Chapter 1

Overview

See how various the forms, and how unvarying the principles.

Owen Jones
The grammar of ornament, p. 157
Portland House, New York, NY, USA, 1986

A bird's eye view of research on sculptured thin films is presented in this chapter. Its scope is wider than the combined scopes of the remaining chapters, but the discussion is, of course, shallower. We recommend that this chapter be read before any other in this book.

Sculptured thin films (STFs) are nanostructured inorganic materials with anisotropic and unidirectionally varying properties that can be designed and realized in a controllable manner using physical vapor deposition (PVD). This overview chapter traces the development of STFs from their precursors, with emphasis on two seminal events that occurred in 1959 and 1966, as well as on the sculptured columnar morphology of these materials. The defining continuum electromagnetic constitutive relations of STFs are presented, along with a control model to link the nanostructure of STFs to their continuum properties via a local homogenization formalism, for optical purposes. Finally, a tour of accomplished and emerging applications is taken.

1.1 Introduction

In its decadal survey entitled *Physics in a New Era* conducted during the 1990s, the U.S. National Research Council (NRC) explored research trends and requirements in the materials sciences [1]. A dominant theme that emerged is of nanosciences and nanotechnologies. The nanoscale is Janusian: matter at the 10- to 100-nm length scale exhibits continuum characteristics, but molecules and their clusters of small size can still display their individuality. For that reason, the U.S. National Science Foundation (NSF) has begun to focus on material morphologies and architectures with at least one dimension smaller than 100 nm in its research initiatives.

Among the nanoengineered materials identified by the NRC are STFs [1, p. 123]. These nanostructured inorganic materials with anisotropic and unidirectionally varying properties can be designed and fabricated in a controllable manner [2–5] using PVD, a century-old technique.[1] The ability to virtually instantaneously change the growth direction of their columnar morphology, through simple variations in the direction of the incident vapor flux, leads to a wide spectrum of columnar forms. These forms can be

    (i) two-dimensional, ranging from the simple slanted columns and chevrons to the more complex C- and S-shaped morphologies [6]; or
    (ii) three-dimensional, including simple helixes and superhelixes [7].

A few examples of STFs are presented in Figs. 1.1 and 1.2, and a representative list of materials deposited as STFs is provided in Table 1.1.

For most optical applications envisioned, the column diameter and the column separation normal to the thickness direction of any STF should be constant. The

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[1]An excellent history of vacuum coating technologies by D.M. Mattox was serialized in the February 2002, March 2002, May 2002, August 2002, October 2002, November 2002, and February 2003 issues of the magazine *Vacuum Technology & Coating*. The complete work recently became available as a book [8].
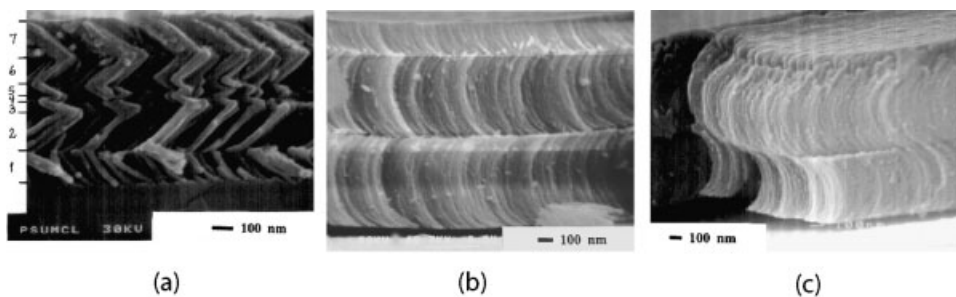
Figure 1.1 SEM micrographs of STFs made of magnesium fluoride (MgF_2) with two-dimensional morphologies: (a) 7-section zigzag; (b) C-shaped; (c) S-shaped.
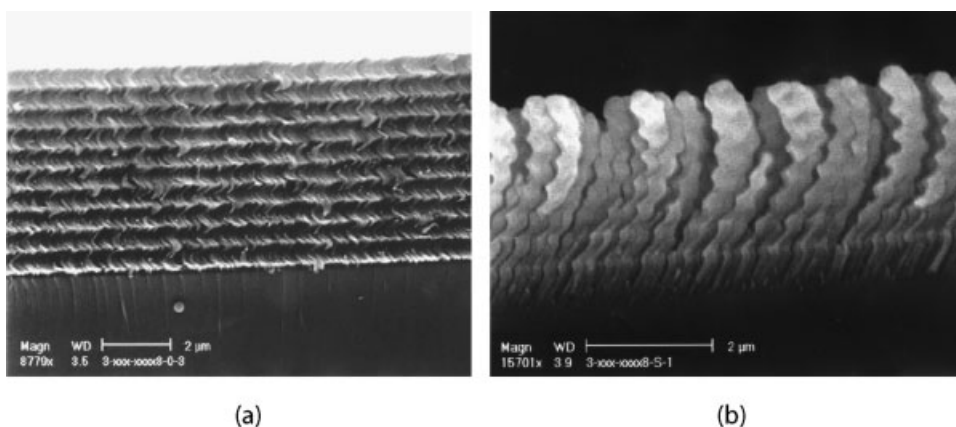

Figure 1.2 SEM micrographs of STFs with three-dimensional morphologies: (a) helical, made of silicon oxide (SiO); (b) superhelical, made of MgF_2.

Table 1.1 Materials deposited as STFs.

oxides	metals	semiconductors
aluminum oxide	aluminum	carbon
silicon oxide	bismuth	germanium
silicon dioxide	chromium	silicon
tantalum oxide	copper	
titanium oxide	iron	polymers
zirconium oxide	platinum	parylene
	titanium	teflon
	tungsten	
fluorides		
calcium fluoride		
magnesium fluoride		

column diameter can range from ~ 10 to 300 nm, while the density may lie between its theoretical maximum value and less than 20% thereof. The crystallinity must be at a scale smaller than the column diameter. The chemical composition is essentially unlimited, ranging from insulators to semiconductors to metals. De-

spite the fact that precursors of STFs have been made for over a century [9–16], systematic exploration of the science and technology of STFs began only during the mid-1990s. What is emerging from recent research [17–23] is that STF technology has a bright future.

At visible and infrared wavelengths, a single-section STF is a unidirectionally nonhomogeneous continuum with anisotropic constitutive properties. Several sections can be grown consecutively into a multisection STF, which can be conceived of as an optical circuit that can be integrated with electronic circuitry on a chip. Being porous, an STF can act as a sensor of fluids and can be impregnated with liquid crystals for switching applications too. Their application as low-permittivity barrier layers in electronic chips as well as for solar cells has also been suggested. Optical applications of STFs began to be systematically reported in 1999, although earlier instances can be found in the literature [12, 16, 24].

Looking back at the histories of various technologies, one finds two distinct patterns of early evolution. More often than not, a set of key experimental observations spurs theoretical developments. Less often, experimental research is engendered by theory—as exemplified by STFs. Right from the beginning, STF research was theoretical [2, 25]. STFs were conceived for optical purposes to be nonhomogeneous in the thickness direction but transversely homogeneous, in effect. In addition, anisotropy was incorporated as a key attribute of STFs. These features gave rise to a mathematical framework for enabling precise and predictable engineering of the polarization state of light, in addition to the widely practiced spectrum engineering and bandwidth control. Much experimental effort has been subsequently directed toward the realization of that goal. Therefore, nanoengineering of thin-film morphology, if not consonant with the theoretical conceptualization of STFs, lies outside the scope of this book.

1.2 From columnar to sculptured thin films

1.2.1 Columnar thin films

Chronologically as well as morphologically, it is sensible to begin with the so-called columnar thin films (CTFs). The growth of oblique-angle CTFs by PVD is usually credited to Kundt in 1886 [9]. At low temperature and pressure, material in a source boat evaporates toward a substrate held at an angle to the incoming directional vapor flux, as shown in Fig. 1.3, and the arriving atoms settle on it to form a thin film. Nucleation clusters 1 to 3 nm in diameter initially form on the substrate. The clusters evolve into expanding and competing cone-shaped columns as the film thickness increases, provided the film temperature is maintained below about a third of its melting point [26]. This results in a fractal-like array of surface features and an associated void network defining the features.

The cross-section morphologies of a thin film of hydrogenated amorphous silicon, a thick film of pyrolytic graphite, and an agate are shown in Fig. 1.4. All of
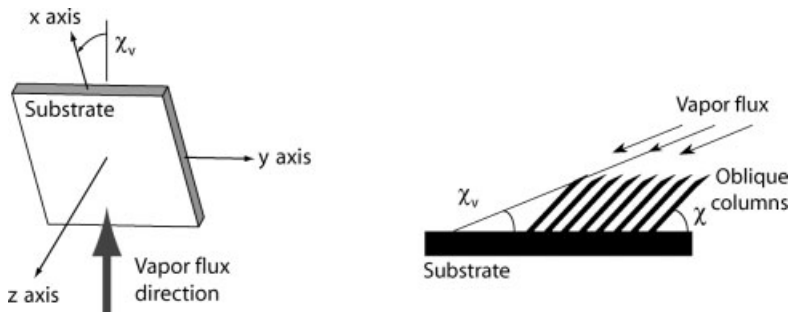
Figure 1.6 Coordinate system, the vapor incidence angle χ_v, and the column inclination angle χ.

1.2.2 Growth mechanics

Columnar thin films are the direct result of self-shadowing at the length scale of the arriving adatoms (which are atoms on the growing film surface before they attain their final free energy state). CTFs are fabricated under low-adatom-mobility conditions—where the sticking coefficient for adatoms is essentially unity and when the vapor arrives from a specific direction, either totally (e.g., in evaporation from a point source at 10^{-5} Torr) or on average (e.g., in sputtering from a planar source at 10^{-3} to 10^{-1} Torr). Only two issues need to be addressed in order to understand the origin of CTFs:

(i) whether the arriving adatoms form a continuous, and thus uniform, network or do they cluster; and

(ii) if they form clusters, then do the clusters grow independently or do they compete for growth much like the leaves of a tree vying for sunlight?

Extensive research has revealed that clusters with associated honeycomblike density deficit regions (commonly called void networks) are formed. Furthermore, the clusters do compete for growth, leading to power-law-shaped columns that are hierarchical cluster aggregates resembling a cauliflower when viewed from above their top surface. This has been seen experimentally [29–31] and has also been modeled via ballistic aggregation [32] and molecular dynamics [33] simulation studies.

For deposition normal to the substrate surface (i.e., $\chi_v = 90$ deg), the adatoms arrive on rectilineal trajectories and form clusters 1- to 3-nm in size [26, 31]. The sizes of these clusters have a statistical variation, and the larger clusters tend to capture more of the arriving adatoms. But the clusters do not simply get larger; rather, more clusters of similar size-distribution continue to form atop the clusters formed earlier, and the clusters tend to aggregate hierarchically, which leads to competitive columnar growth [26]. The edges of the dominant columns have a capture radius that extends beyond the perimeter of the cluster/column boundary,

thus making columnar expansion a possibility. This statistically favorable expansion of the tallest columns leads to shadowing of the smaller adjoining columns. As the top surface area is virtually fixed, at least one column must contract for every column that expands. In the absence of any additional moderating mechanism, the columns evolve eventually to yield a cauliflowerlike surface morphology observable with conventional scanning electron microscopes for films greater than $\sim 1\ \mu$m thickness. This has been classified as the Zone 1 morphology in the well-known structure zone model (SZM) [34, 35]. The column diameters expand according to a power-law dependence in which the power-law exponent is a function of the deposition conditions [29, 36].

The columns *can* become noncompetitive in their growth evolution [28]. These parallel columnar structures constitute the so–called matchstick morphology, since they resemble a bundle of wooden matchsticks when viewed from the top and the sides [7, 37]—not unlike the parallel pins in the toy Round Pin Point™ in Fig. 1.7

Figure 1.7 The parallel steel pins of the toy Round Pin Point™ replicate the matchstick morphology of Zone M quite well.

Figure 1.8 In contrast to the steel pins in the toy of Fig. 1.7, the primary and the secondary trunks as well as the aerial roots of a banyan tree (*Ficus indica*) are irregularly arranged and are, perhaps, closer to the morphology of CTFs.

1.2.4 Primitive STFs with nematic morphology

A seminal event occurred in 1966 that eventually led to the emergence of the STF concept in 1994 [2]. While a CTF was growing, Nieuwenhuizen and Haanstra deliberately altered χ_v to prove that columnar morphology "cannot be a result of the method of preparation itself" [15]. The resulting change in χ was accomplished while the film thickness grew ~ 3 nm, the transition being practically abrupt in the visible and infrared regimes. Some two decades later, Motohiro and Taga demonstrated that χ can be abruptly altered easily during growth [16], which was confirmed a few years later [59]. This ability is the basis for realizing STFs with bent nematic morphologies.

Thus, primitive STFs with zigzag and chevronic morphologies came into existence. The similarity of CTFs to crystals had long been noticed in the optical literature [42], so that the primitive STFs with nematic morphology can be considered as stacked crystalline plates. This has been astutely exploited for designing, fabricating, and testing various optical devices [43, 60]. Furthermore, serial as well as simultaneous bideposition of CTFs and chevronic STFs are now routine in the manufacture of wave plates for the automobile industry [61–63].

1.2.5 Chiral STFs

Another seminal event toward the emergence of the STF concept had already occurred in 1959. Although that event went largely unnoticed, all credit for periodic STFs with chiral (i.e., handed) morphology should be accorded to Young and Kowal [12]. Without actually seeing the anisotropic morphology of CTFs via scanning electron microscopy or otherwise, these two pioneers consciously [64] rotated the substrate about the z axis constantly during growth to create thin films of calcium fluoride with morphology predicted to display transmission optical activity. Most likely, they were the first researchers to deliberately engineer thin-film morphology for producing a nontrivial STF—one with a fully three-dimensional morphology.

The concept of *voids* in thin films was to become common 12 years later. Remarkably, however, Young and Kowal actually used that word to conjecture that "the [optical] activity of a helically deposited film could be due to the co-operative action of a helically symmetrical arrangement of crystallites, crystal growth or voids." Furthermore, they conjectured that the columnar direction could change virtually instantaneously and continuously with changes in the position and the orientation of the substrate. Happily, the Young–Kowal technique of rotating the substrate, the helicoidal morphology realized thereby, and the transmission optical activity of chiral STFs, were rediscovered in the last decade [65–67].

1.2.6 Sculptured thin films

Recognition finally came, during the 1990s, that

(i) a very wide variety of columnar morphologies is possible through control of two fundamental axes of substrate rotation;

(ii) multisections with different columnar morphologies and/or different materials are possible;

(iii) a wide range of potential applications exists; and

(iv) preparation–property–application connections can be truly engineered by coupling theoretical and experimental results.

The concept of STFs then emerged in short order [2, 3].

STFs are modifications of CTFs in which the column direction can be changed almost abruptly and often, even continuously, during growth. When CTFs are obliquely deposited, a wide variety of STF morphologies tailored at the nanoscale are realizable by simple variations of two fundamental axes of rotation, either separately or concurrently [6, 37, 65, 68–75]. These fundamental axes lead to two canonical classes of STFs that have been termed

(i) sculptured nematic thin films (SNTFs) [6], and

(ii) thin-film helicoidal bianisotropic mediums (TFHBMs) [2, 65].

More complex shapes and even multisections, in which either the material or the shape or both are changed from section to section along the z axis, have been executed [76, 77].

SNTF morphologies include such simple two-dimensional shapes as slanted columns, chevrons, and zigzags as well as the more complex C- and S-shapes; see Fig. 1.1. The substrate has to be rotated about the y axis, which lies in the substrate plane and is perpendicular to the vapor incidence direction, while χ_v is varied either episodically or continuously [6]. One concern with this approach is related to the fact that the density of a CTF is highly dependent upon χ_v [5, 6, 70] and, therefore, density variations arise as an SNTF grows. As discussed in Sec. 8.2.3, the compensation of these variations is an area of future research.

TFHBMs are fabricated by tilting the substrate at some oblique angle to the incident vapor flux (i.e., $\chi_v < 90$ deg), followed by substrate rotation about the z axis. Helicoidal morphologies result for constant rotational velocity about the z axis [12, 65]. By varying the rotational velocity in some prescribed manner throughout a rotational cycle, a slanted helicoidal structure occurs with the slant angle controllable over all χ above its minimum value for static glancing angle deposition. Furthermore, by making the rotational cycle $\Delta + 360$ deg, where $\Delta \neq 0$ deg is some chosen phase-shift angle, it is possible to engineer a wide range of superhelixes with controlled handedness [5, 37]. The mass density as a function of film thickness is expected to remain constant since χ_v is fixed for TFHBMs, so long as the columns attain a steady-state diameter in the early nucleation and growth stages.

However, as seen in Fig. 1.2, the column width of the superhelix increases with growth evolution, which begs the scientific question: Why? In many reports

on STFs, the columns shown by cross-section scanning electron microscopy usually appear parallel with cross-section diameters ranging between 10 and 300 nm and with a similar range in separation distances. Since most optical applications of STFs will require that the column diameter, the separation distance between columns, and the connectivity between columns all remain constant during growth, this steady-state column size condition has practical advantages. For instance, when an STF deposition cycle is repeated for a multiple-period TFHBM prepared by both evaporation and sputtering at constant angular velocities of substrate rotation, it is important that the last turn has the same pitch and porosity as all previous turns. This morphological reproducibility leads to, for instance, predictable optical activity spectrums [67, 73], since the column sizes and shapes allow the STFs to effectively act as rotationally nonhomogeneous continuums at optical frequencies [4]. This can only occur if the films evolve from the initial clusters into steady-state, noncompetitive, parallel columns within a small fraction of the total film thickness, and constant cross-section as well as constant porosity is maintained for the remainder of the film growth.

1.3 Time-harmonic electromagnetic fields

Although nonoptical applications of STFs are certainly possible [3, 78, 79], optical applications have been the chief drivers of STF research [17, 18, 77, 80, 81]. Moreover, optical monitoring of STF growth appears necessary in a production setting. Therefore, the linear electromagnetic properties—mostly for application in the visible and the infrared regimes—of STFs are recounted in this section.

1.3.1 Linear constitutive relations

By definition, the morphology of a single-section STF in any plane $z = z_1$ can be made to coincide with the morphology in another plane $z = z_2$ with the help of a suitable rotation. In other words, the *local* morphology is spatially uniform, but the *global* morphology is unidirectionally nonhomogeneous. Naturally, this leads to the concept of local constitutive properties of an STF. The global constitutive properties of an STF can be connected to the local ones by means of rotation dyadics.

The most general linear medium is bianisotropic; i.e., both $\mathbf{D}(\mathbf{r}, \omega)$ and $\mathbf{B}(\mathbf{r}, \omega)$ are linear functions of both $\mathbf{E}(\mathbf{r}, \omega)$ and $\mathbf{H}(\mathbf{r}, \omega)$, in a direction-dependent manner [82]. Accordingly, the linear frequency-domain (or time-harmonic) constitutive relations of a single-section STF are set up as

$$\mathbf{D}(\mathbf{r}, \omega) = \epsilon_0 \underline{S}(z) \cdot \left[\underline{\underline{\epsilon}}_{ref}(\omega) \cdot \underline{S}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega) \right.$$

$$\left. + \underline{\underline{\alpha}}_{ref}(\omega) \cdot \underline{S}^T(z) \cdot \mathbf{H}(\mathbf{r}, \omega) \right], \tag{1.11}$$

$$\mathbf{B}(\mathbf{r}, \omega) = \mu_0 \underline{S}(z) \cdot \left[\underline{\underline{\beta}}_{ref}(\omega) \cdot \underline{S}^T(z) \cdot \mathbf{E}(\mathbf{r}, \omega) \right.$$

$$\left. + \underline{\underline{\mu}}_{ref}(\omega) \cdot \underline{S}^T(z) \cdot \mathbf{H}(\mathbf{r}, \omega) \right], \tag{1.12}$$

where the superscript ^{T} denotes the transpose. These equations model the STF as a bianisotropic continuum. Whereas the relative permittivity dyadic $\underline{\underline{\epsilon}}_{ref}(\omega)$ and the relative permeability dyadic $\underline{\underline{\mu}}_{ref}(\omega)$ represent the reference (or local) electric and magnetic properties, respectively, the dyadics $\underline{\underline{\alpha}}_{ref}(\omega)$ and $\underline{\underline{\beta}}_{ref}(\omega)$ delineate the reference magnetoelectric properties. All four of these constitutive dyadics have the same form as the right side of Eq. (1.6). Gyrotropic terms (of the type $\mathbf{v} \times \underline{I}$, where $\mathbf{v}$ is some vector and $\underline{I}$ is the identity dyadic) can be added to any or all of the four reference constitutive dyadics [83]. For a purely dielectric STF, both $\underline{\underline{\alpha}}_{ref}(\omega)$ and $\underline{\underline{\beta}}_{ref}(\omega)$ are equal to the null dyadic, and $\underline{\underline{\mu}}_{ref}(\omega)$ is equal to the identity dyadic.

Nominally, all columns in an STF twist and bend identically as z changes, a feature that is captured by the rotation dyadic $\underline{\underline{S}}(z)$. This dyadic is some composition of the following three elementary rotation dyadics:

$$\underline{\underline{S}}_x(z) = \mathbf{u}_x\mathbf{u}_x + (\mathbf{u}_y\mathbf{u}_y + \mathbf{u}_z\mathbf{u}_z)\cos\xi(z)$$
$$+ (\mathbf{u}_z\mathbf{u}_y - \mathbf{u}_y\mathbf{u}_z)\sin\xi(z), \tag{1.13}$$

$$\underline{\underline{S}}_y(z) = \mathbf{u}_y\mathbf{u}_y + (\mathbf{u}_x\mathbf{u}_x + \mathbf{u}_z\mathbf{u}_z)\cos\tau(z)$$
$$+ (\mathbf{u}_z\mathbf{u}_x - \mathbf{u}_x\mathbf{u}_z)\sin\tau(z), \tag{1.14}$$

$$\underline{\underline{S}}_z(z) = \mathbf{u}_z\mathbf{u}_z + (\mathbf{u}_x\mathbf{u}_x + \mathbf{u}_y\mathbf{u}_y)\cos\zeta(z)$$
$$+ (\mathbf{u}_y\mathbf{u}_x - \mathbf{u}_x\mathbf{u}_y)\sin\zeta(z). \tag{1.15}$$

The angular functions of z in these equations may be specified piecewise: either $\underline{\underline{S}}(z) = \underline{\underline{S}}_x(z)$ or $\underline{\underline{S}}(z) = \underline{\underline{S}}_y(z)$ for SNTFs, while $\underline{\underline{S}}(z) = \underline{\underline{S}}_z(z)$ for TFHBMs. Although TFHBMs need not be periodically nonhomogeneous along the z axis, it is easy to fabricate them with periods chosen anywhere between 50 and 2000 nm. Chiral STFs are generally analyzed as periodic dielectric TFHBMs with $\zeta(z) = \pi z / \Omega$, with 2Ω as the structural period [84].

Multisection STFs are cascades of single-section STFs fabricated in an integrated manner [3]. The five dyadics $\underline{\underline{S}}(z), \underline{\underline{\epsilon}}_{ref}(\omega), \underline{\underline{\mu}}_{ref}(\omega), \underline{\underline{\alpha}}_{ref}(\omega)$, and $\underline{\underline{\beta}}_{ref}(\omega)$ are defined differently for each section, the transitions between the sections being virtually abrupt and, therefore, optically inconsequential [76, 77].

1.3.2 Electromagnetic wave propagation

The foregoing section makes it clear that an STF is transversely homogeneous (at least in the wavelength regimes of interest) but nonhomogeneous along the z axis. Therefore, electromagnetic wave propagation in an STF is best handled using 4×4 matrixes and column vectors of size 4. At any given frequency, with the transverse wavenumber κ and the angle ψ fixed by excitation conditions, the following spatial