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Viewpoint Paper

Oblique-angle deposition: Evolution from sculptured thin films to bioreplication

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Abstract—The versatile oblique-angle deposition (OAD) technique, which is based on traditional vapor-deposition processes, allows the growth of thin films comprising one-, two- and three-dimensional complex nanostructures. The OAD technique has evolved into the conformal-evaporated-film-by-rotation (CEFR) and the modified CEFR (mod-CEFR) techniques, which have been successfully used to coat biotemplates for possible replication. Finally, the Nano4Bio technique – which is the sequential combination of the mod-CEFR technique, electroforming, plasma ashing and stamping/casting – is emerging as a robust and industrially scalable manufacturing process to fabricate bioreplicas.

Keywords: Oblique-angle deposition; Conformal-evaporated-film-by-rotation (CEFR) technique; Modified CEFR technique; Nano4Bio technique; Columnar thin film

Condensation of a collimated vapor directed obliquely onto a planar substrate has long been used to fabricate thin films with morphology at the nanoscale [1,2]. The vapor is generated by either evaporation or sputtering, the entire process of physical vapor deposition taking place in a low-pressure chamber. The collimated vapor can be directed at an angle (with respect to the substrate plane) that varies from a value slightly greater than 0° to 90°. As the thin film comprises parallel, tilted nanocolumns, it is called a columnar thin film (CTF) [1,3,4].

The direction of the collimated vapor can be changed dynamically and/or the substrate can be rotated about a fixed axis passing through it in order to control the morphology of the growing thin film. Exercising control of the substrate motion, one can grow sculptured thin films (STFs), which are assemblies of parallel nanocolumns of almost identical shapes [2].

During the last 5 years, this oblique-angle deposition (OAD) technique has evolved into the conformal-evaporated-film-by-rotation (CEFR) technique [5–7] and the modified CEFR (mod-CEFR) technique [8] for the deposition of nanostructured thin films on nonplanar substrates. Finally, the Nano4Bio technique for the manufacture of high-fidelity replicas of biotemplates with features at the micrometer and nanometer scales has been developed from the CEFR and mod-CEFR techniques [9–12].

In the following paragraphs, we discuss the fundamentals of the newly developed techniques that have allowed us to move from traditional optical applications [2–4] to novel applications in engineered biomimicry [9,11], forensic science [13–15] and plasmonics [16–18].

OAD is commonly used to fabricate thin films with columnar morphology [1,3,19]. The vapor is directed at an oblique angle χ_v between 0° and 90° with respect to the substrate plane. As a result of shadowing effects, the arriving adatoms are preferentially deposited on top of surface features with large height [19]. When the substrate is stationary, a CTF grows, provided that the temperature and pressure are appropriately chosen [1,3,4]. A CTF comprises parallel, tilted nanocolumns, whose cross-sectional dimensions are strongly dependent on the deposition conditions. In the visible and infrared regimes, a CTF functions optically like a biaxial crystal. All three principal refractive indexes of a CTF depend not only on χ_v, but also on the choice of the evaporated material and the deposition conditions [3].

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CTFs of many different materials – including metals, semiconductors, insulators and organics – have been successfully deposited using the OAD technique. Exemplifying these materials are magnesium fluoride, titanium dioxide, gold, silver, nickel, titanium, silicon, germanium, indium tin oxide, chalcogenide glasses and tris(8-hydroxyquinolinato)aluminum.

Sculptured thin films are thin films grown using the OAD technique in which the growth direction of the columns has been varied instantaneously during the fabrication process [2,20]. Accordingly, STFs are fabricated by:

(i) rocking the substrate about a tangential axis during the deposition process, leading to columns with a two-dimensional shape, and/or
(ii) rotating the substrate about a central normal axis, leading to columns with a three-dimensional shape.

Depending on the particular application envisaged, rocking and rotation can be combined or used sequentially during the fabrication process to create thin films with radically different physical properties [21], thus adding various functionalities to the intrinsic properties of a given material. Accordingly, the morphology of the thin film and consequently its physical response properties can be tailored by controlling the deposition conditions and substrate motion. Substrate movements can be used to induce the growth of various micro- and nanostructures, including vertical columns, helical columns, slanted columns, spirals and chevrons [20,22].

The high porosity and the optical anisotropy and nonhomogeneity of STFs, together with the possibility of engineering their nanostructure into a variety of useful shapes, make them useful in several practical applications. Thus, optical devices based on STFs include polarization filters and transformers [2], as well as optical sensors exploiting the Bragg phenomenon [23–25]. More recently, STFs were theoretically proposed as vehicles for launching multiple surface-plasmon-polariton waves [26,27], the theory being experimentally validated [16,17] and even exploited for optical sensing [18]. Furthermore, STFs have been proposed as candidates for electroluminescent devices, high-speed and high-efficiency electrochromic films, optically transparent conducting films sculptured from pure metals, and multistate electronic switches based on filamentary conduction [2,20].

As an example of a particular optical application, Figure 1 shows a cross-sectional scanning electron micrograph of an STF grown using the OAD technique. The helical shape of the constituent columns is evident in the figure. As this STF is structurally chiral, it discriminates between incident left- and right-circularly polarized radiation. The material and the morphology were chosen so that this chiral STF functions as a wideband-rejection filter for circularly polarized radiation in the shortwave infrared regime [28].

The CEFR technique represents an evolution of the OAD technique. In the CEFR technique, OAD is accompanied by rapid substrate rotation, as shown in Figure 2. This technique was devised for high-fidelity replication of biological templates, as exemplified by the successful replication at the nanoscale of several biological structures, including the compound eyes and several other parts of flies, the wings of butterflies and the exoskeletons of beetles [5,6,12]. As such, the CEFR technique is able to replicate complex micro- and nanoscale features distributed over both planar and curved surfaces.

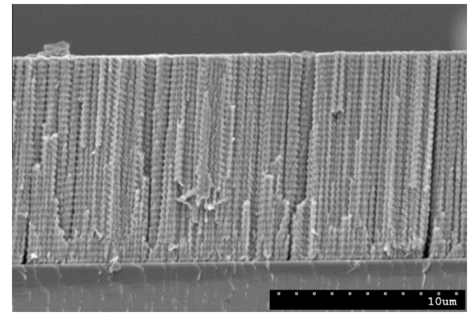

Figure 1. Cross-sectional scanning electron micrograph of a chalcogenide-glass STF that functions as a wideband-rejection filter for circularly polarized shortwave infrared waves [28].

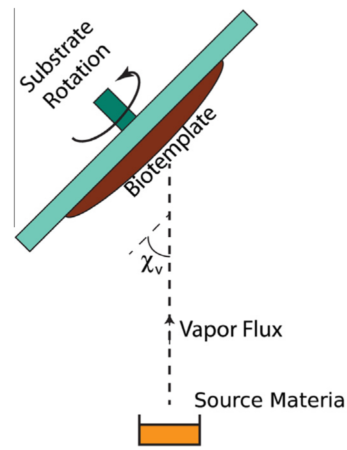

Figure 2. Schematic of the CEFR technique.

To implement the CEFR technique, the specific biotemplate is affixed to a substrate holder and χ_v is fixed at about 5°. The substrate holder is rotated at a high rate, typically between 30 and 120 rpm. The biotemplate is thus coated with a thin film. After the deposition process ends, and if the coating is thick enough, a self-supporting high-fidelity replica is generated by separating the coating from the biotemplate [12].

The CEFR technique is particularly well suited for bioreplication, since damage to the underlying biotemplate is avoided for two main reasons:

(i) the temperature during the deposition process is sufficiently low, and
(ii) the coating process occurs in a non-corrosive environment.

The experimental results also show that neither is there a disturbance of the original biotemplate nor is an observable new structure created by the CEFR technique [5,6,12]. In fact, the optical characteristics of the original biotemplates, mainly due to nanoscale (<100 nm) structural features, are not compromised by the coating process [5,6]. Figures 3 and 4 show two examples of coated