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Self-organization of nanoparticles in a TiO_2 thin film on a glass substrate

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Abstract

Nanocrystalline titanium dioxide colloids have been synthesized using a sol–gel technique followed by growth under hydrothermal conditions in an alkaline environment at temperatures between 190 and 270 °C. Thin films have been made from aqueous suspension of these colloids. Grazing-incidence wide-angle X-ray diffraction (GIWAXD) analysis showed the films to be primarily the anatase crystal phase. This is in agreement with previous scanning electron microscopy (SEM) results, which had revealed a predominantly rod-like particle morphology after growth at lower temperatures. The formation of principally truncated tetragonal or tetrahedral bipyramidal nanocrystallites followed growth at higher temperatures. The rod-like particles self-organize into regular cubic arrays with the long axis of the rods aligned perpendicular to the film surface. This self-organization is dependent upon the base used in colloidal synthesis.

Keywords: Titanium dioxide; Sol–gel; GIWAXD

1. Introduction

Applications of titanium dioxide colloids and thin films are numerous, including photovoltaic, electrochromic, photochromic, electroluminiscence, catalytic devices and sensors [1]. We have explored sol–gel syntheses of nanocrystalline titanium dioxide [2] together with many research groups [3–6]. Both acidic [7] and alkaline environments [8,9] have been used to prepare sol–gel-derived anatase nanocrystals for use as electrode in dye-sensitized solar cell. Formation of hexagonally packed, colloidally derived, ordered thin films has been done by using a base-catalyzed sol–gel synthetic scheme [10,11].

The aim of this work is to use the grazing incidence wide-angle X-ray diffraction (GI-WAXD) method in order to compare with SEM results obtained by Burnside et al. [6] on ordered structures formed from titanium dioxide nanoparticles synthesized using a sol–gel technique.

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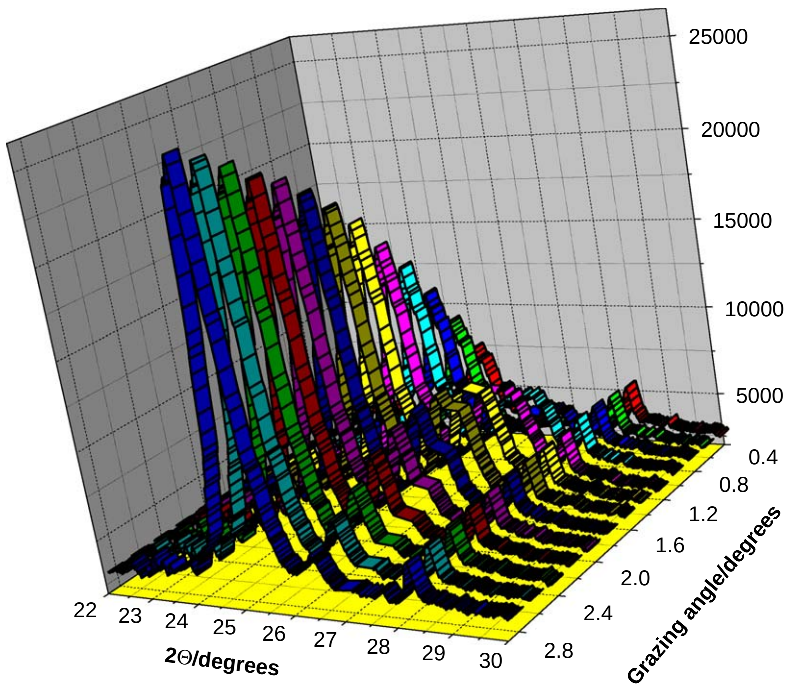

Fig. 1. GIWAXD 3D-pattern of alkaline-ordered TiO_2 film autoclaved at 210 °C; *x*-axes: 2Θ degees, *y*-axes: grazing angles changing by 0.2°, and *z*-axis: intensity of diffraction. At ~25° change of intensity of the line at 24.95° is apparent showing that the surface parallel to the substrate has (1 0 0) orientation.

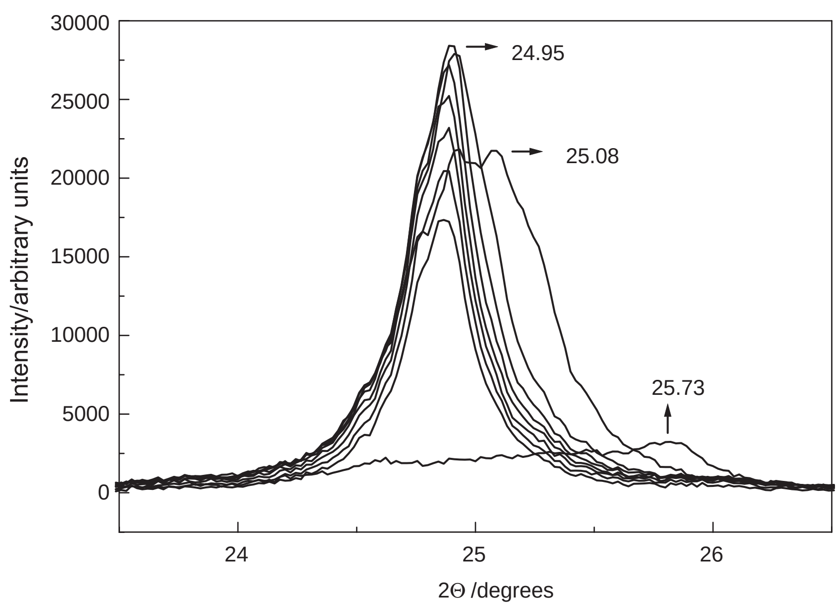

Fig. 2. GIWAXD of alkaline-ordered TiO_2 film on SnO_2-coated glass in 2D-representation with grazing angles changing by 2°.

2. Experimental procedure

Nanocrystalline titanium dioxide colloids have been synthesized using a sol–gel technique followed by growth under hydrothermal conditions in an alkaline environment at temperatures between 190 and 270 °C. Thin films have been made from an aqueous suspension of these colloids on SnO_2-coated glass. The detailed preparation procedure is given elsewhere [6].

GIWAXD measurements were performed at the SAXS beamline at synchrotron ELETTRA, Trieste [12,13]. The beamline is built by the researchers from the Institute for Biophysics and X-ray Structure Research (IBR), Austrian Academy of Science. Its characteristics are: photon beam wavelength is $\lambda = 1.54 \times 10^{-10}$ m, energy resolution $\Delta E/E \leqslant 2.5 \times 10^{-3}$, focal spot size FWHM is $1.2 \times 0.6\,\mathrm{mm}^2$, spot at sample is $5.4 \times 1.8\,\mathrm{mm}^2$ and flux at the sample is 5×10^{12} photons s^{-1} (electron beam energy 2 GeV, beam current 200 mA, X-ray photon energy 8 keV).

3. Results and discussion

In this work we have performed GIWAXD experiments on TiO_2 thin films on a glass substrate. The 2θ angular range was changed from 5° to 35° with a parallel change of the rocking angle for 4°. The grazing angle varied from zero angle by steps of 0.2° till 3° as shown in Fig. 1, while steps of 2° are shown in Fig. 2. Fig. 1 shows 3D-plots for the alkaline sample autoclaved at 210 °C. While focusing on the anatase lines at ~25°, we have followed their behaviour upon change of the rocking angle. In alkaline "ordered" TiO_2 film the intensity of this line, 24.95°, had changed and thus showed that the (1 0 0) orientation plane parallel to the substrate as dominant (Fig. 2). This plane is connected with a predominantly rod-like particle morphology that has primarily (1 0 0) faces irregularly terminated from the (0 0 1) side.

Summary results are presented in Table 1. Transparent "acidic" films are denoted with t. At sample t4, autoclaved at 270 °C, a mixture of orientations (1 0 1) and (1 0 0) are observed (Fig. 3). The figure shows the presence of tetragonal, bipyramidal and rod-like particles. All the lines 1–7 (see Table 1) change with an increase of the grazing angle, which means that the film is anatase without preferential orientation relative to the substrate plane. Sample t3, autoclaved at 190 °C, is anatase in (1 0 0) orientation since the line denoted by 6 changes with the grazing angle. This means that, at lower temperatures, the rod-like particles self-organize into

Table 1
Number of sample, t stands for transparent "acidic" samples and b stands for alkaline samples, scattering angle 2Θ in degrees, d in Å, d/x, ($x = 2.4$) in Å, d in Å from paper of Narita et al. [14], crystallographic table 21–1272, normalized intensity I/I_0 of line, hkl indices and crystallographic phase of film (A stands for anatase)

Sample	2Θ (deg.)	d (Å)	d/x (Å), $x = 2.4$	d (Å)[14]	I/I_0	hkl	Phase
t4							
1	23.40	3.82173	0.95543	0.9550	4	(3 1 6)	A
2	23.77	3.76308	1.88154	1.891	33	(2 0 0)	A
3	24.09	3.71382	0.92845	0.9248	< 2	(3 0 7)	A
4	24.51	3.65113	0.91278	0.914	2	(4 1 1)	A
5	24.73	3.61915	0.89835	0.8960	3	(2 1 9)	A
6	24.91	3.59340		3.785		(1 0 0)	A
7	25.47	3.51566		3.510	100	(1 0 1)	A
t3							
1	17.67	5.04591		4.785		(0 0 2)	A
2	28.46	3.15277		3.171		(0 0 3)	A
6	24.95	3.58770		3.785		(1 0 0)	A
8	25.73	3.48072		3.510	100	(1 0 1)	A
b24							
1	17.66	5.04875		4.785		(0 0 2)	A
2	28.49	3.14952		3.171		(0 0 3)	A
5	24.78	3.61196		3.785		(1 0 0)	A
8	25.72	3.48205		3.510	100	(1 0 1)	A
b23							
5	24.75	3.61627		3.785		(1 0 0)	A
8	25.58	3.50079		3.510	100	(1 0 1)	A
b22							
5	24.77	3.61339		3.785		(1 0 0)	A
8	25.73	3.48072		3.510	100	(1 0 1)	A
b21							
5	25.09	3.56803		3.510	100	(1 0 1)	A
6	24.93	3.58770		3.785		(1 0 0)	A
8	26.57	3.37257	1.68628	1.666	19	(2 1 1)	A

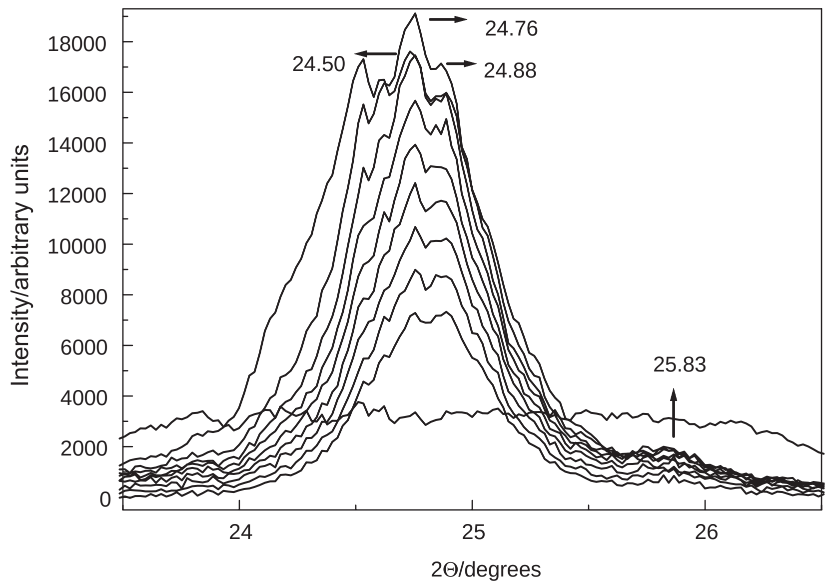

Fig. 3. GIWAXD of transparent acidic TiO_2 film on SnO_2-coated glass in 2D-representation with grazing angles changing by 2°.

regular cubic arrays with the long axis of the rods perpendicular to the film surface.

Samples prepared in an alkaline environment are denoted by b. Sample b24 is in the (1 0 1) orientation since this line increases in intensity as the X-ray penetrates into the bulk. This is connected with the tetragonal and bipyramidal particles that have primarily (1 0 1) surfaces, as observed previously for anatase nanocrystallites [11]. Sample b23 is similar to b24, but without weak lines at 17.66° and 28.49°, which we assigned as (0 0 2) and (0 0 3) lines. Sample b22 behaves as sample b23. Sample b21 is in (1 0 0) orientation where only the line at 24.93° drastically changes with the grazing angle. Samples b21–b24 are alkaline "ordered" samples obtained by the sol–gel method followed by growth under hydrothermal conditions in an alkaline environment at temperatures between 190 and 270 °C. Sample b21 with a rod-like prismatic shape is a low-temperature species, while sample b24 represents a higher temperature nanofilm, with tetrahedral bypiramidal or truncated tetragonal shapes with primarily (1 0 1) surfaces. Growth of colloids in this case occurs by agglomeration of smaller, primary rod-like particles to form larger bypiramidal particles, which can be observed by the narrowing of diffraction lines during a rise in temperature. Broader lines are present with low temperature species thus revealing smaller grain sizes of particles than at higher temperatures.

4. Conclusion

GIWAXD results are in agreement with the previous scanning electron microscopy (SEM) results, which had revealed a predominantly rod-like particle morphology after growth at lower temperatures. The formation of principally truncated tetragonal or tetrahedral bipyramidal nanocrystallites followed the growth at higher temperatures. The rod-like particles self-organize into regular cubic arrays with the long axis of the rods aligned perpendicular to the film surface. This self-organization is dependent upon the base used in the colloidal synthesis.

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