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Porosity engineering in glancing angle deposition thin films

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ABSTRACT We present a new technique for the fabrication of thin films at highly oblique flux incidence angles, in which the direction of film growth and the direction of incoming deposition flux are decoupled. The technique offers a high level of control over the porosity of thin films, and has been used to make thin films with a uniform and highly porous microstructure of tightly interwoven nanoscale fibres. The nanofibrous films have been analysed using scanning and transmission electron microscopy, and will be useful for thin film applications relying on high porosity, such as humidity sensors and supercapacitors.

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1 Introduction

As simple, uniform coatings, thin films play central roles in optical devices, sensors, and many other applications, while as patterned layers, lithographically processed thin films are vital in micro- and optoelectronic circuits. A third approach to the application of thin films is now emerging, in which functionality is realized not just through uniformity or post deposition patterning, but by bottom-up tailoring of the film microstructure during the deposition or fabrication process itself. Examples of intrinsically structured thin films include the work on birefringence by Taga and Motohiro [1], the optical thin film theory by Azzam [2], Hodgkinson's studies on thin film anisotropy [3], Robbie and Brett's development of glancing angle deposition [4, 5], and recently Steltz's proposal for using sculptured thin films for biosensing [6].

This paper deals exclusively with glancing angle deposition (GLAD) thin films. GLAD is a physical vapour deposition technique, in which the substrate is rotated about two axes rather than being held fixed normal to the direction of incoming flux (see Fig. 1a). One rotation axis is in the plane of the substrate, and enables highly oblique flux incidence angles α to be achieved (typically $> 80°$). At such highly oblique angles, porous, low-density thin films with a columnar microstructure are produced. The other rotation axis φ is normal to the substrate, and enables the columns to be engineered into structures such as freestanding vertical posts, chevrons, spirals, and polygonal helices (the latter being slanted posts bent at regular intervals, so that the column shape resembles a polygonal when observed along the substrate normal) [4, 5, 7].

When deposited on bare substrates, GLAD films consist of randomly distributed columns with strong competition and extinction effects among the growing columns. The randomness of the columns results in the film properties being inhomogeneous in the plane parallel to the substrate, whereas column competition makes the films non-uniform in the direction along the substrate normal. Uniform, periodic films, in which the columns are arranged in highly symmetrical patterns, can be fabricated by preparing the substrate with a seed pattern prior to deposition [8, 9]. Provided that the aspect ratio of the seeds is sufficiently high, each seed effectively acts as a nucleation site for one GLAD column and hence induces periodicity. Figure 1b schematically shows the growth of random square helix GLAD films (i.e., polygonal helix films with one full turn of the helix for every four 90° bends [10]).

In this paper we describe a new method for making GLAD films, in which we achieve a higher level of control on the thin film fine structure. The new growth method allows us to engineer the film porosity, i.e., to influence the diameter and spacing of columns and hence the distribution and size of the tiny voids present in any obliquely deposited thin film. This has led to the discovery of a new thin film type with a compact, fibrous structure not previously seen in oblique evaporation. The new GLAD growth method not only represents an innovation in thin film engineering, but also has immediate applications. GLAD thin films are currently being developed for ultra-fast humidity sensors [11], super-capacitors [12], and catalysts [13], and for these uses, better control of the film microstructure and porosity is highly desirable.

2 Experimental approach

2.1 *Decoupling of the flux incidence and film growth directions*

The growth of thin films is governed by three mechanisms: geometrical shadowing (the limited ability of a co-linear flux to reach all parts of a rough surface), surface diffusion (movement of adatoms along the substrate, film surface, and grain boundaries), and bulk diffusion (leading to oriented crystallization). The importance of each

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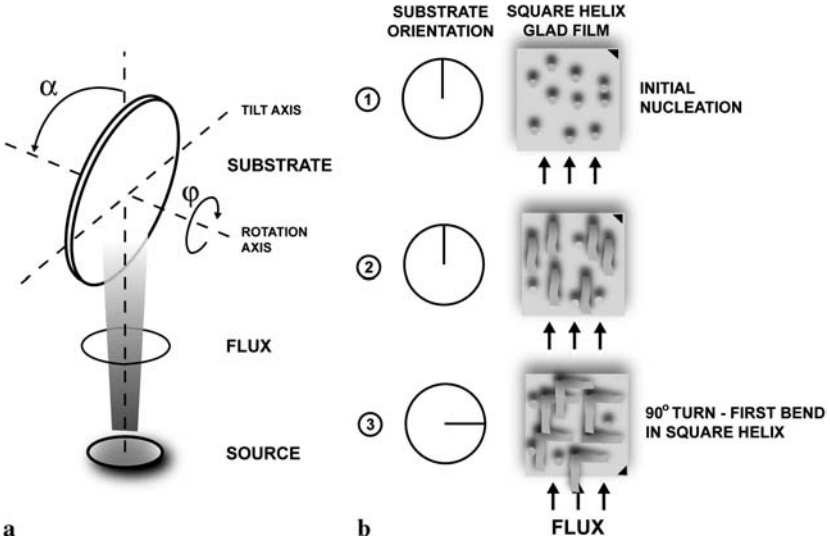

FIGURE 1 **a** Schematic diagram of the glancing angle deposition technique for oblique physical vapour deposition onto rotating substrates. **b** Schematic illustration of traditional GLAD film growth on a bare substrate. Shown here are the initial substrate rotation steps for a square helix film

mechanism depends on the temperature of the film and substrate during growth, as described in various structure zone models [14–16]. In low temperature thin film depositions the geometrical effects dominate and give a voided film structure, whereas thermal effects (i.e., diffusion) dominate at higher deposition temperatures, yielding increasingly ordered, crystalline films.

GLAD films are fabricated at low temperatures, with the only sources of film and substrate heating being thermal irradiation from the molten deposition source, and the release of condensation energy as flux impinges on the substrate. The highly porous GLAD film structures are thus predominantly the result of geometrical shadowing [17, 18]. Depending on the thermal and crystalline properties of the evaporant, the produced films are amorphous, polycrystalline, or single crystalline. For most materials GLAD yields an amorphous film structure, but if polycrystallinity is desired (e.g., when using GLAD films in solar cells or for photoluminescence), recent research have indicated that careful annealing post deposition permits some recrystallization without loss of the porous structure.

In its most basic form, the GLAD process gives a fixed relationship between column inclination angle and film density, the latter usually being measured relative to bulk density [5]. With the advent of advanced GLAD based on non-uniform substrate movement, these two parameters were partially decoupled so that for any column inclination angle a range of film densities could be obtained [7]. However, there were still no means with which to control the way in which a given film porosity would manifest itself in the film microstructure, i.e., in the distribution and size of pores in the film.

To this end, we have developed a new GLAD growth method applicable to any film in which the columnar microstructure consists of linear segments. In contrast to traditional GLAD, where the substrate is kept static for each straight column segment, the new method regularly sweeps the substrate from side to side about a central axis defining the direction of the straight column segments. At each outer extreme of the sweep curve, the substrate is paused for a period of time corresponding to a certain, constant thickness of film growth, called the sweep pitch. One half of the angle covered by each sweep is called the sweep angle. For example, a film with a 45° sweep angle and a 15 nm sweep pitch would have the substrate turn 45° to each side of the direction of the straight post segments (for a full 90° sweep range between the outer extremes), and between sweeps it would keep the substrate fixed at an outer extreme for 15 nm worth of thin film growth, measured normal to the substrate. A schematic illustration of the new GLAD method, called "PhiSweep", is found in Fig. 2.

When neither the sweep pitch nor the sweep angle is too large, the resulting film will consist of straight columns growing in a direction equal to the centre of the sweep (as was shown to be generally valid in [7]). PhiSweep can therefore reproduce all known GLAD structures except circular helices. Polygonal helices, for example, can be grown with ease as long as the polygon side length is not too small. In comparison with traditional, non-sweep GLAD, the key feature of the PhiSweep modification is that it decouples the direction of incoming flux with the direction of column growth. As will be demonstrated below, this leads to significant changes in the film microstructure and porosity.

2.2 *Experimental details of the performed thin film depositions*

All thin film depositions were performed in a CHA Industries electron beam evaporator, fitted with a mount for two stepper motors inside the evaporator chamber. Substrates were attached to a chuck mounted on the axis of the first stepper motor (the φ axis in Fig. 1a). The second stepper motor rotated the φ motor about an axis passing through the plane of the substrate chuck (the α axis in Fig. 1a). Both stepper motors were controlled by a computer running National Instruments' Labview program, in which the parameters of the desired GLAD films were entered and translated into motor rotation commands. In order to account for random fluctuations in the film deposition rate, the computer received feedback from a Sycom STM-100 crystal thickness monitor.

For all films described here the deposited material was silicon, while the substrates were dies cut from silicon wafers.

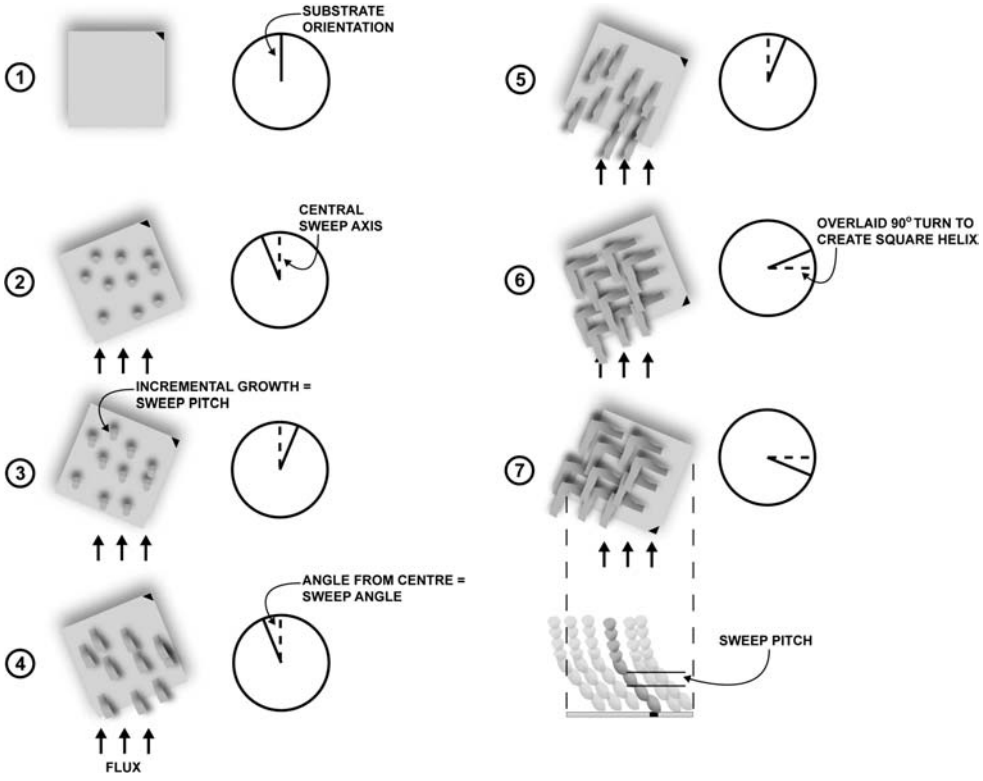

FIGURE 2 Schematic of the Phi-Sweep method for decoupling the directions of incident flux and column growth in GLAD. The substrate axis φ is rotated from side to side about the direction of intended column growth, pausing at each end of the sweep curve to generate incremental column growth. Any post or polygonal helix structure can be fabricated, such as in this case the first two segments of a square helix film

Square helices were used as the fundamental GLAD column shape. The deposition parameters were kept constant for all the depositions, with chamber pressures around 2×10^{-4} Pa and deposition rates of 1.5–2.0 nm/s.

3 Results and discussion

3.1 *Investigation of the ability to engineer the film porosity*

A number of PhiSweep films were fabricated, covering a range of sweep pitches and angles. Figure 3a and b show SEM side view micrographs of square helix PhiSweep films with 45 and 15 nm sweep pitches, respectively, while Fig. 3c shows a traditional GLAD square helix film deposited without PhiSweep (the only φ rotation in this case being the 90° turns required to fabricate the basic square helix). The substrate inclination angle α was kept at 84°, and for the PhiSweep films the sweep angle was 45°. Figure 4 depicts the same films, but in top views. The films obtained with a sweep pitch of 45 nm (Figs. 3a and 4a) look extremely compact, with none of the voiding and competition that is otherwise so characteristic of obliquely deposited films. It appears that the films consist of a large number of densely packed fine fibres, each growing all the way from the substrate to the top of the film with almost constant width, and with no competition among or extinction of individual fibres. The films with

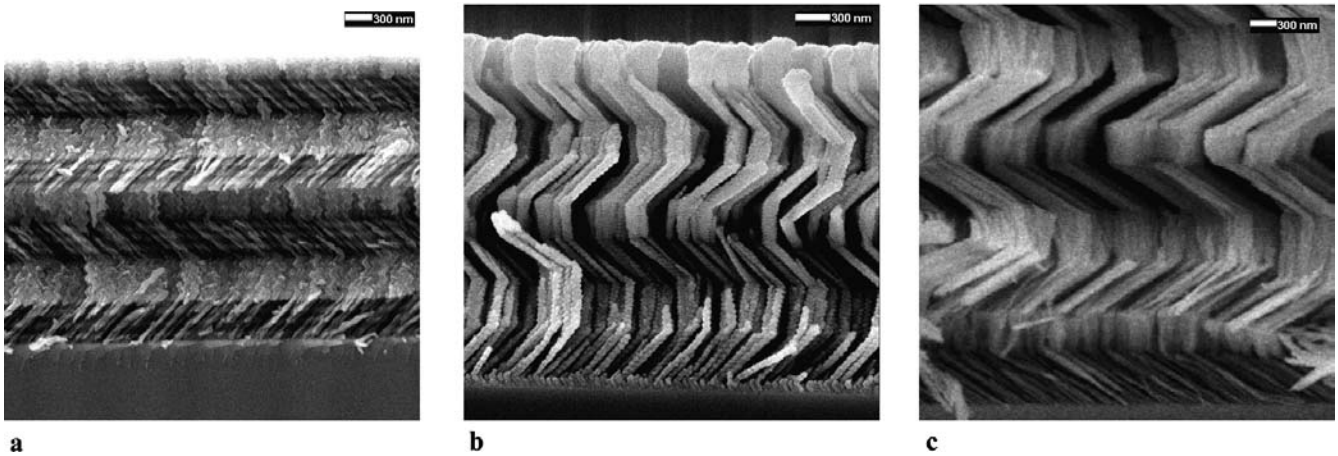

FIGURE 3 SEM side view images of GLAD thin films made with **a** the PhiSweep method with a sweep pitch of 45 nm and a sweep angle of 45°, **b** the PhiSweep method with a sweep pitch of 15 nm and a sweep angle of 45°, **c** the traditional GLAD method. All three films are random silicon square helix films on bare substrates, and were intentionally deposited with different thicknesses

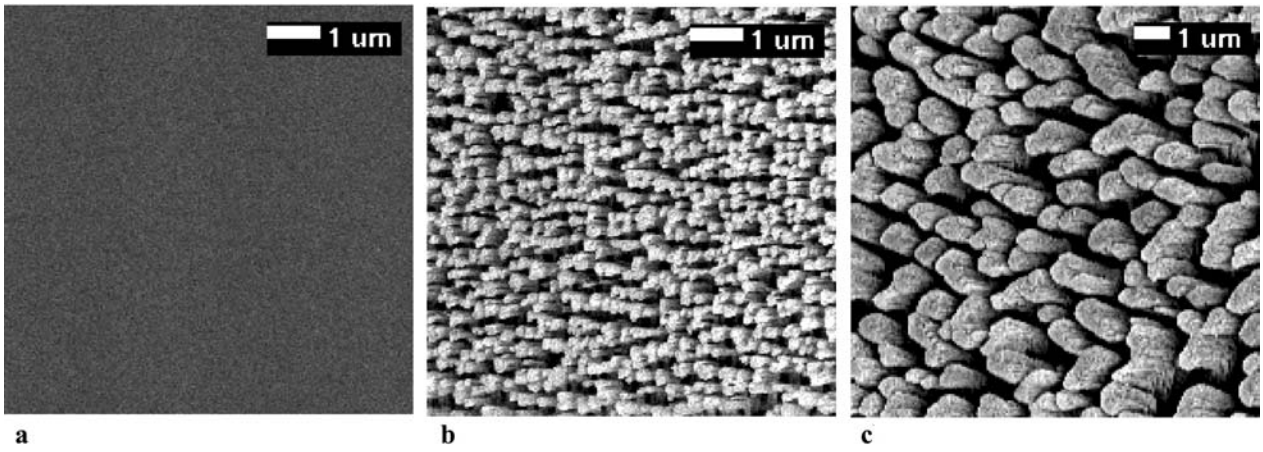

FIGURE 4 SEM top view images of GLAD thin films made with **a** the PhiSweep method with a sweep pitch of 45 nm and a sweep angle of 45°, **b** the PhiSweep method with a sweep pitch of 15 nm and a sweep angle of 45°, **c** the traditional GLAD method. All three films are random silicon square helix films on bare substrates, and are the same as shown in Fig. 3

a 15 nm sweep pitch, on the other hand, have a much more open structure (Figs. 3b and 4b). Rather than a fibrous structure, the 15 nm sweep pitch films consist of larger, freestanding columns, with significant competition effects among the columns. In fact, these PhiSweep films are quite similar to traditional, non-sweep GLAD films (Figs. 3c and 4c), although with less relative column broadening and competition. The sweep pitch consequently appears to have crucial impact on the fine structure of the PhiSweep GLAD films, with certain sweep pitch values yielding an extremely compact "nanofibrous" structure.

Although the nanofibrous films look "dense", the actual film density, defined as mass per volume film, is the same as for traditional, open GLAD films, which themselves have a lower density than the bulk density of the deposited material [19]. This was realized by comparing a 45 nm pitch nanofibrous PhiSweep film and a traditional GLAD film, with each film having received the same amount of deposition material per unit substrate area, as verified by an independent crystal thickness monitor facing the deposition source (in a different experiment from the films shown in Figs. 3 and 4). Any change in density would manifest itself as a difference in thickness between the nanofibrous and the traditional GLAD films, but in the experiment the thickness was in fact observed to be the same for the two films. To maintain the overall film density, the nanofibrous PhiSweep film has instead a high number of smaller, finer pores between the individual fibres, as will be seen in the TEM analysis below. Thus, what really distinguishes the nanofibrous films from traditional, open GLAD films are the size and distribution of the microstructural fibres and pores.

The sweep pitch evidently determines the fine structure of PhiSweep GLAD films, and for the case of silicon we believe that the nanofibrous film microstructure can be explained by the magnitude of the sweep pitch relative to the width of the silicon fibres. This is based on the following observations. A sweep pitch of 15 nm is below the average fibre width of 20–30 nm, and gives an open GLAD film, but when the sweep pitch is raised to 45 nm, and hence slightly above the average fibre width, we get the compact film unique to the PhiSweep method.

To understand the importance of this observation, we must first compare nanofibrous growth with the column growth processes seen in traditional GLAD films. Once nucleation and agglomeration has taken place, the highly oblique incidence angle leads to a compact forest of fine columns. The columns are very thin and closely packed, since the columns grow off equally small and close packed nuclei, and since shadowing among columns initially remains insufficient to influence film growth. Hence, for the first tens of nanometers of growth, there is no difference in the film structure of traditional GLAD films and nanofibrous PhiSweep GLAD films. However, an inherent instability in the columnar self-shadowing process gradually leads to broadening of columns in traditional GLAD films. Due to the highly oblique flux incidence angles, and the anisotropic, near-unidirectional flux arrival, random incremental increases in the width of a column along the direction of incoming flux instantly creates enhanced shadowing of the nearest neighbouring column in that direction. The increase in shadowing is irreversible and self-reinforcing, and leads to broadening of some columns as well as extinction of others, in accordance with self-affine (fractal) dynamics. The broadening instability is clearly evident in Fig. 5, where a traditional GLAD film (consisting of slanted posts created by simply holding the substrate at rest) evolves from an initially finely stranded or nanofibrous film structure into an open, non-uniform structure with broadening and competing columns. This familiar characteristic of structural anisotropy in oblique incidence thin films has been studied extensively both computationally [20, 21] and experimentally [22].

Let us now return to the PhiSweep films and the impact of different values of the sweep pitch. If the sweep pitch is smaller than the natural fibre width of the deposited silicon, the alternation of the flux arrival angle will degenerate the fibres into lumps, as flux rapidly accumulates on two different sides of the fibres. These lumps are equivalent to the beginnings of broadening columns in traditional vertical post GLAD films, in which continuous or nearly continuous substrate rotation leads to preferential flux deposition on the periphery of growing columns. The initial lumps hence evolve to become regular, broadening GLAD columns and yield an

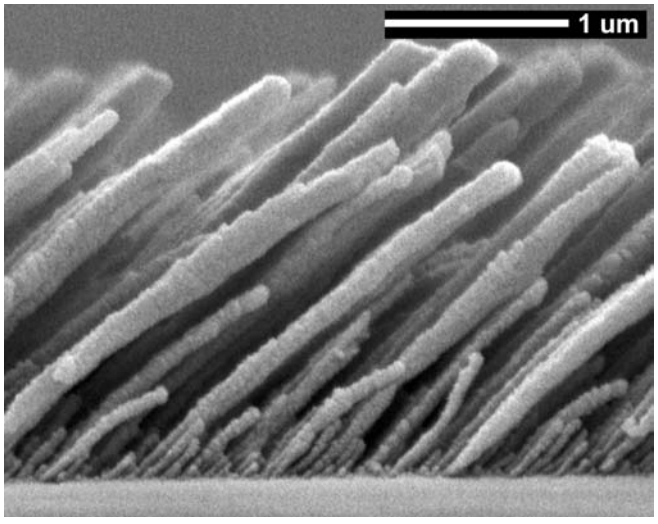

FIGURE 5 SEM micrograph of a traditional SiO_2 GLAD film consisting of slanted posts. At the substrate the film starts out as a dense film of closely packed columns, quite similar to a nanofibrous PhiSweep GLAD film. However, column broadening quickly sets in, leading to severe competition among the columns. As the columns get fewer and fatter, an open, anisotropic film structure develops

open GLAD film, although in this case broadening is not related to structural anisotropy effects. The relative broadening per unit thickness of film does appear to be decreased in the PhiSweep film (compare Figs. 3b with 3c, and Figs. 4b with 4c).

When the sweep pitch is slightly larger than the fibre width, however, the fibres have enough time to redirect between sweeps. In this case, each sweep essentially starts a new column and resets the competition process inherent to GLAD films, hence postponing the adverse effects of competition indefinitely. We then get the nanofibrous film structure, in which closely packed fine strands of deposited material can grow continuously with no observable column broadening. The elimination of broadening can be attributed directly to the frequent changes of the flux incidence direction, since this oscillation of the flux prevents the build-up of a structural anisotropy in the shadowing pattern among the growing columns, and hence removes the precondition for column broadening. By neutralizing the structural anisotropy effect of traditional GLAD, PhiSweep GLAD allows the initial off-the-substrate film structure to keep growing throughout the film, without column competition, extinction, or broadening.

Finally, if the sweep pitch is much larger than the fibre width, the structural anisotropy has enough time to impact the film topography between sweeps, and one reverts to the case of traditional GLAD films with each column broadening between substrate rotations.

Figure 4 clearly demonstrates the ability of the PhiSweep method to engineer the porosity of GLAD thin films, with a full range of possible film textures from very compact (Fig. 4a) to very open (Fig. 4c), and with independence from the film density and the underlying column shape. Through a simple modification of the GLAD technique, this provides significant thin film fabrication flexibility. The absolute sweep pitch values required to obtain a given PhiSweep film structure depends closely on the crystalline and thermal characteristics of the evaporant material, which determine the thin film grain or fibre width, and must be determined experimentally for each material.

3.2 *Characterization of nanofibrous GLAD thin films*

Figure 6 shows transmission electron microscopy (TEM) bright and dark field images of a thin slice of the nanofibrous PhiSweep film. Even on the highly magnified bright field TEM images, the nanofibrous film appears to consist of tightly packed fibres, confirming the previous SEM analysis. Each fibre grows all the way from the substrate to the top of the film, and is shaped according to the overall square helix structure, overlaid with small ripples from the φ sweeps. The width of each fibre is 20–30 nm, and tiny voids or gaps are discernible between the fibres.

The TEM dark field image shows that the nanofibrous silicon film is amorphous, as is the case for all silicon GLAD films. This eliminates crystallographic and thermal effects, such as localized annealing, as explanations for the nanofibrous structure. Energy dispersive X-ray analysis (EDX) was also performed, confirming that the nanofibrous films contain silicon and some oxygen. The oxygen content can be attributed to residual gas present in the deposition chamber and to native oxidation post deposition.

Based on the measured fibre width, taking into account that the nanofibrous GLAD films have the same density as traditional GLAD films (i.e., 30%–40% of bulk density), and approximating the nanofibres to smooth cylinders, we estimate the geometrical surface area of a 3.2 μm thick nanofibrous film to 180 cm^2/cm^2, or 68 m^2/g. Since the nanofibres do in fact have a rough surface texture, rather than a smooth one

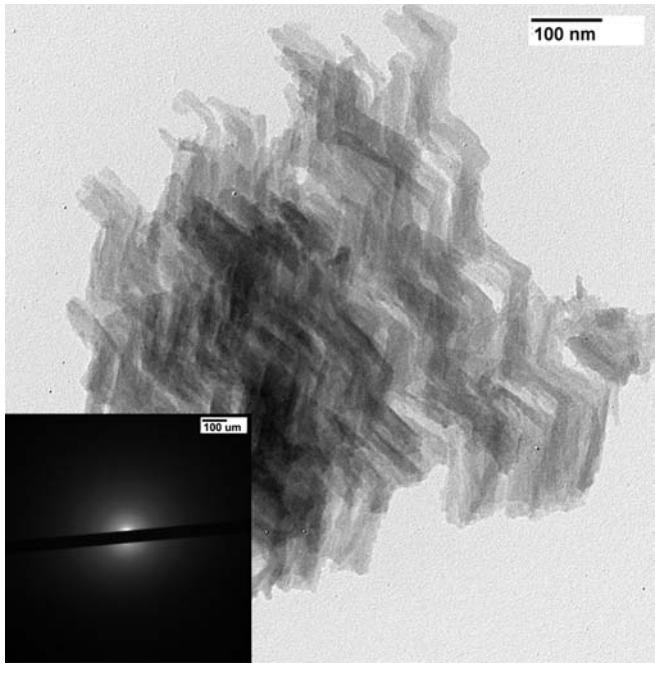

FIGURE 6 TEM bright field image of a piece of nanofibrous silicon square helix PhiSweep GLAD film. The width of individual fibres is 20–30 nm, and each fibre extends all the way from the bottom to the top of the film. *Inset*: TEM dark field image of the same nanofibrous film, revealing that the silicon film is amorphous

(see Fig. 6), the actual surface area will be substantially higher than this conservative estimate. In addition, more surface area can be added simply by growing thicker PhiSweep films. Even so, the geometrical surface area estimate for the nanofibrous films is much higher than the surface areas in traditional GLAD films, which have been measured to $13.2\,\mathrm{cm}^2/\mathrm{cm}^2$ or $6.6\,\mathrm{m}^2/\mathrm{g}$ for GLAD nickel films, using a porosimeter [12], and in another instance was found to be $42\,\mathrm{cm}^2/\mathrm{cm}^2$, based on a geometrical computer simulation that did take column roughness into account [23]. The higher surface area of the nanofibrous films is a direct consequence of these films consisting of more numerous and thinner columns/fibres than traditional GLAD films. Indeed, the estimated nanofibrous film surface area is only one order of magnitude lower than that of activated carbon, whose surface area of $\sim 1000\,\mathrm{m}^2/\mathrm{g}$ is generally considered the highest available for any material today.

4 Conclusion

We have presented a new method for fabricating thin films with engineered porosity, using a variation of the glancing angle deposition technique in which the direction of incoming flux and the direction of growth are decoupled. We have discussed the characteristics of the compact yet highly porous film microstructures obtained for certain deposition conditions, and explained how the new nanofibrous structure arises as the result of suppressing the column competition effects inherent in obliquely deposited thin films. The porosity engineering capability is a powerful tool for continued development of several applications based on GLAD films. Fast humidity sensors and highly efficient catalysts and thermal barriers have already been demonstrated, and will benefit further from the ability to tailor the distribution of microscopic voids within nanofibrous films.

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