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Nanostructural Analysis of Porous Oblique Angle Deposited (OAD) Multilayer Systems by Grazing-Incidence Small-Angle X-Ray Scattering --Manuscript Draft--

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Corresponding Author:	Carmen Lopez-Santos National Agency for Quality Assessment and Accreditation Seville, International SPAIN
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Corresponding Author Secondary Information:	
Corresponding Author's Institution:	National Agency for Quality Assessment and Accreditation
Corresponding Author's Secondary Institution:	
First Author:	Manuel Oliva-Ramirez

First Author Secondary Information:	
Order of Authors:	Manuel Oliva-Ramirez
	Carmen Lopez-Santos
	Francisco Yubero
	Agustín Rodríguez González-Elípe
Order of Authors Secondary Information:	
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Nanostructural Analysis of Porous Oblique Angle Deposited (OAD) Multilayer Systems by Grazing-Incidence Small-Angle X-Ray Scattering

**Manuel Oliva-Ramírez, Carmen López-Santos*, Francisco Yubero, Agustín
R. González-Elípe***

**Institute of Materials Science of Seville (CSIC), Américo Vesputio 49,
41092 Seville (Spain)**

* mclopez@icmse.csic.es; arge@icmse.csic.es

Abstract

This work reports a thorough characterization analysis of various porous thin film multilayers by means of Grazing-Incidence Small-Angle X-Ray Scattering (GISAXS). Alternated $\text{TiO}_2/\text{SiO}_2$ nanocolumnar layers deposited at oblique angles were fabricated in slanted, chiral and zig-zag configurations by rotating azimuthally the substrate from one layer to the next. Multilayer systems formed by the stacking of 3 and 15 alternant thin films of these two oxides were morphologically characterized by scanning electron microscopy (SEM) and structurally by GISAXS. This technique has provided a means to determine series of vertical and lateral correlation lengths and to assess the anisotropic electron density distribution along the structural elements existing in the multilayers. This information can be systematically used to account for the actual arrangement of nanostructural elements in multilayer systems.

Introduction

Control of the growth processes are of paramount importance for self-organized nanostructures prepared by physical vapor deposition at oblique angles (PV-OAD or PV-GLAD, glancing angle deposition) and related methods for the control of their performance in a large variety of applications ^[1]. For example, the optical and optoelectronic behaviors of the so-called sculptured thin films prepared by this method ^[2] have demonstrated to be tightly dependent on material distribution and arrangement. In this line, we have recently shown that the special polarization and wave retarder behavior of planar Bragg microcavity (BM) devices prepared by OAD were critical for liquid monitoring applications and depended on the asymmetric association of the nanocolumns forming their microstructure ^[3]. In these systems, it has been claimed that the occurrence of autocorrelation phenomena resulting from shadowing effects during the ballistic deposition and agglomeration of deposition particles are controlling the growth and, in some cases, the lateral association of their elemental nanostructures.^[4] This gives rise to the appearance of asymmetries and some correlation distances between nanocolumns that have not been yet properly determined. ^[5]

A large variety of methods have been utilized to characterize the morphology of these nanostructured thin films. Among them, grazing incidence small angle X-ray scattering (GISAXS) is recognized as a nondestructive and surface sensitive technique well suited to determine different structural and morphological parameters of thin films.^[6] This method may be advantageous with respect to different microscopies (SEM or AFM) because it provides an average description of the system. Moreover, since X-ray can penetrate through relatively thick layers from microns to cm, it is possible to perform in-situ

GISAXS experiments to probe materials in their native states and in other environmental conditions.^[7] Examples of the possibilities of this technique for the characterization of the microstructural order and its correlation with optical properties have been reported for nanoparticles grown on polymeric substrates^[8] or optical antireflective mesoporous coatings.^[9] For system morphologies similar to those studied in the present work (i.e., thin film configuration), this technique has provided useful information about the mesoporous structure of a SiO₂/VO₂ double-layer systems used as prototype smart windows^[9] or on the distribution of Ge quantum dots in a multilayer systems.^[10] In the present work, we want to further characterize ordered two-oxide-layered systems formed by the alternant stacking of porous SiO₂ and TiO₂ thin films deposited by PV-OAD which in previous works were utilized as Bragg photonic structures.^[11] This type of 1D photonic structures is formed by the staking of various equally thick layers of two materials with different refraction index and incorporate a central thicker layer of the lower refraction index material that act as optical defect. The transmission spectrum of this structure is characterized by an optical gap and a resonant peak in the center. When fabricated by OAD the constituent layers are very porous and the resulting multilayer structure is particularly interesting for its anisotropic optical response properties and its potential use for optofluidic responsive applications.^[15] This investigation can be considered as the continuation of preliminary GISAXS investigation of single oxide layers prepared by PV-OAD where we set the basis for the interpretation of some of the characteristic features of this kind of porous nanocolumnar films depicting a highly anisotropic arrangement of their constituent nanocolumns.^[12] For this GISAXS analysis of PV-OAD multilayers we firstly set the basis of the

1 procedure studying a multilayer system composed of 3 layers arranged as
2 $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$, where layer nanocolumns are oriented according to slanted,
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4 chiral and zig-zag configurations. Previous works with block copolymer systems
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6 [13] or silicon nanowires [14] have reported that GISAXS analysis is highly
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8 sensitive to the orientation of the nanostructural units with respect to the X-ray
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10 incident beam. For the herein studied three-layer stacks, GISAXS has provided
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12 information about vertical and lateral correlation distances and about the distinct
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14 electron density distributions existing in these systems. The methodology of
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16 analysis developed with the simple three layer structures has been then applied
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18 to characterize planar Bragg microcavity (BM) devices formed by the stacking of
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20 15 alternant layers. The analysis of this more complex system has provided
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22 morphological information about the nanocolumns arrangement in these
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24 structures and may constitute a starting point to apply the GISAXS technique for
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26 the systematic characterization of complex multilayer systems and devices.
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38 **Experimental**

39 Fabrication and morphological characterization

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44
45 Highly porous stacked multilayer systems made of alternated layers of TiO_2
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47 and SiO_2 have been prepared by oblique angle deposition (OAD) according to a
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49 previously reported procedure [12a, 15]. The formation of the nanocolumnar
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51 structure in the oblique e-beam evaporation process occurs when the vapor
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53 arrives and condenses forming three-dimensional nuclei during the deposition,
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55 generating a random roughness. Then, the material that arrives during the
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57 growth process is deposited preferentially on these formed nuclei due to
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shadow effects that, in the absence of diffusion, give rise to a microstructure formed by nanocolumns tilted in the direction of the incident flow. These layered structures were e-beam-evaporated on silicon and glass plates of $1.2 \times 2.5 \text{ cm}^2$ at a zenithal angle of 70° . A first set of samples consisted of three layers stacks ($\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$) with an approximated total thicknesses of 250nm. The BMs were fabricated in a similar way and consisted of 2×7 individual layers with a thickness of approximately 85 nm and a SiO_2 middle layer of 200nm thickness. These nanostructured porous thin films were fabricated in three different configurations: *slanted*, *zigzag* and *chiral* and their characterization results were compared with those of a *reference* multilayer prepared at a normal deposition configuration (i.e., at 0°). This *reference system was characterized by a compact and non-porous microstructure*. These three sculptural morphologies of nanocolumns were prepared by keeping fixed the substrate for the *slanted* configuration or azimuthally turned from one layer to the next for the *chiral* (90°) and *zig-zag* (180°) configurations. According to previous SEM characterization analysis ^[3] and a Monte Carlo based computer modeling ^[5] of the surface trapping during the oblique nanocolumnar growth in this type of films, the fabricated BMs present a preferential association of nanocolumns in the direction perpendicular to the flux of evaporated material that will be dubbed here as *growing direction*. Top view and cross section SEM images of the studied multilayers were taken in a Hitachi S4800 field emission microscope at 2keV primary beam energy.

GISAXS analysis

In GISAXS, the refractive index for X-rays is assumed to be described by:

$$\mathbf{n} = 1 - \delta(\lambda) + i\beta(\lambda) \quad (1)$$

where λ is the X-ray wavelength, $1 - \delta(\lambda)$ the real part and $\beta(\lambda)$ the absorption imaginary part. In first instance, these λ dependent functions vary with the mass density (i.e., porosity), the atomic molar ratio and elemental mass of the system components. The basic phenomenology of a GISAXS experiment is presented in Figure 1 showing the impinging, α_i , and reflected, α_f , angles taken in the same direction (characterized by k_i and k_f vectors) and the in-plane lateral scattering angle θ_f . The critical angle for total external reflection depends on the material characteristics (i.e., on $\mathbf{n}$) through the relation $\alpha_c = \sqrt{2\delta}$. In a GISAXS experiment, when the incident X-ray beam impinges onto the surface at a grazing angle close to α_c , it is diffusely scattered by nanometer-sized heterogeneities of the electron density distribution and gives rise to patterns along the directions perpendicular and parallel to the surface. The intensity of the obtained GISAXS patterns is related to the Fourier transforms of the motif shape (form factor $F(q)$) and the correlation function (interference function $S(q)$) where q is the momentum transfer.^[16] Consequently, average lateral size and height distributions within the system can be taken as inversely proportional to the spread of the scattered beam parallel (i.e., through the wave vector q_y) and normal (i.e., through q_z) to the surface.

Figure 1.- Schematic geometry of the GISAXS experiments

GISAXS patterns were recorded at the P03/MiNaXS beamline of the PETRA III storage ring at DESY (Hamburg, Germany). An incident photon energy of 11.4 keV with a beam size of $22.6 \times 23.3 \text{ } \mu\text{m}^2$ at the sample position was used for the analysis. Direct and reflected beam positions have been determined with a photodiode and a calibration standard of silver behenate. The sample was aligned horizontally with the long edge parallel to the X-ray beam and was rotated selecting a grazing incidence angle. The primary and reflected beams leave the sample plane forming an angle $2\alpha_i$. They were blocked by beam-stops. The calibration standard was used to determine the sample-detector distance. The sample to detector distance was set at 2450 mm and a PILATUS 300 K system (Dectris Ltd., Switzerland) with a pixel size of $172 \times 172 \text{ } \mu\text{m}^2$ was used as 2D detector. The beam impinged at an incident angle of 0.4° with respect to the substrate surface. Although theoretical critical angles of bulk TiO_2 and SiO_2 for the used X-ray energy are estimated to be 0.25° and 0.16° , respectively, we proved in a previous work that the chosen incident angle provided the best intensity/penetration depth ratio to analyze the lateral

correlation features in TiO₂ and SiO₂ columnar single layers.^[12a] Samples were oriented at azimuthal angles of 0° and 90° for the x-y sample plane with respect to the X-ray beam, i.e., impinging either parallel or normal to the material *growing direction*, respectively. GISAXS data were analyzed using the DPDAK software package. ^[17] GISAXS patterns are presented with an intensity normalization of the color scale representation.

Results and Discussion

Morphology and microstructure of three layers OAD stacks

The fabricated TiO₂/SiO₂/TiO₂ stacks presented different nanocolumnar arrangements: *slanted*, if the azimuthal orientation of the substrate is kept constant during deposition, and *chiral* and *zig-zag* when the substrate was turned by 90° and 180° for the deposition of subsequent layers of the stack. Figure 2 shows top-view and cross sections SEM micrographs, together with schemes describing the nanocolumnar microstructure of these three layer systems. Table 1 collects the total thickness of the different studied stacks and an estimation of the bilayer period (sum of TiO₂ and SiO₂ film thicknesses) in each case. In the normal and top view micrographs in Figure 2, it is possible to appreciate a certain lateral association of nanocolumns in the direction perpendicular to the *growing direction*, a feature that is common in this type of OAD systems (guiding eyes lines are added in yellow to highlight this nanocolumns association). This preferential arrangement is more evident for the *slanted* and *zig-zag* geometries. The 2D-Fourier transforms in this figure clearly illustrate an anisotropic morphology in these three OAD stacks, in contrast with

the uncorrelated microstructure of the *reference* system deduced from its highly symmetric FT shape. In a previous work [3] we have shown that this lateral association of nanocolumns extends along the whole multilayer thickness passing from one layer to the next in an arrangement that we have named *fence-bundling* association. [5]

Figure 2.- SEM micrographs showing the top-view and cross sections (insets at the left side of the images) of the porous three layer stacks with *chiral*, *slanted* and *zig-zag* configurations and the *reference* three layer stack included for comparison. Schemes describing the nanocolumnar microstructure as well as Fourier transforms images are included as insets in the right side of each panel. Lateral association of nanocolumns in the direction perpendicular to the growing direction has been highlighted with yellow lines drawn in the top view micrographs.

Table 1.- Bilayer period estimated by SEM, vertical (d^V) and lateral (d^L) correlation distances, Yoneda shifts and porosity values according to the waveguiding approximation (q^Y_z) estimated by GISAXS analysis for two orthogonal directions of the X-ray beam with respect to the growing direction of films. Bottom: Schematic diagrams featuring these correlation distances in the real space for the different porous multilayer structures.

TiO ₂ /SiO ₂ /TiO ₂ multilayer	reference	slanted		zig-zag		chiral	
		0°	90°	0°	90°	0°	90°
SEM bilayer period (nm)	296	205	-	172	-	187	-
d^{V*} (nm)	251	178	189	172	184	210	215
d^L (nm)	-	-	10,3	-	10,7	-	10,9
q^Y_z (nm ⁻¹)	0,579	0,547	0,546	0,546	0,564	0,554	0,554
Porosity (%)	15	43	-	43	-	36	-

* relatively large errors can be expected by this determinations because a deviation of one pixel of the detector would render a change of ca. 15% in the estimated correlation distances.

GISAXS analysis of three layer systems

Figure 3 presents selected two-dimensional normalized GISAXS patterns obtained for two orthogonal azimuthal orientations of the samples with respect of the X-ray beam (0° and 90° , as indicated in the scheme) and different microstructural configurations of the $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ stacks. Typical features directly identified in these GISAXS spectra are the following: i) the Yoneda peak [18], characterized by a strong X-ray reflection zone confined around $q_y=0$ and spread along q_z and ii) two series of high intensity rings named diffuse Debye–Scherrer rings (DDSRs) that result from the random orientation of microstructural units with respect to the X-ray beam along q_y and q_z . A first series (iia) appear as regular Bragg sheet patterns along the q_z direction at $q_y=0$ and a second (iib) as Bragg rods, i.e. high intensity wing-like features along q_y at $q_z=0$. To gain more detailed information about these features, Figure 4 plots a series of linear profiles taken along q_z and q_y directions on the patterns in Figure 3.

Figure 3.- GISAXS patterns of *slanted* (b), *chiral* (c) and *zig-zag* (d) $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ stacks in comparison with a *reference* three layer system taken as reference (a). GISAXS patterns are presented for two orthogonal azimuthal orientations of the sample with respect to the X-ray beam: 0° and 90° .

Regarding features i) and ii) Figures 3 and 4a shows that GISAXS signal is vertically patterned in q_z for all the investigated systems, including the *reference* sample. In layered systems, similar modulated distributions of intensity have been previously linked to a certain repetitive order perpendicular to the substrate. [6a] A first observation from the off-detector q_z profiles in Figure 4a is that the maximum of the Yoneda feature, and therefore the critical angle of reflection α_c , takes approximate values of 0.175° and 0.142° for the nanocolumnar and *reference* multilayers, respectively. Since the square of the critical angle is proportional to the average electron density [18-19], this shift confirms the highly porous character of the OAD thin films and provides a means to quantitatively estimate void volume fraction in these stacks.

Figure 4.- Out-of-plane (a) and in-plane (b) one-dimensional GISAXS intensity profiles as a function of q_z and q_y respectively. Plots are shown for *slanted*, *chiral* and *zig-zag* TiO₂/SiO₂/TiO₂ stacks for 0° and 90° orientation of the X-rays beam and are compared with the profiles of the *reference* stack. Guiding lines are added to identify Yoneda peak' shifts (a) and lateral correlation maxima (b).

Porosity φ can be estimated according to:

$$\varphi = 1 - \frac{\rho}{\rho_0} \quad (2)$$

where ρ_0 is the theoretical bulk mass density and ρ the actual mass density of the porous material under investigation. [20] Since the Yoneda peak maxima yield the real part of the scattering length density $Re(\rho \text{ SLD})$, a parameter that depends on the actual electron density ρ_e of the porous structure, the mass density can be estimated using the expression:

$$\rho = \frac{4\pi\epsilon_0 m_e c^2 M u}{e^2 (f^0 + f')} Re(\rho^{SLD}) \quad (3)$$

where M is the molar mass [79,9 and 60,1 kg/mol for TiO_2 and SiO_2 respectively], e is the elementary charge [$-1,6 \times 10^{-19}$ C], u is the atomic mass unit [$1,66 \times 10^{-27}$ kg], ϵ_0 the permittivity of free space [$8,85 \times 10^{-12}$ C²/Nm²], m_e the electron mass [$9,1 \times 10^{-31}$ kg], c the speed of light in a vacuum [3×10^8 m/s], and f^0 and f' are dispersion corrections of the atomic factor within the dipole approximation. [21] According to this expression and taking average values of these parameters for TiO_2 and SiO_2 , the *reference* stack system would present a pore volume fraction of 15%, whereas the nanocolumnar stacks would have a pore volume fraction of 36% for the *chiral* and 43% for the *slanted* and *zig-zag* configurations (cf. Table 1). These values are in good agreement with the porosity of single TiO_2 GLAD thin films of similar thickness, previously estimated by adsorption/desorption isotherms [12a] and optical simulations. [15] For the *zig-zag* and to a lesser extend the *slanted* stacks it is also noteworthy in Figure 4a that the position of the Yoneda maxima vary for the profiles at 0° or 90°. The

observed difference suggests a higher electron density distribution along the perpendicular to the vapor flux arrival direction (i.e., coinciding with nanocolumn association direction evidenced by the SEM micrographs in Figure 2).

Figure 4a also shows the appearance of regularly spaced diffuse scattering resonances at the right of the total reflection peak. A first possible interpretation of these secondary maxima is to take them as Kiessig-like fringes^[8a] formed by the constructive interference of partially scattered radiation at each interface in the multilayer stack (i.e., due to the X rays reflection at consecutive interfaces modulated by roughness and linked with the thickness of two consecutive layers, d , according to $\Delta q_z = 2\pi/d$). Calculations based on this assumption gave values between 350 and 450 nm, much larger than the bilayer parameters determined from the SEM micrographs (c.f., Table 1) and that, therefore, disregard interface scattering as the origin of these features. An alternative explanation relies on the total reflection of the partially transmitted X-ray wave at the interfaces between the $\text{TiO}_2/\text{SiO}_2$ layers and its guiding through the SiO_2 film just like in a typical waveguide.^[22] Bragg-like resonant lines resulting from this phenomenon would appear at: $\Delta q_z = \pi/d^V$, where d^V corresponds to the bilayer $\text{TiO}_2/\text{SiO}_2$ thickness. The d^V values in Table 1 calculated under this assumption show a reasonably good correlation with the bilayer $\text{TiO}_2/\text{SiO}_2$ period retrieved from the SEM images and support a wave guiding effect as the origin of these secondary maxima along q_z . The approximate 15% variation found between some SEM bilayer distances and calculated d^V values can be attributed to the difficulty to accurately estimate the bilayer period from the contrast in SEM images, i.e. between darker and clearer zones of the very thin

stacked layers. The higher differences found for the *chiral* structure can be also linked with to a stronger roughness correlation as evidenced by the similar intensity of scattered maxima and that of the Yoneda peak (c.f. Figure 4a).

The in-plane profiles along q_y in Figure 4b are characterized by an intense Yoneda peak and one or two broad wings at high q_y values. The Yoneda peak profiles could be fitted with Lorentzian curves that were narrower for the nanocolumnar than for the reference stack (FWHM values between 0.95×10^{-2} and $0.99 \times 10^{-2} \text{ nm}^{-1}$ for the *nanocolumnar* stacks and $1.05 \times 10^{-2} \text{ nm}^{-1}$ for the *reference* sample). The width of the Yoneda peak may stem from diffuse scattering events, usually resulting from the surface roughness of the system, and/or from scattering contributions at large associated arrays of material that appear at very small angles and cannot be resolved in the GISAXS spectrum.

[8a] Another interesting feature of the Yoneda peaks in the *slanted*, *zig-zag* and *chiral* samples measured at 90° is the appearance of an asymmetric larger tail at the side opposite to the broad and intense lateral wings observed at high q_y values (similar features also appears in GISAXS spectra of single TiO_2 OAD samples^[23]). Although there is not yet a clear explanation for this asymmetric intensity distribution of the Yoneda peak, we tentatively link its appearance to the effect of an asymmetrical distribution of roughness at the surface (previous studies in the literature have demonstrated the influence of an oriented roughness on the Yoneda peak ^[24]).

According to previous studies on OAD thin films, the asymmetry spectral wing features appearing in the *slanted* and *zig-zag* samples can be discussed in terms of the distinct scattering phenomena ^[25] resulting from the particular

arrangement of nanocolumns in the studied stacks. In general, for the $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ nanocolumnar stacks, X-rays will be preferentially scattered by the Ti atoms at the bottom and top layers since these atoms have much higher scattering cross section than Si.^[26] (i.e., most GISAXS features can be accounted for by the effect of TiO_2 nanocolumns). In the *zig-zag* and *slanted* a three layer configuration stacks, TiO_2 nanocolumns in the bottom and top layer present a *parallel* titling orientation (c.f. Figure 1) which we deem as the main microstructural factor giving rise to the single broad side wing observed at high q_y in the 90° pattern of these two samples. Therefore, from the point of view of the GISAXS scattering, the *zig-zag* microstructural arrangement is equivalent to that of the *slanted* case. However, such asymmetry in the arrangement of TiO_2 nanocolumns is lost in the *chiral* multilayer where TiO_2 nanocolumns have opposite orientations in the first and third layer of the stack. Nevertheless, the symmetric shape of the q_y profile of the *chiral* sample suggests the existence of correlation distances along the two q_y directions, in agreement with the fact that the tilted TiO_2 nanocolumns in the bottom and top layers are azimuthally turned 90° one with respect to the other. In particular, we associate this latter feature to the existence of a correlation distance in the film plane only in the direction perpendicular to the *growing direction*. The fact that no lateral wings were detected for *zig-zag* and *slanted* samples at 0° , suggest the absence of any lateral correlation between microstructural elements in that direction. The actual value of lateral correlation distances measured at 90° can be deduced from the q_y value of the lateral wings maximum according to $d^L = 2\pi/q_{y(\text{max})}$. The obtained values varied between 10-11nm and were slightly higher for the *chiral* than for the *slanted* stack (c.f., Table 1). It is also apparent in Figure 4a that the

1 narrowest lateral wing band corresponds to the *zig-zag* structure (FWHM of
2 0.24 nm^{-1}), suggesting a better defined lateral arrangement of nanostructures in
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4 this sample. According to Dendooven et al. ^[19], TiO_2 /void interfaces may act as
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6 scattering centers with the scattering intensity reflecting the internal surface
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8 area in the top layers of mesoporous titania thin films. Following this
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10 interpretation, d^L values determined here for the OAD stacks can be taken as
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12 the average size of partially ordered mesopores extending along the whole
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14 layer thickness within the array of associated tilted nanocolumns (c.f SEM
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16 images in Figure 2 and schemes in Table 1). This assumption and the absence
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18 of any scattering wing at 0° imply a wide and randomized distribution of pore
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20 sizes separating the nanocolumns in the growing direction, in agreement with
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22 our previous assumptions about lateral association of nanocolumns in OAD thin
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24 films. ^[5] Similar wing asymmetry and correlation length values determined
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26 previously for single TiO_2 OAD thin films were also associated with the average
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28 distance separating tilted nanocolumns preferentially associated along the
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30 perpendicular to the growing direction. ^[12a] To clarify the meaning of the
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32 different correlation parameters discussed above a series of schematic
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34 diagrams of the different structures are included as part of Table 1, indicating
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36 the geometrical features in real space responsible for these correlations.
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49 Planar BM multilayer structures

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52 Previous considerations on the GISAXS patterns of the three stacked layers
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54 can be extrapolated to multilayer structures formed by a larger number of
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56 stacked TiO_2 / SiO_2 alternated layers. As a model example, results are reported
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58 here for a porous Bragg microcavity formed by 15 stacked layers, alternating
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TiO₂ and SiO₂ layers of around 70nm thickness, and a *slanted* configuration.

SEM cross-sections and normal micrographs of this 1D-photonic structure are shown in Figure 5 (a).

Figure 5.- GISAXS and SEM analysis of a nanostructured TiO₂/SiO₂ Bragg microcavity with a *slanted* configuration. (a) Top-view and cross section SEM micrographs, these latter for two orthogonal azimuthal orientations (left) and Fourier transform image included as inset (right). (b) GISAXS patterns of the for 0° and 90° orientations of the X-rays beam with respect to the films growing direction. c) and d) out-of-plane and in-plane GISAXS intensity line profiles along q_z and q_y . Guidelines are added to identify Yoneda peaks' shifts and lateral correlation maxima. Inset shows the out-of plane GISAXS profile in an enlarge scale to show the replica features along q_z .

Figure 5 (b) collects the two-dimensional normalized GISAXS patterns obtained at 0° and 90° orientations. At first sight, these patterns are similar to those of the three layers stack. For example, characteristic vertical patterns are observed along the q_z axis at the Yoneda peak, while similar wing maxima at large q_y values are found when the sample is measured at 90°. This similarity suggests that, despite that the BM multilayer has a thickness of around 1.4 μm , more than 3 times higher than that of the three layer stack, vertical correlation in a distance between 175 - 194 nm (Table 2) can be estimated using the typical formula of a wave guiding mechanism, i.e., $\Delta q_z = \pi/d^V$, with d^V corresponding to the actual interface period for the alternated $\text{TiO}_2/\text{SiO}_2$ bilayers present in this system. Another difference with respect to the three layer stacks is the considerable broadening of the Yoneda peak (c.f., Figures 5 (b, c)) that can be attributed to a progressive roughness increase at the $\text{TiO}_2/\text{SiO}_2$ interfaces from the bottom to the top of the 1D structure and at its final surface. ^[8a] AFM analysis of samples roughness reported as Figure S1 from supporting information confirms that roughness increases by one order of magnitude for the 15-layer system with respect to the 3-layer stacks. The high asymmetric tail of the Yoneda band at 90° follows the same tendency found for three layers *zigzag* and *slanted* systems and can similarly be attributed to a different electron density distribution along the two analysis directions due to differences in roughness distribution.^[3] Since the asymmetry found in the BM multilayer system is more pronounced than that found for the three layer *zig-zag/slanted/chiral* systems (c.f., Figure 4) we may conclude that the difference in the in-plane distribution of electron density becomes enhanced in the former case.

Table 2.- Bilayer period estimated by SEM and vertical (d^V) and lateral (d^L) correlation distances and Yoneda shifts estimated according to the waveguiding approximation (q^Y_z) estimated by GISAXFS for two orthogonal directions of the X-ray beam with respect to the growing direction of films.

Porous multilayer		SEM bilayer period	d^V	d^L	q^Y_z
		(nm)	(nm)	(nm)	(nm ⁻¹)
slanted	0°	210	175	-	- 0,550
	90°		194	11 155	0,575

Similarly, the appearance of only one lateral Bragg wing along the q_y direction (c.f., Figures 5 (b and d)) evidences the existence in the multilayer system of a correlation distance at 10-11 nm (Table 2), similar to those found in the three layer stacks. This suggests that mesopores between nanocolumns have a similar average diameter along the perpendicular to the growing direction. A close observation of the lateral profiles taken for the multilayer at 90° reveals the existence of a second maximum close to the Yoneda peak (i.e. with much smaller q_y values) which also points to the existence of a larger lateral correlation distance in this system. The calculated average value of 155nm is in the order of the distance between laterally associated rows of nanocolumns in the so-called fence-bundling association distribution (see Figure 5 (b)), which further supports the existence of such a lateral arrangement of nanocolumns in this type of OAD thin films and multilayers.^[3, 5]

Conclusion

In this work, we have applied the GISAXS procedure to analyze the microstructure of porous $\text{TiO}_2/\text{SiO}_2$ stacked film structures consisting of three and fifteen layers. For the three layer stack samples, the assessment of the features observed in the patterns taken at two azimuthal orientations with respect to the X-ray beam, revealed information about the following microstructural features and scattering processes:

- a) a roughness correlation of the porous layers may induce a waveguide effect that result in a vertical correlation length with a value in the order of the thickness of an alternated $\text{TiO}_2/\text{SiO}_2$ bilayer stack.
- b) the existence of a similar lateral correlation length of 10-11nm between the three and fifteen layer stack systems, observable only in one direction, has been linked to the size of mesopores between nanocolumns and with a preferential orientation of nanocolumns in one direction that gives rise to an anisotropic electron density distribution. The asymmetrical in-plane electron density distribution appears enhanced for the multilayer system with respect to the three layer stacks.
- c) in the case of the multilayer system, the lateral arrangement of nanocolumns known as fence-bundling association distribution is characterized by a correlation length of 155nm.
- d) using the GISAXS analysis as an indirect measuring method we have also estimated a pore volume of 36-43% for the nanocolumnar structures (15%

for the reference). A higher porosity has been found for the *slanted* and *zig-zag* configurations.

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References

- [1] a) A. Barranco, A. Borrás, A. R. González-Elipe, A. Palmero, *Progress in Materials Science* **2016**, 76, 59; b) M. Wiesing, T. d. I. Arcos, G. Grundmeier, *Advanced Materials Interfaces* **2017**, 4, 1600861; c) M. Laurenti, S. Stassi, G. Canavese, V. Cauda, *Advanced Materials Interfaces* **2017**, 4, 1600758.
- [2] M. M. Hawkeye, M. J. Brett, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2007**, 25, 1317.
- [3] M. Oliva-Ramirez, A. Barranco, M. Löffler, F. Yubero, A. R. González-Elipe, *ACS Nano* **2016**, 10, 1256.
- [4] R. Alvarez, C. Lopez-Santos, J. Parra-Barranco, V. Rico, A. Barranco, J. Cotrino, A. R. González-Elipe, A. Palmero, *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena* **2014**, 32, 041802.
- [5] C. Lopez-Santos, R. Alvarez, A. García-Valenzuela, V. Rico, M. Loeffler, A. R. González-Elipe, A. Palmero, *Nanotechnology* **2016**, 27, 395702.
- [6] a) P. Müller-Buschbaum, *Advanced Materials* **2014**, 26, 7692; b) G. Renaud, R. Lazzari, F. Leroy, *Surface Science Reports* **2009**, 64, 255.

- [7] A. Bhattacharyya, M. K. Sanyal, U. Mogera, S. J. George, M. K. Mukhopadhyay, S. Maiti, G. U. Kulkarni, *Scientific Reports* **2017**, 7, 246.
- [8] a) M. Schwartzkopf, G. Santoro, C. J. Brett, A. Rothkirch, O. Polonskyi, A. Hinz, E. Metwalli, Y. Yao, T. Strunskus, F. Faupel, P. Müller-Buschbaum, S. V. Roth, *ACS Applied Materials & Interfaces* **2015**, 7, 13547; b) A. Meyer, N. Franz, H. P. Oepen, J. Perlich, G. Carbone, T. H. Metzger, *Nano Research* **2017**, 10, 456.
- [9] J. Sun, C. Zhang, C. Zhang, R. Ding, Y. Xu, *RSC Advances* **2014**, 4, 50873.
- [10] B. Pivac, P. Dubcek, J. Popovic, J. Dasovic, S. Bernstorff, N. Radic, J. Zavasnik, *Journal of Applied Crystallography* **2016**, 49, 1957.
- [11] M. Oliva-Ramirez, J. Gil-Rostra, M. C. López-Santos, A. R. González-Elípe, F. Yubero, *Journal of Nanophotonics* **2017**, 11.
- [12] a) G.-G. Lola, P.-B. Julián, R. S.-V. Juan, B. Angel, B. Ana, R. G.-E. Agustín, G.-G. Mari-Cruz, J. H. Jaime, R. R. Daniel, A. E. Tiberio, *Nanotechnology* **2012**, 23, 205701; b) J. Parra-Barranco, F. J. García-García, V. Rico, A. Borrás, C. López-Santos, F. Frutos, A. Barranco, A. R. González-Elípe, *ACS Applied Materials and Interfaces* **2015**, 7, 10993; c) L. Gonzalez-García, J. Parra-Barranco, J. R. Sanchez-Valencia, J. Ferrer, M.-C. Garcia-Gutierrez, A. Barranco, A. R. Gonzalez-Elípe, *Advanced Functional Materials* **2013**, 23, 1655.
- [13] a) J. Zhang, D. Posselt, D.-M. Smilgies, J. Perlich, K. Kyriakos, S. Jaksch, C. M. Papadakis, *Macromolecules* **2014**, 47, 5711; b) K. A. Cavicchi, T. P. Russell, *Macromolecules* **2007**, 40, 1181.
- [14] T. David, D. Buttard, T. Schüllli, F. Dallhuin, P. Gentile, *Surface Science* **2008**, 602, 2675.
- [15] M. Oliva-Ramirez, L. González-García, J. Parra-Barranco, F. Yubero, A. Barranco, A. R. González-Elípe, *ACS Applied Materials & Interfaces* **2013**, 5, 6743.
- [16] P. Müller-Buschbaum, in *Applications of Synchrotron Light to Scattering and Diffraction in Materials and Life Sciences*, DOI: 10.1007/978-3-540-95968-7_3 (Eds: M. Gomez, A. Nogales, M. C. Garcia-Gutierrez, T. A. Ezquerra), Springer Berlin Heidelberg, Berlin, Heidelberg **2009**, p. 61.
- [17] G. Benecke, W. Wagermaier, C. Li, M. Schwartzkopf, G. Flucke, R. Hoerth, I. Zizak, M. Burghammer, E. Metwalli, P. Muller-Buschbaum, M. Trebbin, S. Forster, O. Paris, S. V. Roth, P. Fratzl, *Journal of Applied Crystallography* **2014**, 47, 1797.
- [18] K. Hoydalsvik, T. Barnardo, R. Winter, S. Haas, D. Tatchev, A. Hoell, *Physical Chemistry Chemical Physics* **2010**, 12, 14492.
- [19] J. Dendooven, K. Devloo-Casier, M. Ide, K. Grandfield, M. Kurttepli, K. F. Ludwig, S. Bals, P. Van Der Voort, C. Detavernier, *Nanoscale* **2014**, 6, 14991.
- [20] M. Rawolle, M. A. Ruderer, S. M. Prams, Q. Zhong, D. Magerl, J. Perlich, S. V. Roth, P. Lellig, J. S. Gutmann, P. Müller-Buschbaum, *Small* **2011**, 7, 884.
- [21] T. Hanashima, <http://lipro/msl.titech.ac.jp/scatfac/scatfac.html>.
- [22] a) S. V. Roth, P. Müller-Buschbaum, M. Burghammer, H. Walter, P. Panagiotou, A. Diethert, C. Riekel, *Spectrochimica Acta Part B: Atomic Spectroscopy* **2004**, 59, 1765; b) M. M. A. Kashem, J. Perlich, L. Schulz, S. V. Roth, P. Müller-Buschbaum, *Macromolecules* **2008**, 41, 2186.
- [23] G. G. Lola, B. Angel, P. A. Muñoz, G. E. A. R., G. G. Mari-Cruz, H. J. J., R. D. R., E. T. A., B. David, *ChemPhysChem* **2010**, 11, 2205.
- [24] I. Pape, T. P. A. Hase, B. K. Tanner, M. Wormington, *Physica B: Condensed Matter* **1998**, 253, 278.
- [25] a) T. H. Metzger, I. Kegel, R. Paniago, A. Lorke, J. Peisl, J. Schulze, I. Eisele, P. Schittenhelm, G. Abstreiter, *Thin Solid Films* **1998**, 336, 1; b) G. Renaud, R. Lazzari, C. Revenant, A. Barbier, M. Noblet, O. Ulrich, F. Leroy, J. Jupille, Y. Borensztein, C. R. Henry, J.-P. Deville, F. Scheurer, J. Mane-Mane, O. Fruchart, *Science* **2003**, 300, 1416.
- [26] K. Golovin, S. P. R. Kobaku, D. H. Lee, E. T. DiLoreto, J. M. Mabry, A. Tuteja, *Science Advances* **2016**, 2.

List of Figure Captions

Figure 5.- Schematic geometry of the GISAXS experiments

Figure 6.- SEM micrographs showing the top-view and cross sections (insets at the left side of the images) of the porous three layer stacks with *chiral*, *slanted* and *zig-zag* configurations and the *reference* three layer stack included for comparison. Schemes describing the nanocolumnar microstructure as well as Fourier transforms images are included as insets in the right side of each panel. Lateral association of nanocolumns in the direction perpendicular to the growing direction has been highlighted with yellow lines drawn in the top view micrographs.

Figure 7.- GISAXS patterns of *slanted* (b), *chiral* (c) and *zig-zag* (d) $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ stacks in comparison with a *reference* three layer system taken as reference (a). GISAXS patterns are presented for two orthogonal azimuthal orientations of the sample with respect to the X-ray beam: 0° and 90° .

Figure 8.- Out-of-plane (a) and in-plane (b) one-dimensional GISAXS intensity profiles as a function of q_z and q_y respectively. Plots are shown for *slanted*, *chiral* and *zig-zag* $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ stacks for 0° and 90° orientation of the X-rays beam and are compared with the profiles of the *reference* stack. Guiding lines are added to identify Yoneda peak' shifts (a) and lateral correlation maxima (b).

Figure 5.- GISAXS and SEM analysis of a nanostructured $\text{TiO}_2/\text{SiO}_2$ Bragg microcavity with a *slanted* configuration. (a) Top-view and cross section SEM micrographs, these latter for two orthogonal azimuthal orientations (left) and Fourier transform image included as inset (right). (b) GISAXS patterns of the for 0° and 90° orientations of the X-rays beam with respect to the films growing direction. c) and d) out-of-plane and in-plane GISAXS intensity line profiles along q_z and q_y . Guidelines are added to identify Yoneda peaks' shifts and lateral correlation maxima. Inset shows the out-of plane GISAXS profile in an enlarge scale to show the replica features along q_z .

Supporting Information

Figure S1.- AFM topographical images at $5\mu\text{m} \times 5\mu\text{m}$ of the slanted multilayers with 3 and 15 alternant layers and the reference stacks included for comparison. RMS roughness values and line profiles along the growing and bundling directions on the slanted systems are included.

3-multilayer

15-multilayer

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