossing [67]. While embossing requires the use of a master, it retains most of the flexibility of the lithography techniques, but should be much faster since patterned substrate copies can be rapidly produced.

Figure 13.10: The first examples of the methods used to force nucleation in GLAD films: (a) electron beam [114]; (b) colloidal crystals [127]; (c) embossing [67]; and (d) block co-polymers [138]. ((a) Reprinted with permission from [114], © 1999 American Institute of Physics, (b) reproduced from [127] with permission from Elsevier, (c) reprinted with permission from [67], © 2001 American Chemical Society, (d) reproduced from [138].)
The other methods for seeding substrates for GLAD growth use self-assembly, and trade flexibility for speed. These include the use of colloidal crystals [124–131, 134, 135] and block co-polymers [138]. Such techniques can produce very large areas, but are typically confined to hexagonal geometries. Self-assembly techniques are also subject to crystal defects [130, 138, 141], which will adversely affect GLAD film column separation and broadening. An additional limitation of the self-assembly methods is the fixed seed spacing. As seen from the rules of thumb above, this is equivalent to reducing available deposition angles.

In practice, development of a seeding strategy might require several of these techniques in series: electron-beam lithography to explore the parameter space, and embossing or nanoprint lithography once the optimal conditions are understood. Forcing the nucleation of GLAD thin films can be a powerful technique for controlling resulting film properties. However, it is best used in combination with the advanced motion control techniques discussed in the next section.

### 13.3.2 Advanced Deposition Methods

In this section, we discuss modifications to the GLAD process during deposition, including advanced motion control methods, GLAD co-deposition, and substrate temperature control.

#### 13.3.2.1 Substrate Motion Control

Columns in GLAD films tend to broaden into fan-like shapes during deposition, which can detrimentally affect film properties. To improve individual column structure, two techniques based on dynamic shadowing have been developed. As discussed in Section 13.2.1, shadowing is anisotropic, acting parallel to the deposition plane. Shadowing anisotropy may be reduced by rotating the substrate, and thus the column shadow, during deposition. Active control of the shadow forms the conceptual basis of the PhiSweep and substrate swing rotation techniques.

PhiSweep was introduced by Jensen and Brett [142]. The substrate motion in the PhiSweep method is defined by a sweep angle $\gamma$ and a sweep pitch, along with the standard $\alpha$ and $\phi$ angles. The PhiSweep method, given schematically in Figure 13.11, deposits a thickness defined by the sweep pitch at a substrate orientation of $(\alpha, \phi + \gamma/2)$. The substrate is then rotated to an orientation of $(\alpha, \phi - \gamma/2)$ for a second segment, also equal to the sweep pitch. Once deposition is complete, the substrate returns to the original position for another cycle. These cycles are continued until the desired column length is obtained. Because of the symmetry of the substrate sweep, the column’s net growth follows the central axis lying between the two segments along an orientation defined by $(\alpha, \phi)$.

Jensen and Brett have shown that the morphology of Si columns is very sensitive to the values chosen for the PhiSweep method [142]. With a sweep pitch approximately equal to the column diameter, the PhiSweep technique produces a film composed of densely packed individual fibers 20–30 nm in width. It is thought that each change in substrate position acts as a new
Figure 13.11: Offset angle as a function of thickness for the PhiSweep and substrate swing motion algorithms. The step function is the PhiSweep motion, the sawtooth is the substrate swing motion. Both algorithms will produce net column growth with an offset angle of 0°.

GLAD column, effectively suppressing the effects of competitive growth and column broadening.

One effect of the PhiSweep technique is a change in the effective deposition angle. Gish et al. have studied the $\beta$ for PhiSweep columns deposited onto patterned substrates [143]. They have shown that the tilt angle of the PhiSweep fibers $\beta_{PS}$ is related to the tilt angle of the traditional GLAD columns $\beta_{TG}$ by

$$\tan \beta_{PS} = \tan \beta_{TG} \cos \gamma$$  \hspace{1cm} (13.7)

Ye et al. introduced substrate swing rotation to eliminate anisotropic broadening in GLAD structures [122]. Unlike the PhiSweep method, the substrate is periodically rotated through a given angle (defined as swing angle $\phi$). The motion of a substrate under this algorithm is also shown in Figure 13.11. The effects of the substrate swing method on column morphology is similar to that seen with the PhiSweep method. Column broadening is reduced, and column chaining is prevented. As seen in Figure 13.12, better defined columns are achieved, with approximately circular cross-sections in the plane of the substrate. As in the PhiSweep method, periodic rotation of the substrate changes effective deposition angle, $\alpha'$, given by

$$\tan \alpha' = \frac{2 \tan \alpha \sin \phi}{\phi}$$  \hspace{1cm} (13.8)

For both the PhiSweep and substrate swing methods, the column tilt angle $\beta$ will deviate from the expressions given in Section 13.2.1. The degree of deviation can be controlled using the
analytic results of Eqs. (13.7) and (13.8). Both techniques offer an additional avenue for controlling tilt angle, partially decoupling $\beta$ from $\alpha$. Another method for decoupling $\beta$ from $\alpha$ is the spin–pause method, developed by Robbie et al. [144]. In the spin–pause method, GLAD structures are fabricated by combining the growth of vertical posts (spin) and slanted posts (pause) in small segments. Although a constant $\alpha$ is maintained, varying the ratio of the spin mode growth and pause mode growth produces a reduced $\beta$.

The PhiSweep and substrate swing methods were introduced to minimize anisotropy in the planar cross-section of the columns. However, many physical properties of GLAD films are a product of structural anisotropy in the substrate plane. Thus, it can be desirable to maximize column broadening and enhance these properties. This has been achieved by Hodgkinson et al., who developed serial bideposition (SBD) [145]. In SBD, deposition occurs at oblique angles of incidence with rapid 180° rotations of the substrate every few nanometers of growth. In a plot like Figure 13.11, SBD would look like the PhiSweep method with an amplitude of ± 90° and a period of a few nanometers. The time-averaged source direction is normal to the substrate and the net growth of the structures will be in the vertical direction. The shadowing mechanism is preserved, producing a highly pronounced structural anisotropy due to lateral broadening perpendicular to the deposition plane. This has been exploited to produce films with very high birefringence (see Section 13.5.1.1, Engineered birefringence). In a slanted column, the planar cross-section is elliptical due to competition between two effects. The first, broadening, orients the semi-major axis perpendicular to the deposition plane. The second, column tilting, orients the semi-major axis parallel to the deposition plane.

The advanced substrate motion techniques described here have the effect of modifying the available $\beta$ for GLAD films. The trend for an unperturbed GLAD deposition is given by Tait’s rule (Eq. 13.2). Column tilt angles below those predicted by Tait’s rule can be accessed through the PhiSweep, substrate swing, SBD, and spin–pause methods. Column tilt angles above those predicted by Tait’s rule are more difficult to obtain. The only method yet
demonstrated in the literature is ion-assisted deposition, discussed below in Section 13.3.2.4. Using ion-assisted depositions, a small increase in $\beta$ at high $\alpha$ can be achieved.

13.3.2.2 GLAD Co-deposition

Co-deposition techniques have long been used for GLAD films, [146–149], and have recently been the subject of intensive development [63, 71, 127, 135, 150–155]. Configurations that have been demonstrated include a single material deposited from two directions [126, 146], two materials deposited from similar directions [63, 154, 155], and two materials deposited from different directions [135, 148].

Su et al. and He et al. have studied the optical properties of oxide films with embedded Au [154] and Ag [63] nanoparticles, respectively. Such films exhibit interesting polarization properties. He et al. have produced Ti-doped Mg structures, which may have application as hydrogen storage structures [155]. Films composed of both anatase TiO$_2$ and monoclinic WO$_3$ were produced by Tesfamichael et al. for gas sensing applications [152].

Kesapragada and Gall have used GLAD co-deposition to modify the normal growth of a GLAD column [127]. First, single crystal 1.5 $\mu$m Cu columns were deposited using conventional GLAD. Then two sources located at ($\alpha = 84^\circ$, $\phi = 0^\circ$) and ($\alpha = 84^\circ$, $\phi = 180^\circ$) are used simultaneously to form Y-shaped structures, with each branch oriented toward their respective sputter source. Zhou and Gall have recently extended this work to produce columns composed of Si and Ta, shown in Figure 13.13 [135]. The columns are split longitudinally along the axis of the column, a morphology that may have piezo-activated or energy-scavenging applications.

![Figure 13.13: Co-deposition of Si and Ta to produce GLAD columns composed of two different materials, split along the longitudinal axis. (Reproduced with permission from [135], © Wiley-VCH.)](image-url)
The use of co-deposition techniques in a GLAD system may require modification to the GLAD apparatus described in Section 13.2.3. For co-deposition methods, non-stoichiometric evaporation or sputtering will require careful calibration. In the case of sequential depositions with two different sources, a single vapor flux monitor is sufficient to control the GLAD process. For high-quality structures produced using two or more sources, independent, simultaneous measurements of each source will be required. In this case, individual vapor flux monitors must be shielded such that only one source contributes to each monitor.

### 13.3.2.3 Substrate Temperature Control

One of the key conditions of the GLAD deposition process is that surface diffusion is insufficient to allow adatoms to fill in ballistic shadows. During deposition, the substrate will heat through two mechanisms: direct radiative heating from the vapor source, and heating from vapor condensation on the substrate. Adatom diffusion length increases with temperature, so the effectiveness of ballistic shadowing decreases with temperature as adatoms diffuse further. Direct control of substrate temperature for GLAD has been studied by several groups [49, 69, 156–158]. GLAD depositions of Pd [69], Co [49], and TiO₂ [157] at cryogenic substrate temperatures have been reported.

A general degradation of GLAD helical structure quality has been reported by Schubert et al., who deposited Si spirals at substrate temperatures up to 475 °C [156]. Work by the same group, reported by Patzig and Rauschenbach [158], has shown that a single GLAD column can evolve through several of the classic GLAD structures: spirals, screws, and vertical posts, with carefully selected deposition conditions. Similar observations were reported by Robbie et al. for an S:O column [159].

The combination of material, deposition rate, substrate rotation rate (or algorithm), and substrate temperature together define a morphological phase space which will control the precise column morphologies produced during a GLAD deposition. The experiments reported by Robbie et al. [159] and Patzig and Rauschenbach [158] can be thought of as tracing a route through this space. There is a vast parameter space available for GLAD depositions, and only in isolated cases is the dependence of column structure on deposition parameters well understood. The careful experiments needed to understand these effects have begun, but much work remains. Another aspect of these issues, column crystallinity, is discussed in Section 13.4.1.1.

### 13.3.2.4 Other Advanced Methods

**Ion-assisted GLAD**

Ion-assisted GLAD has been studied by a few groups [50, 160–162]. The use of low-energy ion bombardment during GLAD deposition has been shown to increase β in slanted posts when the incident angle of the ion beam is less than the vapor flux deposition angle α.
Glancing Angle Deposition [50, 161]. This is likely due to resputtering of column top surfaces, leading to redeposition on the bottom surface of adjacent columns. Hodgkinson and Wu [50] and Fleischauer et al. [161] studied this effect for optical applications. Kitagawa et al. have optimized deposition angle for a scalable ion-assisted GLAD process to produce smooth diamond-like coatings [160]. Taschuk et al. have used ion-assisted GLAD to modify the density of vertical post films in an effort to improve the responsivity of relative humidity sensors [162].

**External shadowing**

Krause and Brett developed a modification to the GLAD technique, imposing an additional, macroscopic shadowing element which modifies GLAD depositions [163]. Their set-up and images of the resulting films are given in Figure 13.14. The addition of a cylinder at the center of a deposition chuck produces a region shadowed from incoming vapor flux. As a substrate rotates through this region, it experiences a periodic, momentary reduction in vapor flux which modifies GLAD structures. The response of helical thin films to such shadowing is seen in Figure 13.14(c–e).

![Figure 13.14: Shadowed GLAD method:](image)

*Figure 13.14: Shadowed GLAD method: (a) A shadow block placed in the center of the obliquely inclined substrate casts a shadow, resulting in (b) a graded thin film with structure defined by substrate motion. SEM images of $\alpha = 85^\circ$ helices located (c) 1 mm, (d) 13 mm, and (e) 56 mm from shadow block edge. (Reproduced with permission from [163], © Wiley-VCH.)*
Sequential GLAD
A simple way to combine the properties of different materials within a single GLAD film is to deposit different materials sequentially; a few recent examples are discussed here. A GLAD structure is grown with one material, followed by an additional deposition with a different material [153, 164–166]. This method is distinct from co-deposition, where two vapor sources are used simultaneously. Alouach et al. have deposited a GLAD Cu layer as seeds for Permalloy (Ni$_{80}$Fe$_{20}$) nanowire arrays [165]. Anisotropic Ag nanoparticles have been deposited on SBD SiO$_2$ posts for surface-enhanced Raman applications [166]. Photocatalytic properties of TiO$_2$ have been enhanced using WO$_3$ support structures [153].

13.3.3 Postdeposition Treatments

The structures available to GLAD are robust enough to survive several treatments, including annealing, etching, oxidization, chemical functionalization, and templating processes. In this section, postdeposition processing of GLAD thin films is discussed.

13.3.3.1 Annealing

Postdeposition annealing of GLAD structures is one method for achieving a crystalline, nanostructured thin film. The impact of annealing of GLAD thin films has been studied by many groups [15, 57, 60, 61, 69, 156, 157, 167–173]. Film morphologies have been widely observed to survive the annealing process [57, 156, 167, 171], although a reduction in surface area [69, 157] and thickness [61, 170] has been reported for some materials. One common application of annealing has been to activate photoluminescent materials such as Y$_2$O$_3$:Eu [60, 61, 169], ZnO [15], and Si through production of Si nanocrystals [174, 175]. Such annealing processes correct stoichiometric or crystallinity deficiencies in the as-deposited material, greatly improving the photoluminescent efficiency.

Another application of postdeposition annealing has been the blueshift of the wavelength of a circular Bragg peak [170]. In that work, Pursel et al. cite a combination of competing effects: a blueshift due to column thinning and a small reduction in circular pitch, and a redshift from TiO$_2$ transition (amorphous to anatase). Such competing effects complicate the use of annealing processes for GLAD films, but ellipsometric measurements can address the relative magnitude of these effects, allowing good design choices.

13.3.3.2 Density Modification: Etching and Oxidization

Although GLAD structures can take many forms, film density can be constrained. In such cases, it is possible to modify density postdeposition through etching processes which remove material [133, 176, 177], or oxidization processes which add material [178, 179]. Etching processes for GLAD thin films were first investigated in detail by Lakhtakia and Horn for tuning of optical filters [176]. Subsequent work by the same group demonstrated this effect.
experimentally with TiO$_2$ spectral hole filters [177]. In this work, Pursel et al. demonstrated a 25 nm blueshift in the wavelength of a spectral hole filter for an 80 minute etch. The leisurely rate of change suggests that precise adjustments to optical properties can be made.

Another method to modify GLAD film density while retaining the columnar structure is to oxidize the film. This approach has been explored for optical applications by Robbie et al. [178] and Summers and Brett [179]. Robbie et al. oxidized Si rugate optical filters, converting them to silica. This procedure enhances the filter’s visible band transmission and reduces its average optical index. Summers and Brett oxidized Si square spirals in an effort to increase the structure’s fill factor for photonic crystal applications [179]. This approach combines the high-quality structure produced by GLAD with a higher density than is usually attainable by direct deposition. Using these density modification techniques, a desired $\beta$ can be achieved, without necessarily accepting the density produced by GLAD.

### 13.3.3.3 Chemical Functionalization

Owing to the wide selection of materials available to GLAD, it is possible to produce films that are amenable to chemical functionalization [82, 134, 180–184]. Tsoi et al. have demonstrated that GLAD structures can survive functionalization processes, and that the entire film is likely affected [180, 182]. In this work, siloxane-based functionalization was chosen for flexibility and durability of the resulting coatings [180]. Such work expands the available surface chemistry for GLAD films, which has applications in sensors and other devices. It is also possible to adjust the hydrophilicity of TiO$_2$ through ultraviolet irradiation. Taschuk et al. have exploited this effect, along with the photocatalytic nature of TiO$_2$, to develop an anti-aging procedure for relative humidity sensors [185]. The easily accessible, high surface area films produced by GLAD make excellent platforms for chemical functionalization treatments. Some applications for such treatments are discussed in Section 13.5.2.

### 13.3.3.4 GLAD Templating

Some materials, such as low-melting-point metals or complex organics, are difficult or impossible to deposit directly in a GLAD film. In cases where the properties of such materials must be combined with the geometric properties of a GLAD film, templating methods can be used [96, 99, 101, 103, 186]. Harris et al. developed the templating method [103] shown in Figure 13.15.

The template process begins with a GLAD film (Figure 13.15a), which is filled with an intermediate material such as photoresist (Figure 13.15b). The choice of intermediate material is important, since it must be orthogonally etchable with the template material. The intermediate material is etched to expose the top of the original GLAD film (Figure 13.15c), which is subsequently etched to produce a perforated thin film composed of the intermediate material (Figure 13.15d). Au, Ni, and polystyrene perforated thin films were produced by Elias et al. using a similar method [101].
Harris et al. produced Cu and Ni GLAD copies of a SiO$_2$ GLAD film through a double-templating process [99]. A template is first produced using the above process, followed by electrodeposition through the perforated thin film to achieve a copy. This work was extended to organic materials by Elias et al., although vacuum filling was necessary to infiltrate the various acrylates into the perforated thin film template [96].

Summers has developed a low-pressure chemical vapor deposition (LPCVD) process for production of inverse square spirals [110], a photonic crystal structure discussed further in Section 13.5.1.1 (Photonic crystals).

### 13.4 Properties of GLAD Thin Films

This section discusses the properties of GLAD thin films at several different length scales. Below $\approx 100$ nm, properties related to a single column dominate. Such properties include crystallinity, width and magnetic anisotropies. Between $\approx 100$ nm and $\approx 1 \mu$m, an ensemble of columns control properties such as surface area and electrical conductivity. Above $1 \mu$m, the ‘bulk’ properties of the overall film control thermal and optical properties. GLAD’s ability to partially decouple the different length scales in thin film fabrication makes it possible to produce materials with interesting and useful properties.

#### 13.4.1 Column Properties

##### 13.4.1.1 Crystallinity

Since GLAD is a low-temperature process ($T_{\text{substrate}} \approx 0.3 \ T_{\text{melting}}$), one does not expect a thin film with long range crystalline order to be produced during deposition. However, owing to the small size of individual GLAD columns, adatom mobility can be sufficient to produce single-crystal columns during deposition. Such columns have been produced for a wide range of materials: Al [30], Co [115], CrN [187], Cu [125, 126], Ge [54, 55], Mg [62], Sn [188], Ti-doped Mg [63], Ru [76], $\beta$-phase W [90, 189], and ZnO [190]. Crystalline organic GLAD
films have also been produced for C₆₀ and pentacene [83]; partially crystalline films composed of PPX derivatives have recently been reported [91]. No catalyst was required to achieve single-crystal nanorods, unlike conventional vapor–liquid–solid techniques.

Van der Drift identifies three principal factors which may introduce texture in a thin film: preferentially oriented nucleation, evolutionary or competitive selection of initially random nucleation, and postdeposition crystallization [191]. Annealing of GLAD films is discussed in Section 13.3.3; here we discuss texture formation during GLAD processes. Since different crystal faces grow at different rates, the vertical growth rate of a crystal is sensitive to its orientation. Assuming randomly oriented crystallites at the substrate, the orientation with the greatest vertical growth rate will be the most likely to survive and emerge as the dominant texture in the film. Because of its competitive nature, this principle is reminiscent of the competitive growth process found in GLAD.

Conditions under which GLAD columns become textured have been reported by many groups [25, 26, 49, 54, 55, 59, 90]. Okamoto et al. have been studying oblique deposition of Fe thin films for many years [25, 26, 59], culminating in a detailed mapping of Fe crystallinity as a function of deposition angle and deposition rate, as shown in Figure 13.16. Similar studies for Co [49] and Ge [54, 55] have been performed.

Karabacak et al. have studied single-crystal β-W formation [90]. A schematic for Karabacak’s model is given in Figure 13.17. During initial growth, a mixture of α-W and β-W islands form on the substrate. However, the β-W islands are favored in GLAD growth since they have lower adatom mobilities and act as diffusion sinks for deposited adatoms. Once the β-W islands start collecting more adatoms, they will grow faster and thus tend to capture more incoming vapor flux, reinforcing the faster growth.
The relationship between column growth direction and crystallinity has been studied for several materials [24, 76, 192–197]. A preferential crystalline orientation is observed in many cases, but no general trend exists. Hagemeyer et al. have studied the deposition of Co–Cr magnetic thin films for a variety of substrates and deposition conditions for a fixed $\alpha$ of 45° [24]. Hagemeyer et al. note that the c axes of their films were always oriented along the column growth direction. However, Moon and Shin report that the $\langle 111 \rangle$ axes of Co-Pt films were not aligned with column growth direction [192]. The situation becomes more complicated for the case of rotating substrates [76, 193, 194]. Yamaguchi et al. observed an optimum rotation rate for producing crystalline YSZ layers by GLAD [193]. Alouach and Mankey have found a dependence of Cu crystal orientation on $\alpha$ and substrate rotation rate [194]. Similar results were obtained for Ru columns by Morrow et al. [76]. One final avenue of control is the expected dependence of film crystallinity on substrate material and crystallinity [24, 195].

Grain boundaries can influence column morphology during growth. Wang et al. have demonstrated that stacking faults can cause bifurcation in Cu vertical post films [125]. Through a combination of molecular dynamics simulations and experimental investigations, they were able to attribute the formation of Y-shaped columns to the interaction of stacking faults and a large diffusion barrier between different facets of the Cu crystal. By manipulating the deposition conditions, it may be possible to control this branching and use it to fabricate more complicated nanostructures.

Nanocrystallites have been observed within and on GLAD columns [119, 154, 171, 174, 175]. Indutnyy et al. have produced Si nanocrystals within SiO$_2$ columns by annealing SiO$_2$ films at
700 °C and 950 °C, followed by radio-frequency (RF) plasma passivation in a mixed H₂/N₂ atmosphere [174]. Photoluminescence from the Si nanocrystals was observed in the original report, and studied further as a function of several chemical treatments [175]. Summers et al. [119] and Schubert et al. [156] have observed the presence of similar nanocrystals, though photoluminescence was not investigated. Using a co-sputtering GLAD technique, amorphous SiO₂ columns with Au nanocrystals have been produced by Su et al. [154].

The empirical studies discussed here are ahead of theoretical or modeling efforts in this area. While some molecular dynamics work, such as that performed by Wang et al., is offering useful insights into the underlying physics governing GLAD columns, in general the size of physically interesting domains renders molecular dynamics simulations intractable. One avenue for development of this area is to make further use of the literature on magnetic materials deposited by oblique angle sputtering techniques. While the magnetic work is typically confined to α ≤ 60° and stationary substrates, it does offer some useful insight into GLAD processes.

In general, the impact of crystallinity on a particular material in a GLAD film must be evaluated on a case by case basis. While it may not be possible to control crystallinity or texture in all cases, the dependence of crystallinity on deposition angle reported by Alouach et al. and Morrow et al. suggests that the GLAD technique might offer an opportunity to control thin film crystallinity in an interesting manner. One of the common characteristics of the work presented in this section is the relatively high rotation rates: 30 rpm or higher. This may have the effect of isolating adatoms on the surface, such that crystal–adatom interactions would dominate column growth. While much work remains to be done in this area, the wide range of behaviors observed to date indicates that this is a promising area.

13.4.1.2 Column Width

Vertical post films are deposited at oblique incidence with a constant substrate rotation. Column diameter of vertical post films has been studied as a function of deposition angle and film height by many groups [91, 112, 198–202]. Column diameter is described using a power law:

\[ w (t, \alpha) \propto t^{p(\alpha)} \]  

where \( w \) is column width, \( t \) is film thickness, and \( p \) is a characteristic growth coefficient which depends on deposition angle \( \alpha \). Literature results for several materials are given in Figure 13.18. This work started with Karabacak et al., who derived theoretical limits for \( p \) based on interface growth models [198]. Such models exhibit two characteristic growth coefficients, describing growth parallel and perpendicular to the substrate plane projection of the incoming vapor flux. Karabacak et al. extended results applicable to the case of stationary substrates to the GLAD case by taking a geometric average of the growth coefficients. A limited range for \( p \)
Figure 13.18: Literature values for $p$ from the column growth model described in the text. The theoretical limits for $p$ for shadowing dominated (KPZ limit, 0.5) and diffusion dominated growth (MH limit, 0.3) are given on the right side of the plot. Both limits are violated by experimental data points. Experimental data are described in the table. Several data points and error bars are not visible due to overlap with other results.

was obtained:

$$\frac{5}{16} \leq p \leq \frac{1}{2} \quad (13.10)$$

The upper limit corresponds to shadowing dominated growth, imposed by the Kardar–Parisi–Zhang (KPZ) model. The lower limit corresponds to growth with shadowing and diffusion, imposed by the Mullins–Herring (MH) model. The interface models are well described by Barabási and Stanley [203]. Experimental values for $p$ are given in Figure 13.18. The limits derived by Karabacak et al. are shown on the right side of the plot, denoted by KPZ$'$ and MH$'$. The minimum and maximum values for the stationary cases (MH$_{\text{min}}$ and KPZ$_{\text{max}}$) are also given.

The data in Figure 13.18 show that no consensus has yet emerged for literature values. The data given here are for many materials, listed in the table inset in Figure 13.18. While the data from Karabacak et al. and Cetinkaya et al. suggests that $p$ varies with material, it is clear from the Buzea and Taschuk data that significant scatter exists even for a single material. This scatter is also observed between different groups, as seen by the scatter for Si columns at an $\alpha$ of 85°. As a result, the variation in $p$ as a function of material reported by Karabacak and Cetinkaya may not be statistically significant.

More serious is the violation of the theoretical limits proposed by Karabacak et al. While most data are within the range given by Eq. (13.10), data from multiple groups are outside.
Interestingly, some of the values are beyond the minimum and maximum values for the stationary interface models, though this is less conclusive for the $KPZ_{\text{max}}$ limit. Further experimental and theoretical work will be required to quantify this property of GLAD films. Given the incomplete understanding of the issues controlling the scaling of column width in GLAD films, an empirical approach for each deposited material will be necessary.

### 13.4.1.3 Magnetic Anisotropy

On a sufficiently small scale, surface effects and boundary conditions strongly influence the magnetic properties of structured material. Much research has examined magnetic properties of such materials and how they can be controlled by GLAD. Early studies in oblique deposition of magnetic materials observed pronounced anisotropy, where the material possesses a hard and an easy magnetization axis [28, 59, 204–209]. This anisotropy is created by the columnar structure of the deposited film and is not a product of crystallinity or strain.

Magnetic properties of slanted post films can be explained using two anisotropy fields, $H_1$ and $H_2$ [59]. Field orientation is determined by the columnar structure: $H_1$ is parallel to the column axis and $H_2$ lies in the substrate plane, orthogonal to $H_1$. The film planar anisotropy is the difference between $H_2$ and the planar projection of $H_1$. By varying film structure, it is possible to control the magnetic anisotropy magnitude. The magnetic anisotropy can further be tailored by simultaneously depositing two different materials from opposite directions [147, 210–213]. This produces compositionally graded columns with complicated ferromagnetic and non-ferromagnetic domain structures.

Recent research continues to examine the magnetic properties of GLAD films, with new approaches including magnetic force microscopy [46, 214], optical techniques [46, 215], and scanning tunneling microscopy [216]. These studies provide more information about anisotropy, coercivity, and domain formation in these structures.

### 13.4.1.4 Organic Materials

Direct organic material deposition with GLAD has been studied by several groups [78, 79, 83, 87, 91, 92]. Pursel et al. used a nozzle to direct vaporized parylene C onto a substrate at an oblique angle [87]. The parylene C subsequently polymerizes, but retains GLAD film structures. One of the more remarkable results in this area has been the Alq$_3$ structures produced by Hrudey et al. [78]. Scanning electron microscope (SEM) images of characteristic Alq$_3$ helical GLAD thin films are shown in Figure 13.19. These films are extremely smooth, exhibit excellent uniformity, and self-organize over short distances into hexagonal-close packed ordering. The deposition of organic materials with GLAD is a rapidly developing field, and interesting results are expected as these new materials are investigated.
13.4.2 Column Ensemble Properties

13.4.2.1 Interface Width

Interface width is defined by the statistical distribution of column heights. Similar to column width, it has been found to follow a power law with film thickness:

\[ T_{\text{interface}} (t, \alpha) \propto t^{\beta(\alpha)} \]  \hspace{1cm} (13.11)

where \( T_{\text{interface}} \) is the interface thickness, \( t \) is film thickness, \( \alpha \) is deposition angle, and \( \beta \) is a characteristic growth coefficient which depends on deposition angle \( \alpha \). Note that the use of \( \beta \) here does not represent column tilt angle. Surface roughness of GLAD films has been studied by several groups [68, 71, 73, 84, 102, 217, 218]. A summary of results for \( \beta \) from the literature is given in Figure 13.20. A strong dependence on deposition angle is observed, rising to a nearly linear scaling of surface roughness with film thickness for highly oblique depositions. Although only a limited data set is available from the literature, the report of Vick et al. [218] and the strong trend observed here suggests that this parameter depends less on material than the column width parameter discussed in Section 13.4.1.2.

Another measure of GLAD surface roughness can be made by treating it as a self-affine surface; this measure depends only weakly on deposition angle [73, 84]. A final point is that surface roughness depends on rotation rate [70], which may offer an additional degree of control over this property.
13.4.2.2 Areal Column Density

Areal column density has not been studied as much as other properties, although a few reports of specific materials have been made [38, 91, 130, 158, 219, 220]. Typical values in the range of ≈ 20 columns per square micrometer are observed for films at least a few hundred nanometers thick. For specific materials, a few general trends do exist. As a result of column competition, areal column density decreases with film thickness [91, 219, 220]. Similarly, increasing substrate temperature has been shown to decrease column number density [130, 158].

Column number density is closely related to column width, which is not yet well understood (see Section 13.4.1.2). In general, understanding GLAD column areal density scaling will require an improved understanding of column width scaling, which remains an open research question. Column density varies with film thickness, deposition angle, and material, and must be evaluated for any given application. In some cases, it should be possible to exert some influence over column density through the advanced substrate motion control techniques discussed in Section 13.3.2.1.

13.4.2.3 Surface Area

The columnar microstructure of GLAD films can result in large surface areas. The surface area of GLAD films has been studied in several reports, including experimental measurements [53, 69, 157, 221–226], simulations [227], and geometric estimates [142]. Figure 13.21 summarizes the experimental literature values as a function of \( \alpha \) and material.

Surface area increases with deposition angle up to \( \approx 70^\circ \), and then decreases slightly; peak location varies with material. The surface area magnitude also depends on material, with oxides tending to exhibit higher surface areas than pure elements. The data reported by Kim et al. for Pd are an exception to this general trend, deposited at an extremely low temperature of 22 K [69]. It is clear that deposition temperature does play a significant role from the TiO\(_2\).
Figure 13.21: Literature values for surface area of GLAD thin films as a function of deposition angle and material. A strong dependence on material is observed. The Flaherty data and Krause data are for TiO$_2$. The discrepancy is attributed to different substrate temperatures during deposition: Flaherty deposited at 100 K, while Krause left substrate temperature uncontrolled. Experimental data are described in the table. Several data points are not visible due to overlap with other results.

![Graph showing surface area vs. deposition angle for different materials]

The data from Flaherty et al. and Krause et al., who deposited at 100 K and above room temperature, respectively [157, 226]. However, further work will be required to evaluate the impact of deposition temperature on GLAD surface area.

13.4.2.4 Mechanical Properties

Because GLAD films are composed of separated columns rather than a continuous solid film, interesting mechanical properties are observed. GLAD films can act as stress relief layers, and stiffness can be adjusted through film microstructure. In general, these properties are the product of an ensemble of columns, but some work has successfully isolated the mechanical properties of single GLAD columns. Some studies have also been made of the mechanical response of GLAD films to droplets encompassing an ensemble of columns.

**Hardness**

Hardness of GLAD films has been studied by several groups [27, 43, 95, 160, 228]. Researchers have found that hardness decreases with $\alpha$, and a summary of literature results is found in Figure 13.22. Lintymer et al. have studied hardness for Cr films composed of slanted posts [27] and chevrons [43]. The data suggest that structure type and period number of a GLAD film have an effect on hardness. However, the data are noisy, and further work will be required to ascertain the magnitude of such effects.

**Young’s modulus**

Helical columns fabricated using GLAD closely resemble springs, and many reports have been made on the Young’s modulus of such structures [27, 37, 38, 43, 44, 186, 229–233]. For many
Figure 13.22: Literature values for GLAD thin film hardness. Hardness decreases with increasing deposition angle. The Lintymer data are for Cr slanted posts (2003) and Cr chevrons (2005). Although noisy, the Lintymer data suggest that the structure type and period number of a GLAD film can affect hardness. Experimental data are described in the table. DLC: diamond-like carbon.

measurements, indentor size is large enough that an array of springs is probed in parallel, although atomic force microscopy (AFM) measurements have been made of isolated columns [229–231]. Limited measurements of shear resistance have been reported, but the result for Ta$_2$O$_5$ indicates, as expected, that GLAD films are more resistant to normally oriented stress than shear stress. The Young’s modulus values exhibited by GLAD films depend on material and deposition angle. Table 13.3 summarizes literature results.

**Stress**

Stress in GLAD films tends to be much reduced from that found in films deposited at $\alpha = 0^\circ$, assuming equivalent thickness. Since a GLAD film is made up of isolated columns, it is free to

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s (GPa)</th>
<th>Shear (GPa)</th>
<th>Structure</th>
<th>Deflection (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq$_3$</td>
<td>0.93</td>
<td>-</td>
<td>Helix</td>
<td>3.2</td>
<td>[233]</td>
</tr>
<tr>
<td>Cr</td>
<td>140</td>
<td>-</td>
<td>Helix</td>
<td>60–70</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>80–170$^a$</td>
<td>-</td>
<td>Slanted post</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>100–250$^a$</td>
<td>-</td>
<td>Chevron</td>
<td>-</td>
<td>[43]</td>
</tr>
<tr>
<td>Ni</td>
<td>154</td>
<td>-</td>
<td>Inverse helix</td>
<td>25</td>
<td>[186]</td>
</tr>
<tr>
<td>Si</td>
<td>94 ± 10</td>
<td>-</td>
<td>Slanted post</td>
<td>-</td>
<td>[231]</td>
</tr>
<tr>
<td>SiO</td>
<td>92</td>
<td>-</td>
<td>Helix</td>
<td>60–70</td>
<td>[38]</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>0.375</td>
<td>0.06</td>
<td>Helix</td>
<td>60–70</td>
<td>[44]</td>
</tr>
<tr>
<td>Ti</td>
<td>110</td>
<td>-</td>
<td>Helix</td>
<td>60–70</td>
<td>[38]</td>
</tr>
</tbody>
</table>

$^a$ Non-monotonic dependence on $\alpha$, measured for 0–50°.
undergo movement that is uncoupled over short length scales, which reduces stress. Stress in GLAD films has been the subject of, or noted in, many reports [39, 159, 234–237]. Using GLAD films as stress-reduction layers has been studied by Karabacak et al. [235] for W slanted post films and Sumigawa et al. [236] for Ta₂O₅ helical films. Initial work by Robbie et al. reported a 0.01 GPa residual stress in MgF₂ thin films deposited at α = 85° [159, 234]. Similar results were reported by Jaing et al., who studied residual stress in MgF₂ films as a function of deposition angle [237]. Jaing’s data indicate that stress depends non-linearly on α, but remains below 0.3 GPa in magnitude for 0° < α < 70°. Cuomo et al. report that stress decreases in diamond-like carbon films as deposition angle increases [39].

**Nanocarpet effect**

The mechanical response of an ensemble of columns to a droplet introduced to the film has been the subject of a few reports [238–240]. Such studies are important because they speak to the robustness of GLAD devices outside a controlled laboratory environment. Fan et al. studied the damage which occurs when a droplet strikes a vertical post GLAD film [238]. The authors identify a central damage region due to droplet impact, a surrounding region of columns which are tilted toward the center of the droplet as it spreads, and a final randomized region as the droplet edge percolates through the film. This work has been followed up by theoretical studies [239], and a study of droplet-induced damage as a function of GLAD structure [240]. Slanted posts were found to be the most resistant to droplet-induced damage; vertical posts the most susceptible.

**13.4.2.5 Electrical Properties**

Electrical properties of GLAD films have been studied by several groups [26, 27, 39, 241–243]. The development of columns can strongly affect the electrical properties of a GLAD thin film, and a few trends are observed in literature reports. First, increasing α increases in-plane resistivity as film density decreases, reducing the number of electrical pathways available [27, 243]. For thin diamond-like carbon films, resistivity decreases as incidence angle increases, probably due to an increasing number of sp² bonds [39]. Second, the development of columnar microstructure breaks the electrical symmetry of a GLAD thin film, exhibited as different electrical resistivities in directions parallel and perpendicular to the GLAD nanocolumns. This anisotropy also increases with α [26, 241, 243], although a maximum has been observed in Fe–Si multilayered structures [242]. GLAD film conductivity is important in sensor and solar applications.

**13.4.3 Bulk Properties**

**13.4.3.1 Optical Properties**

The microstructural and nanostructural control provided by GLAD makes it ideally suited to fabricating engineered optical materials, where optical properties are determined by the
structure. In thin films produced by PVD, the link between columnar structure and the film’s optical properties is well known [244, 245]. The traditional focus of PVD optical coatings is to produce homogeneous, robust, dense films. GLAD is a departure from this goal, aiming to create unique properties in thin film materials. The optics of GLAD thin films has been studied in great detail, so a very good understanding exists in the literature. Correspondingly, the dominant application of GLAD thin films has been optical.

In the earliest works on oblique deposition, researchers observed polarization-sensitive properties in obliquely deposited films [246]. Metallic films deposited at oblique incidence were found to preferentially absorb one polarization state over the other, a property known as dichroism. Similarly, transparent materials display birefringence [247]. The anisotropy observed in obliquely deposited films is not generated by crystal structure or stress, rather it is created by film structure.

In a stationary oblique deposition corresponding to a slanted post structure, the resulting film will be optically biaxial [248]. To describe such a material, three refractive indices and their respective orientations are required. These orientations are determined by the structure of the slanted post and are (i) along the column axis, (ii) lying in the plane and parallel to the broadening direction, and (iii) mutually orthogonal to the other two. A vertical post film is also anisotropic. However, because the structure is symmetric in the substrate plane only two refractive indices are required, one lying in and one perpendicular to the substrate plane [249]. The film is no longer biaxial, but instead the anisotropy is uniaxial.

Because of the structural control provided by the GLAD technique, optically isotropic materials can be engineered into anisotropic forms. Furthermore, the anisotropic magnitude and orientation can be varied throughout the thickness of the film via deposition angle adjustment. These two properties of the GLAD technique are used to fabricate polarization discriminating optics, discussed in Section 13.5.1.1.

**Effective medium theories**

GLAD thin films exhibit a distribution in column size, shape, and separation. Therefore, predicting film optical properties from first principles is very difficult. However, in any practical measurement, the beam spot is macroscopic in size and therefore averages over a number of columns. This immediately suggests theoretically approaching GLAD films with some sort of averaging method: exactly the basis of effective medium (EM) theory, which attempts to replace a heterogeneous structured system with a homogeneous uniform approximation that is much more amenable to further calculations [250, 251]. In general, the refractive index of a two-component mixture will depend on many parameters. We therefore define an effective refractive index $n_e$,

$$n_e = f (n_1, n_2, \rho_1, \lambda, \text{geometry})$$

(13.12)
where \( n_1 \) and \( n_2 \) are the indices of the two components, \( \rho_1 \) is the fraction of total volume occupied by component 1 (\( \rho_1 + \rho_2 = 1 \)), and \( \lambda \) is the wavelength of light (which is most often ignored based on a quasistatic approximation). \( n_e \) is also influenced by system geometry, which dictates the particular EM theory used. For example, the Maxwell–Garnett and Bruggeman EM equations can be respectively derived from a separated-grain structure and an aggregate structure [252]. The accuracy of a given EM theory depends on how well it represents the underlying microstructure of the real sample, in addition to knowing precise values for \( n_1, n_2, \) and \( \rho_2 \). That said, EM approaches have been successfully used by many researchers to approximate the properties of GLAD thin films [42, 253–256]. The anisotropy seen in GLAD films can be quantitatively understood using generalized versions of the classic Maxwell–Garnett and Bruggeman theories [257–260]. The Maxwell–Garnett equation is

\[
\frac{n_e^2 - n_2^2}{n_2^2 + q_2 (n_e^2 - n_2^2)} + \frac{n_2^2 - n_1^2}{n_2^2 + q_1 (n_1^2 - n_2^2)} \rho_1 = 0 \quad (13.13)
\]

and the Bruggeman equation is

\[
\frac{n_1^2 - n_e^2}{n_e^2 + q_1 (n_1^2 - n_e^2)} \rho_1 + \frac{n_2^2 - n_e^2}{n_e^2 + q_2 (n_1^2 - n_e^2)} \rho_2 = 0 \quad (13.14)
\]

In these theories, the constituent phases can adopt ellipsoidal shapes, providing a rough approximation of columnar structure, through the depolarization tensors \( q_1 \) and \( q_2 \). (In application, the approximation \( q_1 = q_2 \) is often used.) For an ellipsoid with axes \( a, b, c \), the principal axes of the depolarization tensor are aligned with the ellipsoid and are given by

\[
q_i = \frac{xyz}{2} \int_0^\infty \frac{ds}{(s + i^2) \sqrt{(s + a^2) (s + b^2) (s + c^2)}}, \quad i = a, b, c \quad (13.15)
\]

Tabulation of this integral for different ratios of the axes can be found in the literature [261]. In practice, however, the depolarization values \( q_a, q_b, \) and \( q_c \) are used as fitting parameters in numerical optimization, with the added constraint that \( q_a + q_b + q_c = 1 \).

**Optical indices**

The deposited film’s planar density is determined by shadow length and can, therefore, be controlled with deposition angle. Varying the amount of bulk material in the film provides a means of tuning the film’s refractive index. This has been demonstrated by many researchers investigating various important optical materials. Optical constants have been reported for many materials including dielectrics (\( \text{TiO}_2 \) [256, 262, 263], \( \text{Ta}_2\text{O}_5 \) [247, 256], \( \text{WO}_3 \) [247], \( \text{Nb}_2\text{O}_5 \) [34], \( \text{ZrO}_2 \) [256, 264], \( \text{HfO}_2 \) [106], \( \text{SiO}_2 \) [42], \( \text{MgF}_2 \) [42], \( \text{ZnS} \) [68]), semiconductors
Figure 13.23: Optical index as a function of $\alpha$ for several optical materials. The top figure shows the full range, while the bottom figure focuses on highly oblique angles. Literature references for these and other materials may be found in the text.

(Si [249]), chalcogenides ($a$-As$_2$S$_3$ [95, 265], $a$-As$_2$Se$_3$ [265], $a$-GeSe$_2$ [266], GeSbSe [104]), transparent conductors (ITO [267, 268]), and organics (Alq$_3$ [269]).

Figure 13.23 shows several data sets taken from the literature. The general relationship between $n$ and $\alpha$ is continuous and monotonic; increasing $\alpha$ lowers the film’s planar density and reduces $n$. At low $\alpha$, the deposited film is dense, with only a small fraction of void region, and $n$ approaches bulk thin film values. At high $\alpha$, the film is highly porous and $n$ asymptotically approaches unity. This can be seen in Figure 13.23, where as $\alpha$ nears 90°, the data sets converge toward $n = 1$, regardless of material.

Of particular note in Figure 13.23 are the data sets of the same material from different publications. Wang et al., Hawkeye and Brett, and Hodgkinson et al. all studied TiO$_2$ structures. Wang et al. [262] and Hodgkinson et al. [256] studied slanted post structures and Hawkeye and Brett [263] examined vertical post structures. Additionally, these investigations used different measurement techniques, with Wang et al. using Swaneopel’s method, Hawkeye and Brett fitting reflectance data, and Hodgkinson et al. using an ellipsometric technique. What can be seen in the data sets is good but not perfect agreement, which is quite reasonable given
the sensitivity of TiO$_2$ films to preparation conditions [270]. A similar conclusion can be reached in the reported optical constants of ITO from Zhong et al. [268] and Kim et al. [267], and of ZrO$_2$ from Wang et al. [264] and Hodgkinson et al. [256]. The agreement between these data sets highlights the applicability and reproducibility of the GLAD technique in controlling refractive index. While sensitivity to preparation conditions is an issue, it is a concern in any thin film manufacturing and process variables must always be optimized.

13.4.4 GLAD Properties Summary

One of the challenges for GLAD is rooted in the very aspect that makes GLAD films of such interest: the combination of different length scales together with the corresponding physics, into a single material. As we have seen in this section, understanding the behavior of GLAD columns requires well-developed nanoscale physics. In many cases, this understanding has not yet developed. While ballistic and Monte Carlo simulation methods are well developed, they are limited by our knowledge of the physics. Molecular dynamics simulations are one way to discover new phenomena from the bottom up, and current practical simulation sizes are nearly at a useful scale for GLAD films. While increasing computer speed and improved molecular dynamics simulation techniques will ease this burden, an increased theoretical effort will be required.

As the length scale increases, the physical understanding improves. The mid-range effects, such as surface area and mechanical properties, are more easily addressed experimentally, and have a better developed set of models on which to draw. The large-scale effects, such as optical properties, are well understood, and here the design of GLAD films for particular applications becomes much more straightforward. As we will see in the next section, the dominant applications of GLAD reflect this superior understanding of the long length scale effects. However, as a better understanding of the nanoscale physics present in GLAD develops, exciting new applications of GLAD films are anticipated.

13.5 GLAD Applications

GLAD thin films have found application in many fields, exploiting the properties discussed in the previous section. The dominant application of GLAD thin films is optical, reflecting in part the well-developed theoretical support, combined with the ease with which GLAD can control structure on a scale relevant to optical applications. Many applications, including sensor, catalysis, and energy applications, rely on the extremely large surface areas of GLAD thin films. In this section, we review a selection of the diverse applications to which GLAD films have been applied. The focus is on optical and sensor applications, with brief discussions of mechanical devices, catalysis applications, magnetic data storage, energy applications, and manufacturability of GLAD thin films.
13.5.1 Optical

13.5.1.1 Passive Optical Applications

Engineered birefringence

As discussed in Section 13.4.3.1, slanted post films are inherently birefringent leading to proposed application as optical waveplates and retarding elements. Motohiro and Taga investigated various metal oxide films and developed a Ta$_2$O$_5$ quarter waveplate based on a chevronic columnar structure [247]. Harris et al. fabricated various anisotropic layers from ITO, making birefringent transparent conducting films, for flat panel display applications [109]. Hodgkinson et al. developed the SBD technique to maximize film birefringence [145, 271]. Van Popta et al. combined SBD with annealing treatments, producing TiO$_2$ thin films with a birefringence of $\Delta n = 0.22$, the highest reported value in SBD films [272].

Chiral filters

The ability to control the optical anisotropy orientation has led to one of the most novel applications of the GLAD technique. In a helical columnar film, the optical anisotropy twists following the helical structure. This produces a periodic rotation of the planar anisotropy which is different for circular polarization states of left-and right-handedness. Light of the same handedness as the structure undergoes a Bragg reflection whereas light of the other handedness is transmitted. This leads to an optical filter distinguishing between circular polarization states of opposite handedness, reproducing the properties of cholesteric liquid crystals in an inorganic medium [273]. The optics of such media are complicated and theoretical investigations require either $4 \times 4$ matrix techniques [255, 274, 275] or dyadic approaches [276] to deal with the varying anisotropy. The reflectance band spectral location is determined by the helix pitch (vertical period) and the film’s average refractive index. Controlling the helical pitch is straightforward as it is determined by the substrate rotation speed relative to the deposition rate, allowing production of circular polarization filters for different wavelength regions [277]. By increasing the birefringence of the structure and/or the number of helical periods in the film, very strong optical effects can be achieved [278, 279]. More recent work has focused on increasingly sophisticated structures, such as helices with engineered defects [280], perturbed structures [281], polygonal helices [51], and apodized structures [282].

Optical coatings

Many researchers have fabricated GLAD optical coatings based on controlling refractive index. The refractive index can be controlled along the film thickness by changing $\alpha$ during deposition. Because various materials can be deposited and many refractive index profiles can be realized, the GLAD process provides significant design flexibility. Kennedy and Brett fabricated SiO$_2$ graded index antireflection coatings which strongly increase transmittance over a wide wavelength range [283]. The transmittance data for Kennedy’s film are given in Figure 13.24 for both transverse electric (TE) and transverse magnetic (TM) polarizations and incidence angles up to 30°.
Figure 13.24: GLAD fabricated graded-index antireflection coatings demonstrate excellent performance, with a maximum of 99.9% transmittance at normal incidence. Over 99% of incident light (both TE and TM polarizations) is transmitted through the sample over a broad wavelength range 450–1000 nm even at angles up to $30^\circ$. (Reproduced with permission from [283], © 2003 Optical Society of America.)

This work has been continued and extended in SiO$_2$/TiO$_2$ [284, 285] and ITO [267] (see Figure 13.25). Multiple groups have reported fabrication of optical rugate filters, which are characterized by a sinusoidal refractive index profile. These filters have been deposited using MgF$_2$ [234], Si [249], SiO$_2$ [178], and TiO$_2$ [286, 287]. Bragg multilayers have also been fabricated using Si [288], TiO$_2$ [289], ITO [108], and Eu-doped Y$_2$O$_3$ [61]. Rugate and Bragg

Figure 13.25: Reflectivity (TE) at 632 nm as a function of incidence angle. Closed squares are from Kennedy et al. [283] and are direct measurements of transmission. Open symbols are from Xi et al. [284] and Kuo et al. [285], and are reflectivity measurements. Vertical scales have been aligned assuming no scattering; reflectivity measurements thus represent an upper bound.
optical filter structures produce reflectance bands due to interference of light propagating through the film. Incorporating defects into the periodic index profile produces narrow peaks within the reflectance band of the film.

**Photonic crystals**

Another interesting application of GLAD is in the fabrication of three-dimensional (3D) photonic crystals (PCs). In a PC, the material is precisely structured to form a 3D dielectric crystal lattice. The combined effects of interference and scattering form photonic stopbands, analogous to the electronic stopbands in semiconductor crystals. The square spiral PC proposed by Toader and John, based on connecting nearest neighbors of the diamond lattice with dielectric cylinders, is amenable to fabrication with the GLAD technique [290]. SEMs of square spiral structures are shown in Figure 13.26(a, b). Inverse square spirals have also been predicted to exhibit good photonic band gap properties. Through an LPCVD process,

![Square spiral structures](image)

Figure 13.26: Square spiral structures, when arranged in a tetragonal lattice, are 3D photonic crystals. Direct square spirals are shown in (a) and (b), an inverse is shown in (c). ((a) Reproduced with permission from [291], © 2005 Optical Society of America, (c) reproduced with permission from [110].)
Although an initial increase in band gap reflectivity is observed, after three periods the reflectivity decreases. Data from Summers et al. and Ye et al. (Adapted from [110].)

Summers has produced a Si inverse structure, using a square spiral as a template [110]. A cross-sectional SEM is shown in Figure 13.26(c).

Achieving the planar ordering of square spiral columns requires deposition onto lithographically patterned substrates, which was first demonstrated by Kennedy et al. [292, 293]. Through simple modification of the underlying seed template, different defects can be engineered into the PC, a prerequisite for ultracompact integrated optic device proposals [123]. Much work has been devoted to optimizing the square spiral structure, eliminating problems such as broadening and bifurcation [140, 294]. The PhiSweep and substrate swing techniques have been used to maximize the optical properties of the square spiral PC, with recent results reporting forbidden bands with bandwidths of 16.1% [140] and 14.7% [294], respectively. In the results reported by both Ye et al. [294] and Summers and Brett [140], the stopband reflectivity increases with the number of PC periods up to three periods (Figure 13.27). At this point, structural degradation becomes problematic and the reflectivity decreases.

### 13.5.1.2 Active Optical Applications

#### Liquid crystal devices

Because the GLAD films are porous, it is possible to infiltrate the film with optically interesting materials such as nematic liquid crystals (LCs) [295, 296]. Nematic LCs are electrically controllable and have been used to create a switchable GLAD device [297]. In this device, helical columns were deposited onto an electrode layer. Another electrode layer was placed on top and the resulting cell was vacuum-filled with the LCs. In the unaddressed state (zero voltage) the LCs align with the helical structure and increase the polarization selectivity of the filter. Addressing the device aligns the LC and reduces selectivity. The device can therefore be electrically switched between states. Other recent work on GLAD/LC hybrids has examined the alignment of LC molecules in the GLAD structures [298, 299].
Luminescent devices

The GLAD technique can directly fabricate structures out of luminescent materials, producing polarized light emitters. Hrudey et al. fabricated slanted and helical columnar films from Y$_2$O$_3$:Eu [60, 169]. Depending on the particular structure, these films were found to preferentially emit one polarization state over the other. The slanted posts preferentially emitted linearly polarized light, with electric field vector aligned with the column tilt, and the helical columns emitted circularly polarized light of handedness opposite to the helical structure. The polarization selectivity of these films was relatively low, owing to a degradation of the structure in thicker films. This problem was overcome by Hrudey et al. by depositing helices made of Alq$_3$ [78, 79]. These helices maintained their structure over many periods and displayed much improved photoluminescence properties.

13.5.2 Sensors

The high porosity, large surface area, controlled morphology, and ability to use any PVD-compatible source material make GLAD films strong candidates for sensing applications. Properties such as response time, response shape and magnitude depend on the underlying film morphology. Given the very small pore size in GLAD films, Knudsen diffusivity can be applied to vapor movement through GLAD films. Assuming a pore with 10 nm radius, and an average thermal velocity of $\sim 600 \text{ m s}^{-1}$, a diffusivity of $\approx 4 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$ is expected. Applying Fickian diffusion yields an expected diffusion length scaling of $\sqrt{4Dt}$. Diffusion time through a 1.5 $\mu$m film should take $\approx 140$ ns, orders of magnitude faster than the experimental results, which suggests that adsorption is the limiting factor in GLAD sensors, rather than diffusion. This is opposite from the behavior of typical bulk sensors, and represents an interesting opportunity for GLAD-based sensor technology.

13.5.2.1 Optical Sensors

GLAD films are inherently sensitive to the ambient environment since any fluids moving into the porous film will change the material’s optical properties. This environmental sensitivity is advantageous for optical sensing applications. Lakhtakia et al. fabricated helical columns and monitored changes to the optical spectrum as liquids penetrated the film [280]. One of the weaknesses of GLAD sensors is specificity – the film will react to any gas which enters the film. Sensor specificity has been addressed in one case through chemical functionalization by van Popta et al., who reduced the hydrophilicity of a TiO$_2$ GLAD film [181]. Chemical functionalization was also used by Fu et al., who demonstrated fluorescence detection of Salmonella on Si–Au GLAD films [184].

Surface-enhanced Raman sensors

Another sensing approach which has received significant research attention is surface-enhanced Raman spectroscopy (SERS) [82, 166, 183, 219, 300, 301]. The interaction
of light with metal structures is highly sensitive to the surrounding medium’s dielectric constant. When molecules adsorb to the metal, they can be detected through shifts in the optical absorption peak. GLAD SERS substrates have exhibited enhancement factors as high as $5 \times 10^8$ [183], and are able to discriminate between different bacteria strains [302] and even between distinct RNA strands [301].

**Reflection/transmission monitors**

GLAD films have also been used in transmission or reflection modes for sensing applications [181, 303, 304]. Using a spectral hole filter, van Popta et al. [181] and Chang et al. [304] have produced sensors in which a transmission peak changes in response to changes in relative humidity. Such sensors could be fiber coupled to perform remote measurements. Zhang et al. have used a grating coated with GLAD nanorods in reflection, monitoring the adsorption of proteins on the surface through a change in the peak wavelength of a reflection peak [303].

**13.5.2.2 Electrical Sensors**

Electrically based sensors using GLAD films as sensing layers have been studied using many combinations of material and probe methods [94, 162, 185, 305–307]. GLAD humidity sensors typically exhibit a three order of magnitude change in capacitance combined with response times well below 100 ms. This application area is another example of the empirical development of GLAD exceeding the theoretical work. Initial attempts at modeling the electrical and temporal response of these sensors are underway [94, 202], but much work remains. An interesting use of the GLAD technique in this area was by Kanamori et al., who produced a porous electrode, allowing high-speed access to a fluorinated polyimide sensing layer [308].

**13.5.2.3 Mechanical Sensors**

Kesapragada and Gall created a pressure sensor from sputter-deposited Cr chevronic columns [126]. When a compressive load is applied to the film, each column elastically deforms and can contact neighboring columns. This changes the conduction path through the film, altering the film’s electrical resistance. The authors loaded the film with a pressure of 0.8 MPa (an estimated force of 0.1 nN per column) while monitoring resistance with a two-point probe measurement. The resistance reversibly changed by 50% during loading–unloading cycles. Larger pressures (> 1 MPa) resulted in plastic deformation of the structure and a degradation in sensor performance.

**13.5.2.4 Sensor Aging**

The advantages that render GLAD a promising platform for sensor technology are also a vulnerability, since the sensing medium is open to the environment and susceptible to damage. Relative humidity sensor response has been observed to degrade significantly over a period of several days [185]. The aging process for GLAD RH sensors is not well understood, and
presents an obstacle for application of such systems outside a laboratory setting. However, in the case of TiO$_2$ GLAD films, photocatalytic treatments have been shown to address the aging process, and it may be possible to extend such techniques to other material systems.

### 13.5.3 Mechanical Devices

Various devices have been developed based on the mechanical properties of GLAD microstructures, including electrically actuated devices [230, 233] and sensors [141] (see Section 13.5.2.3). Such technology could find application as standalone resonant devices or when integrated into microelectromechanical platforms. Electrically controlled actuation has been demonstrated with two approaches. Singh et al. deposited Si helical columns and coated them with a thin layer of Co (deposited by chemical vapor deposition) [230]. When a current is passed through the Co layer, a magnetic field is induced which creates an attractive force between the coils of the helix. The current is applied by an atomic force microscope. The compression of the helix can be tuned by varying the current passing through the coils, with a maximum displacement of 6 nm at a 20 mA current demonstrated by the authors. Another electrically based approach was taken by Dice et al., who fabricated Alq$_3$ helices between Al electrical contacts [233]. This parallel-plate capacitor arrangement creates an electrostatic force when the contacts are charged. At an applied voltage of 6 V, a 1.2 nm compression is observed.

Another approach to producing motion of GLAD structures is found in the work of He et al. [151]. Using GLAD, the authors fabricated chevronic Si columns with tips partially coated with Pt. After fabrication, the columns were ultrasonically removed from the substrate and dispersed in water. Upon adding H$_2$O$_2$, the structures rotated and moved in the solution. The structures are propelled by the decomposition of H$_2$O$_2$ into H$_2$O and O$_2$, a reaction catalyzed by the Pt layer. In addition to the chevronic structure, square spiral structures were also fabricated and catalytically propelled in a complicated 3D rolling motion. Through careful design and fabrication, it may be possible to create nanomotors based on this work.

### 13.5.4 Applications in Catalysis

Structured materials with high surface area are of great interest in catalysis where either the catalytic material itself is structured, or it is supported on a high surface area scaffold. Because GLAD is able to sculpt many materials into a high surface area form, there have been interesting examples of GLAD-fabricated catalysts.

Platinum is a widely used catalyst and structured GLAD Pt films have been investigated for various applications. Harris et al. fabricated Pt helices and used them to catalyze the breakdown of typical automotive exhaust compounds [72]. Bonakdarpour et al. used GLAD-fabricated titanium vertical columns as supports for Pt nanoparticles [89]. These
supported catalysts had an order of magnitude greater surface area than smooth Pt films, and were used as oxygen reduction electrocatalysts for fuel cell applications.

Titanium dioxide is a photocatalytic material compatible with the GLAD process. Several groups have studied the photocatalytic properties of TiO₂ thin films [153, 173, 309], or induced changes in the surface chemistry to adjust film properties [185]. Suzuki et al. studied the photocatalytic activity of GLAD films as a function of structure and deposition angle [309], with a maximum occurring at \( \approx 70^\circ \). This corresponds roughly to the maximum internal surface area for TiO₂ films, discussed in Section 13.4.2.3. Improved photocatalytic activity has been demonstrated with annealing of the TiO₂ structure [173], and fabrication of a WO₃/TiO₂ structure that enhances charge transfer [153].

### 13.5.5 Magnetic Tape Data Storage

Magnetic GLAD films possess anisotropic magnetic properties. Such films have high coercivities, a measure of the field required to change the film magnetization, a characteristic which is useful for information storage technologies. In particular, oblique deposition formed the basis of commercially manufactured video tape [310]. In this roll-to-roll coating process, spools of polymer tape substrate are unwound and exposed to the Co or Ni evaporation source. The source is partially shuttered and the tape receives flux from a range of oblique angles as it is pulled through the system. The fabrication of this product provides an interesting example of oblique deposition being scaled to industrial production.

Magnetic tape continues to be a mature, high-performance technology for data storage and oblique deposition is still a prominent manufacturing technique [311]. In order to achieve higher storage densities, the obliquely deposited layers must become thinner. Towards this goal, thinner films and smaller grain sizes can be achieved through the use of underlayers which serve to promote magnetic anisotropy in the subsequently deposited columnar structures [312, 313].

### 13.5.6 Energy Applications

There is increasing scientific, commercial, and social interest in developing clean and affordable energy technologies. In this research, nanofabrication techniques feature prominently and there are multiple examples using GLAD. Applications in this field focus on three main advantages of the GLAD technique: increased surface area, microstructural and nanostructural control, and material flexibility. Furthermore, the proven scalability and reliability of thin film production suggest reduced costs in manufacturing. The current state of research is preliminary, with basic proof-of-principle objectives being studied. More studies focusing on parameter optimization and device integration are required.
13.5.6.1 Charge Storage

Developing new and efficient charge storage devices is an important topic of energy research. Electrochemical capacitors have attracted attention because of their high energy densities, which make them suitable for applications such as battery miniaturization and hybrid vehicles [314]. Because electrochemical capacitors benefit from high surface areas, Broughton and Brett examined GLAD Mn films for application as electrochemical capacitors [222]. They report a measured specific capacitance of 256 F/g, which is only a moderate value. However, they emphasize the suitability of the process for high-throughput fabrication.

Another charge storage application of GLAD is in microbattery fabrication. Microbattery devices are being developed to improve the performance of modern electronics and microdevices such as microelectromechanical systems (MEMS). GLAD has been used to produce high surface area, structured electrodes for Li-ion rechargeable batteries. Figueroa et al. [56] deposited WO3 vertical and helical columns and Fleischauer et al. [315] fabricated Si vertical post structures. Both studies examined the charge storage characteristics of the structured materials.

13.5.6.2 Fuel Cells

Fuel cells are a promising future source of clean energy, but significant work is required on many aspects of these devices. In order to overcome issues with efficiency, hydrogen storage, and cost many nanofabrication techniques, including GLAD, are being applied to various aspects of fuel cell technology [66, 66, 89]. Saraf et al. have studied the use of GLAD to create higher efficiency electrolytes for solid oxide fuel cells [66]. They infiltrated GLAD-fabricated yttria stabilized zirconia (YSZ) columns with a CeO2 sol-gel solution for use as intermediate temperature electrolytes. The authors suggest that the increased CeO2/YSZ interface area will improve the ion conduction properties of the electrolyte and lead to more efficient fuel cell performance. Bonakdarpour et al. have produced columnar Ti supports for Pt catalysts [89]. Oxygen reduction and H2O2 release were characterized, and a 10–15 times enhancement in electrochemical surface area over a conventional smooth Pt surface was observed. Another group is studying the properties of GLAD-fabricated structures for hydrogen storage applications. He and Zhao have fabricated Mg columns using GLAD and coated them with a V catalysis layer in a second deposition process [316]. The combination of high-surface Mg and the presence of V as catalyst improved the hydrogen storage properties of the material.

13.5.6.3 Solar Cells

Solar cells are another intensely studied clean energy source. A common approach in solar cell research is to use high surface area electrodes to improve collection efficiency. Using GLAD, Kiema et al. fabricated and tested a dye-sensitized solar cell based on annealed TiO2 columns [168]. Xie et al. also fabricated TiO2 columns using GLAD for use in solar cells [317]. The ability to precisely control the column structure with GLAD provides an advantage over other approaches, such as using colloidal TiO2. GLAD has also been used in preliminary studies of
organic and hybrid solar cells. Gerein et al. spin cast an organic hole transport material into the void regions of a GLAD TiO$_2$ columnar film creating a very high interface area between the two materials [318]. With the GLAD process, van Dijken et al. fabricated high surface area copper phthalocyanine films for use in bulk heterojunction organic solar cells [86].

### 13.5.7 Microfluidics

Microfluidic applications of GLAD films have been studied for a number of years [319–321]. Seto et al. produced a combination of porous vertical posts and solid walls suitable for microfluidic applications with an engineered substrate [319]. Kiema et al. employed electron-beam lithography to produce an array of ordered columns, surrounded by unseeded areas [320]. The contrast in pore size distribution between the seeded area and unseeded area allows microfluidic flow to be confined to the patterned areas. Recently, Bezuidenhout and Brett demonstrated nanostructured ultrathin layer chromatography plates with 5 $\mu$m thick SiO$_2$ GLAD films [321]. These devices exploit GLAD’s capability to engineer structural anisotropy, and decoupled analyte movement from the solvent flow. With further development, two-dimensional chromatographic devices may be possible.

### 13.5.8 Manufacturability of GLAD Thin Films

The uniformity of GLAD thin films varies with structure and deposition angle, and is well discussed by Buzea et al. [322]. Film thickness for a slanted post film deposited at 70° is given in Figure 13.28. As expected, there is a significant variation with increasing distance between the vapor source and substrate position, and minimal dependence in the transverse direction.

![Figure 13.28: Thickness of a TiO$_2$ slanted post GLAD film as a function of substrate position.](image)

Since no substrate motion was used to produce the slanted posts, this represents a worst case for GLAD thin film uniformity. Directions are as defined in the schematic on the right, with the base of the arrows corresponding to (0,0). Vapor flux incident upon wafer from bottom of page with a 43 cm throw distance. A deposition angle of 70° was used. (Data courtesy of N.G. Wakefield and J.C. Sit.)
An increase in $\alpha$ will lead to larger variations in the longitudinal direction, but have minimal effect in the transverse direction. Since there is no substrate motion, no averaging of film flux can take place; slanted posts represent a worst case. For different structures, such as vertical posts or helices, a significant reduction in variation is observed.

13.6 Summary

GLAD is a highly flexible nanofabrication technique combining oblique angle deposition and precise manipulation of substrate position during deposition. By depositing at oblique angles, columnar structures arise owing to a combination of ballistic shadowing and limited surface diffusion. The resulting columns are tilted toward the incident flux direction, and can be sculpted into various morphologies: slanted and vertical posts, helices, chevrons, square spirals, and combinations thereof. GLAD can partially decouple the different length scales involved in thin film production, yielding novel materials with interesting properties. GLAD is compatible with a large number of materials, further increasing the combinatorial power of the GLAD technique.

Advanced GLAD techniques may offer additional control or modification of the canonical GLAD structures. Such techniques include forced nucleation through seeding and advanced substrate motion control to combat film broadening. GLAD films are robust, such that several postdeposition techniques such as annealing, etching, and oxidization can be used to further modify the structures. Many of these techniques may be applied in parallel, producing high-quality structures that may be tuned to match application needs.

GLAD can produce single-crystal columns without catalysts or postdeposition annealing. GLAD films have extremely large surface areas, and values as high as $10^9 \text{ m}^2 \text{ m}^{-3}$ have been observed. Stress in GLAD films is extremely low, because the porous structure is free to move. The refractive index of GLAD films can be tuned from a material’s bulk value down to $\approx 1$. The flexibility of the GLAD process has produced a variety of interesting properties, and rapid progress in the near future is expected.

While GLAD has been used for many applications, the dominant use to date is in optics. GLAD offers the unique ability to produce an engineered index gradient with a single material in a one-step deposition process, and has been used to produce high-quality optical filters. Control over 3D structure on the same length scale as optical band wavelengths has led to photonic crystal applications. Developing applications include sensors and energy applications, which depend on the large surface area of GLAD films. However, such applications are not as well developed, limited in part by insufficient understanding of the nanoscale physics accessible by GLAD thin films.

Although GLAD has seen impressive developments over the past 15 years, empirical studies are far ahead of theoretical ones. The factors controlling the fine details of column growth are
not yet well understood. However, it is clear from the literature that GLAD has access to an extremely large parameter space, and with further work the full power of GLAD will become available. As physical understanding and experimental techniques improve, exciting new applications for GLAD are expected.

References