Structure of Glancing Incidence Deposited TiO₂ Thin Films as Revealed by Grazing Incidence Small-Angle X-ray Scattering


1. Introduction

Titanium dioxide thin films possess outstanding properties, such as high optical transmittance and refractive index, photoactivity, chemical stability, and so forth, that make them suitable for many technological applications.[1] Regarding film morphologies, the formation of ordered nanorods is important for improving the photocatalytic, photovoltaic or sensor properties of nanostructured TiO₂ thin films.[2, 3] Among the various methods available to produce nanostructured thin films a very versatile procedure is the use of glancing angle physical vapor deposition (GLAD).[4, 5] This method produces porous thin films formed by columns tilted by a certain angle with respect to the substrate. Although different methods of characterization have been used to ascertain the morphology of this type of thin films, to our knowledge grazing incidence small-angle X-ray scattering (GISAXS) [6, 7] has not yet been applied. Herein we report on the GISAXS analysis of TiO₂ thin films prepared by GLAD. One of the advantages of GISAXS is the ability to provide averaged statistical information over the entire illuminated sample area, as well as the ability to access buried structures located well below the surface[8] that are not accessible to local probe techniques like scanning electron microscopy (SEM) or atomic force microscopy (AFM). We found that the GLAD thin films give rise to a new kind of asymmetric GISAXS patterns that may result from a morphological evolution of the columns across the thickness of the films. The data analysis also shows that the GISAXS technique is a powerful tool to describe the nanostructure of this kind of thin films.

Experimental Section

TiO₂ thin films were prepared by GLAD at room temperature on silicon substrates. Evaporation was carried out in an electron bombardment evaporator, using TiO₂ pellets as a target. Stoichiometric and columnar thin films of TiO₂ were obtained by evaporation at 10⁻⁴ torr O₂, placing the substrates at a glancing angle of 80° with respect to the evaporation source. Si-substrates (rectangular pieces of about 1×4 cm²) were positioned with the shortest edge parallel to the vapor flow direction. Films with thicknesses between 45 nm and 600 nm were prepared.

GISAXS experiments were performed at the BW4 beamline (HASYLAB, Hamburg) using a wavelength of λ = 0.138 nm and a sample-to-detector distance of 2.175 m. A moderate microbeam focusing was achieved using beryllium compound refractive lenses (beam size 42×22 mm²). The scattering signal was recorded with a 2D detector (MAR CCD camera with 79 μm² pixel size).

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2. Results and Discussion

SEM cross-section views of the samples investigated were obtained by cleaving the silicon substrates in the direction parallel to the shortest edge. Figure 1 shows a cross-section view of a 600 nm TiO$_2$ film together with a series of normal views of the sample investigated were obtained by cleaving the silicon substrates in the direction parallel to the shortest edge. Figure 1 shows a cross-section view of the sample with the film thickness of 600 nm. The dashed lines plotted in the cross-section view define the height of the thin films used for analysis (i.e., 45, 100, 200, 300, and 600 nm).

![Figure 1](image)

Each point of a GISAXS pattern is defined by two angular coordinates, $\psi$ and $\alpha_y$, where $\psi$ is the horizontal angle measured from the meridian or incidence plane and $\alpha_y$ is the vertical exit angle measured from the sample plane. The pattern is also defined by the scattering vector coordinates, $q_y$ and $q_x$, which can be expressed as functions of the angular coordinates according to the expressions in Equations (1) and (2):

\[
q_y = \frac{2\pi}{\lambda} \sin(\psi) \cos(\alpha_y) \quad (1)
\]

\[
q_x = \frac{2\pi}{\lambda} \sin(\alpha_y) \quad (2)
\]

When the samples investigated with GISAXS are isotropic, that is, have well-aligned scattering objects with an axis of revolution perpendicular to the substrate, the scattered intensity out of the meridian ($q_y \neq 0$) is symmetric with respect to the incidence plane and satisfies the condition in Equation (3):

\[
l(-q_y) = l(q_y) \quad (3)
\]

In this case, the GISAXS patterns are not sensitive to azimuthal rotation along the $z$-axis. However, the samples investigated here show a preferential orientation of the TiO$_2$ columns with respect to the substrate (see Figure 1). Thus, the GISAXS intensity distribution also depends on the azimuth angle ($\omega$) of the substrate. Moreover, the corresponding GISAXS patterns are asymmetric with respect to the incidence plane. Thus, as shown in Figures 3a–c, if the sample is mounted with the columns tilted to the right, the large and broad scattering appears at the left half where $q_y < 0$, and vice versa; columns tilted to the left scatter mostly to the right half where $q_y > 0$ (Figure 3d). To our knowledge, such patterns have not been reported previously for columnar systems although GISAXS patterns from faceted Ge quantum dots have shown non-cen-

![Figure 2](image)
shape of the intensity distribution is similar for all the samples investigated.

Figure 4 shows that the experimental GISAXS pattern of the thinnest sample can be fairly well reproduced within the distorted-wave Born approximation applied to buried scatterers\(^{[12, 13]}\) by means of the FitGISAXS program.\(^{[12]}\) We considered a simple model of monodisperse nanocylinders (diameter = 4.8 nm and aspect ratio = 2.7) tilted by 36° with respect to the z-axis, and randomly distributed in a TiO\(_2\) film with 50% porosity. Such a preliminary simulation suggests that the weak intensity present in the right half of the GISAXS pattern could be related to the second order of the form factor, which would reveal that the height distribution of the columns is quite narrow. Next, we focus on the analysis of the half of the GISAXS pattern which shows the large scattering and exhibits only one broad maximum in the case of the thinnest sample. In contrast, the inset in Figure 5, showing horizontal intensity profiles (\(\gamma\)-cuts) taken at the \(q_y\) value of maximum intensity, illustrates the presence of two scattering maxima in the GISAXS patterns of the TiO\(_2\) samples thicker than 45 nm.

A first approach to extract quantitative information on the samples investigated is obtained from the position of the scattering maxima (\(q_{\text{max}}\)). The corresponding lateral distance \(D_y\) can be derived according to Equation (4):

\[
D_y = \frac{2\pi}{q_{\text{max}}^y}
\]

Thus, the characteristic lateral lengths derived from the two scattering maxima observed are represented as a function of sample thickness in Figure 5. The broad peak observed for the thinnest sample is still present for the thicker samples (Figure 3) and its position is almost constant, suggesting it to be related to the TiO\(_2\) columns formed at the initial stages of the film growth, as evidenced by the morphology observed below the first dashed line plotted in the cross section SEM image shown in Figure 1. The greater characteristic length (\(D_y\)), which is not observed for the thinnest film (45 nm), presents values in the range of 39–160 nm, increasing with film thickness. This suggests the development of a second population of wider and/or more separated columns that, due to the shadowing effects controlling the growth mechanism of GLAD films\(^{[4, 5]}\), grow in length and width at the expense of the initially deposited columns as the thickness of the films increases. This general phenomenology revealed by GISAXS is in agreement with the evolution of the thickness of the columnar microstructure as revealed by the SEM micrographs in Figure 1. Nevertheless, the lateral characteristic length (160 nm) derived for the thickest sample appears to be greater than the inter-column distance revealed by the SEM cross-section image (Figure 1). This discrepancy could be attributed to the influence of the tilting angle of scatters (TiO\(_2\) columns) on the position of GISAXS scattering maxima and/or to the tendency of the GLAD columns to form bundles separated by distances larger than the typical inter-column separation.\(^{[4, 14]}\)
3. Conclusions

For the first time GISAXS was used to characterize the morphology of TiO$_2$ thin films grown by GLAD. Because of the tilting of the TiO$_2$ rods grown on the Si substrate, the obtained GISAXS patterns show a characteristic asymmetry with respect to the meridian or incidence plane. The capability of GISAXS to access buried structures below the surface allowed us to access characteristic lengths which can be assigned to layers with columns of different widths. We anticipate that GISAXS will be a unique technique to elucidate the key parameters of TiO$_2$ thin films to optimize their photocatalytic, photovoltaic or sensor properties.

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