

SCULPTURED THIN FILMS

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Keywords: biological, chemical, circular Bragg phenomenon, constitutive relations, fabrication, nanotechnology, optical, plasmonic, sculptured thin films, thermal.

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Summary

Sculptured thin films (STFs) are assemblies of nanowires that can be fabricated from many different materials, typically via physical vapor deposition onto rotating substrates. The curvilinear-nanowire morphology of STFs is determined by the substrate motions during fabrication. The optical properties, especially, can be tailored by varying the morphology of STFs. In many cases prototype devices have been fabricated for various optical, plasmonic, thermal, chemical, and biological applications.

1. Introduction

A sculptured thin film (STF) is an assembly of nanowires typically grown by physical vapor deposition, whose bent and twisted forms are engineered via the growth process. As a result of the flexibility in controlling the evolving nanostructure of the films during fabrication, their optical and other properties can be engineered.

The curvilinear-nanowire morphology of STFs is exemplified by Figure 1. Note the individual nanowires that make up the STF in this case are helical; they are also nominally identical and parallel. The constituent nanowires of an STF have diameters of ~10–300 nm, and lengths on the order of tens of nanometers to several micrometers. The nanowires are made of clusters 1–3 nm in linear dimension. Therefore, STFs may be classified as nanomaterials. For many applications dependent on optical or infrared

radiation, the closely packed nanowires can be treated effectively as equivalent to an anisotropic and non homogeneous continuum.

Possibly the first STF was fabricated by Young and Kowal in 1959, who made fluorite films via oblique evaporation onto a rotating substrate. Although the structure of the resulting film was not unambiguously determined, the film did display optical activity. Most likely, the film was structurally chiral, as in Figure 1. This development was preceded by about 75 years of growing columnar thin films by thermal evaporation. Columnar thin films are assemblies of parallel straight nanowires, and are optically akin to biaxial crystals. The emergence of scanning electron microscopy in the late 1950s and early 1960s led to the confirmation of nanowire morphology. In 1966, a significant event occurred when Nieuwenhuizen and Haanstra showed that the nanowire inclination could be altered within a transitional distance of about 30 nm.

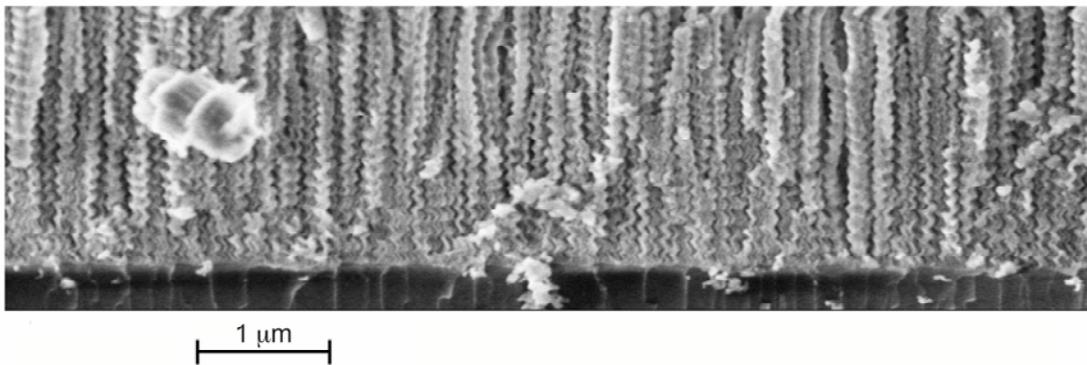


Figure 1: This scanning electron micrograph shows that the helical nanowires of a chiral STF are nominally parallel and identical to each other. Courtesy: M. W. Horn, The Pennsylvania State University.

Messier and colleagues further identified the conditions for the emergence of the nanowire morphology. In 1989, Motohira and Taga showed that the direction of growing nanowires could be altered often within a few nanometers by appropriately switching the direction of the incoming vapor mid-deposition. Lakhtakia and Messier realized that nanowires with almost arbitrary shapes could be fashioned by continuously changing the direction of the incoming vapor during deposition. Robbie and colleagues reported the first STF with unambiguously determined structure. Since that time, hundreds of research papers, a monograph, and many book chapters have been written on STFs.

This brief entry contains a description of STFs and the physical phenomena exhibited by STFs. In many cases, those phenomena are due directly to the symmetries that the structures of the constituent nanowires break.

In Section 2, we briefly review the fabrication of STFs. Then in Section 3, we present the mathematical description of the constitutive relations of STFs. In Section 4, we review the optical, plasmonic, thermal, chemical, and biological applications to which STFs either have been put or have been suggested. The advantages and disadvantages of STF technologies compared to other technologies are presented in Section 5. We end with some concluding remarks in Section 6.

2. Fabrication

STFs are chiefly fabricated by physical vapor deposition. Several variants exist, of which thermal evaporation is the simplest. A source material is evaporated under high vacuum and the vapor allowed to flow at an oblique incidence angle χ_v onto a substrate, as schematically depicted in Figure 2. When the temperature of the source material is less than approximately one-third the melting temperature, there is little surface diffusion, and straight nanowires form. The morphology is enabled by the shadowing of nanowires by those in front of them.

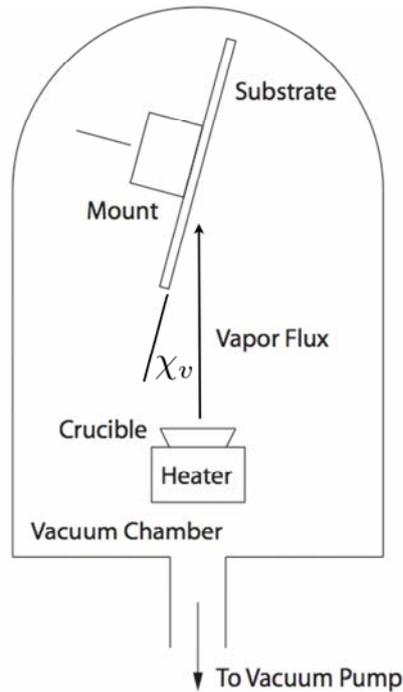


Figure 2: Schematic for fabrication of STFs by thermal evaporation. The source material is placed in a heated crucible, from which the vapor flux is allowed to fall obliquely on a substrate. A motorized mount allows the orientation of the substrate to be varied with time.

The nanowire morphology can be changed during deposition by tilting and rotating the substrate. When the substrate is rotated about a direction perpendicular to the substrate and passing through it, the nanowires become helical. These structures form the basis of chiral STFs, also known as thin-film helicoidal bianisotropic mediums (TFHBMs). Several scanning electron micrographs of STFs, including TFHBMs, are shown in Figure 3.

In addition, the substrate can be rotated about an axis in the plane of the substrate. Changing the tilt along either or both of two such orthogonal axes can lead to zigzag, c-, and s- shaped nanowires. Such STFs are known as sculptured nematic thin films (SNTFs). Several scanning electron micrographs of SNTFs are shown in Figure 3.

Hybrid STFs that consist of both TFHBM and SNTF sections grown one after another are also possible. For example, Suzuki and Taga fabricated hybrid STFs with zigzag,

helicoidal, and straight nanowire sections. More recently, Park et al. grew a hybrid STF comprising three different chiral sections.

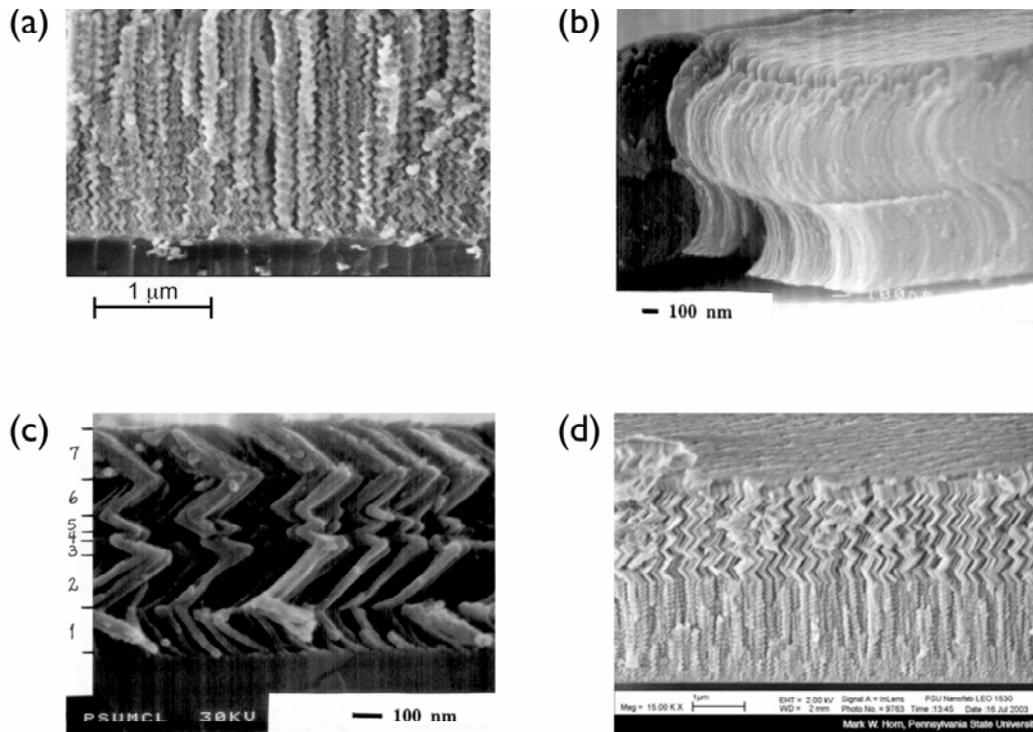


Figure 3: Examples of (a) thin-film helicoidal bianisotropic medium, (b) and (c) sculptured nematic thin films, and (d) hybrid STFs. Courtesy: M. W. Horn and R. Messier, The Pennsylvania State University.

Several variations on the basic scheme are possible, including serial bideposition, multideposition, pre patterning of substrates, and hybrid chemical/physical vapor deposition. In serial bideposition, a single source is used to fabricate films with large local birefringence. For example, when growing chiral STFs, the source is manipulated to deposit alternately on either side of the growing nanowires. Multideposition consists of two or more sources being simultaneously evaporated to grow STFs. Hybrid chemical/physical vapor deposition has been used to fabricate polymeric STFs, because such materials cannot typically be heated to produce a collimated vapor. Inverse structures can be formed by infilling of STF voids via electrodeposition of metal or infiltration of molten polymer, and subsequent removal of the initial STF via etching.

STFs can be fabricated from just about any material that can be evaporated. A wide variety of materials, including dielectrics, metals, and polymers have been used to fabricate STFs. These include oxides (e.g. iron oxide, silicon oxide, tantalum oxide, tin oxide, titanium oxide, zirconium oxide), fluorides and nitrides (e.g. calcium fluoride, magnesium fluoride, indium nitride), metals (e.g. aluminum, chromium, copper, manganese, molybdenum), semiconductors (e.g. silicon), carbon, GeSbSe chalcogenide glasses, luminescent tris(8-hydroxyquinoline) aluminum (Alq₃), and polymers (e.g. parylene). Inverse structures have been made from, for example, gold, nickel, and polystyrene.

The structures into which STFs can be formed have also expanded to include three-dimensional STF architectures. STFs can be deposited on substrates that have been patterned via lithography or other processes. The STF nanowires grow on the raised areas (and, depending on the angle of incidence of the vapor, the side walls) to form three-dimensional structures. Alternatively, the pre-deposition of arrays of small islands, or seeds, of source material can result, after STF deposition, in patterns of single nanowires or clusters of nanowires.

STF technology was recently augmented into the conformal-evaporated-film-by-rotation (CEFR) technique to replicate the intricate surface features of templates of biological origin. The CEFR technique is the combination of thermal evaporation with simultaneous substrate tilting and high-speed rotation. The potential of the CEFR technique has been demonstrated in the replication of planar as well as curved biological templates with surface features on the micro- and nano-scales. The compound eyes of flies, the wings of butterflies, and the exoskeletons of beetles have been replicated with high fidelity. An additional application is the conformal coating of the outermost surfaces of microelectronic circuits.

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Biographical Sketches

Joseph B. Geddes III graduated from the Pennsylvania State University with bachelors and masters degrees in 2001, and with a doctoral degree in 2006—all in Engineering Science and Mechanics. His work focused on the time-domain optical response of nonhomogenous, anisotropic, and nonlinear materials like chiral sculptured thin films to excitation by ultra- short optical pulses. He won the Schreyer Honors College Dean’s Research Award and the Xerox Research Award in 2001 for his BS and MS theses, respectively, and he was awarded a NSF Graduate Fellowship and a SPIE Educational Scholarship. His work centers on the optics of complex natural and synthetic materials, and he has published over 20 journal papers in that field. He is currently a Beckman Postdoctoral Fellow at the University of Illinois at Urbana-Champaign. At the Beckman Institute he has extended his research in the design and optical interrogation of complex materials. His projects have included analysis of curved photodector arrays for improved cameras, design of highly nonlinear metal-dielectric composites, and optical pulse shaping for coherent control of Raman microscopy.

Akhlesh Lakhtakia was born in Lucknow, India on July 1, 1957. He obtained a Bachelor of Technology degree in Electronics Engineering from the Banaras Hindu University, Varanasi, India in 1979; Master of Science and Doctor of Philosophy degrees in Electrical Engineering from the University of Utah, Salt Lake City in 1981 and 1983, respectively. Thereafter, he joined the faculty of the Pennsylvania State University, where he was elevated to the rank of Distinguished Professor of Engineering Science and Mechanics in January 2004. In 2006, he became the Charles Godfrey Binder (Endowed) Professor of Engineering Science and Mechanics. He also serves as a Professor in the Graduate Programs in Materials and Forensic Science. From 2004 to 2007 he also held the rank of a Visiting Professor of Physics at Imperial College, London. He has published more than 690 journal articles; has contributed 20 chapters to research books and encyclopedias; has edited, co-edited, authored or co-authored 16 books and 12 conference proceedings; has reviewed for 122 journals; serves on the editorial boards of four electromagnetics journals; was the Editor-in-Chief of the international journal *Speculations in Science and Technology* from 1993 to 1995; and became the first Editor-in-Chief of the online *Journal of Nanophotonics* published by SPIE from 2007. He served as an international lecturer for the International Commission for Optics and the Optical Society of America; was twice a Visiting Professor of Physics at Universidad de Buenos Aires, a Visiting Professor of Physics at the University of Otago, and a Visiting Fellow in Mathematics at the University of Glasgow; headed the IEEE EMC Technical Committee on

Nonsinusoidal Fields from 1992 to 1994; and is a Fellow of the Optical Society of America, SPIE, the American Association for the Advancement of Sciences, and the Institute of Physics (UK). He also served as the 1995 Scottish Amicable Visiting Lecturer at the University of Glasgow. He received the PSES Outstanding Research Award in 1996, the PSES Premier Research Award in 2008, and the PSES Outstanding Advising Award in 2005. For his research on sculptured thin films and complex-medium electromagnetics, he received the Faculty Scholar Medal in Engineering in 2005 from the Pennsylvania State University, a Doctor of Science degree in Electronics Engineering from the Banaras Hindu University in 2006, and the 2010 SPIE Technical Achievement Award. Nanotech Briefs recognized him in 2006 with a Nano 50 Award for Innovation. The University of Utah made him a Distinguished Alumnus in 2007. His current research interests lie in the electromagnetics of complex materials, sculptured thin films, chiral nanotubes, nanoengineered metamaterials, engineered biomimicry, and surface multiplasmonics. At Penn State, he co-developed a course on green engineering for undergraduate engineering students, as well as a course on fundamentals of engineering principles and design for pre-service elementary schoolteachers.

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