Fine control of the amount of preferential <001> orientation in DC magnetron sputtered nanocrystalline TiO$_2$ films

B Stefanov, C G Granqvist and L Österlund

The Ångström Laboratory, Department of Engineering Sciences, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

E-mail: lars.osterlund@angstrom.uu.se

Abstract. Different crystal facets of anatase TiO$_2$ are known to have different chemical reactivity; in particular the {001} facets which truncates the bi-tetrahedral anatase morphology are reported to be more reactive than the usually dominant {101} facets. Anatase TiO$_2$ thin films were deposited by reactive DC magnetron sputtering in Ar/O$_2$ atmosphere and were characterized using Rietveld refined grazing incidence X-ray diffraction, atomic force microscopy and UV/Vis spectroscopy. By varying the partial O2 pressure in the deposition chamber, the degree of orientation of the grains in the film could be systematically varied with preferred <001> orientation changing from random upto 39% as determined by March-Dollase method. The orientation of the films is shown to correlate with their reactivity, as measured by photo-degradation of methylene blue in water solutions. The results have implications for fabrication of purposefully chemically reactive thin TiO$_2$ films prepared by sputtering methods.

1. Introduction

Nanocrystalline TiO$_2$ films have beneficial physicochemical and optical properties in a number of applications related to environmental photocatalysis and energy conversion technologies [1]. Normally anatase particles are dominated by the low energy {101} surface planes with only a fraction of {001} facets, which gives the particles their characteristic truncated bi-pyramidal morphology.

Thin TiO$_2$ films prepared by reactive DC magnetron sputtering in O$_2$ atmosphere are initially amorphous, but after heat-treatment it has been reported that preferential alignment of grains occurs in the <004> direction, which exposes reactive (001) planes at the film surface [2,3]. This is desirable, since it is known that the reactivity of anatase depends on the surface structure. For example increased orientation in the <001> direction can favor water splitting reactions, or improve the photonic efficiency of anatase photocatalyst [4-6].

In the present work we demonstrate the possibility to purposefully control the fraction of preferred <001> orientation up to approximately 39%, as determined by March-Dollase analysis of x-ray diffraction data, by adjustment of the partial oxygen pressure for the deposition process. The fraction of preferred orientation was estimated using GIXRD and the effect of the deposition parameters on the crystalline and optical properties of the films was reviewed.

2. Deposition and characterization of anatase TiO$_2$ films

Standard microscope glass slides were used as substrates. The deposition was done using a pair of 5 cm diameter Ti targets (99.995% purity) positioned symmetrically at a distance of 13 cm from the substrate in a setup described elsewhere [7]. Sputtering was carried out in Ar/O$_2$ atmosphere (99.998%

purity gases) at a total pressure of 20 mTorr and with O_2 partial pressures in the range 0.65 – 1.54 mTorr (refer to table 1). A constant current of 0.75 A was employed leading to sputtering power in the range of 206 – 280 W with increasing oxygen flow. After deposition the films were heat-treated for 1 h at 500ºC.

The phase composition of the films was investigated by use of grazing incidence X-ray diffraction (GIXRD), employing a Siemens D5000 diffractometer using CuKα1 radiation (1.5406 Å) at 0.5° incidence angle.

Additional information about surface morphology was acquired through atomic force microscopy (AFM) employing a PSIA XE150 SPM/AFM instrument.

Film thicknesses were determined by surface profilometry (Dektak XT Advance from Bruker).

A Perkin-Elmer Lambda 900 spectrophotometer equipped with a $BaSO_4$ coated integrating sphere was used for UV-VIS transmittance and reflectance measurements in the range 300 – 800 nm.

Table 1. Summary of the deposition conditions and structural and optical properties of anatase films, deposited at different partial O_2 pressures. Oxygen partial pressure during sputtering (P_{O_2}), film thickness (d), film deposition rate (r_{dep}), fraction of <001> grain orientation ($\eta_{<hkl>}$), refractive index (n), porosity, surface roughness (R_{rms}), and optical bandgap (E_g).

P_{O2} mTorr	d nm	r_{dep} nm min^{-1}	$\eta_{<001>}$ %	n	Porosity %	R_{rms} nm	E_g eV
0.65	574	16	1.99	2.23	88	1.3	3.31
0.95	578	17	12.1	2.15	84	1.1	3.29
1.25	664	18	25.4	2.04	79	1.4	3.28
1.54	697	20	38.6	1.96	75	1.6	3.27

3. Results and discussion

Film deposition was performed at a rate between 16 and 20 nm min^{-1} (proportional to sputtering power) yielding final thicknesses between 574 to 696 nm, as determined both by profilometry and analysis of UV-VIS transmittance data.

Rietveld refinement of the GIXRD data was done using the PowderCell package [8], and the March-Dollase (MD) method was used to determine the fraction of <001> preferred orientation by means of the Zolotoyabko equation [9]:

$$\eta_{\langle hkl \rangle} = \frac{(1 - r_{\langle hkl \rangle})^3}{(1 - r_{\langle hkl \rangle})^3} \times 100\% \qquad (1)$$

The MD method assumes that the sample has cylindrical orientation symmetry (i.e. the orientation vector does not change by azimuthal rotation, which is applicable in our case since the samples were deposited using a rotating holder). The MD parameter $\eta_{\langle hkl \rangle}$ is a measure of the fraction of crystallites oriented with the crystallographic direction of interest towards the surface (see figure 1).

Analysis of the XRD data shows that $\eta_{\langle 001 \rangle}$ increases with increasing O_2 partial sputtering pressure P_{O2} (as can be seen from figure 2 and table 1). It is also evident from figure 2 that the as-deposited films (lowest diffractogram) are amorphous.

The inset in figure 2 also shows photography images of the as-deposited films. The color of the films reveals that films deposited at low P_{O2} are under-stoichiometric. All post-heat treated films were transparent. It has been reported that sputter deposited TiO_2 is usually <001> orientated [3].
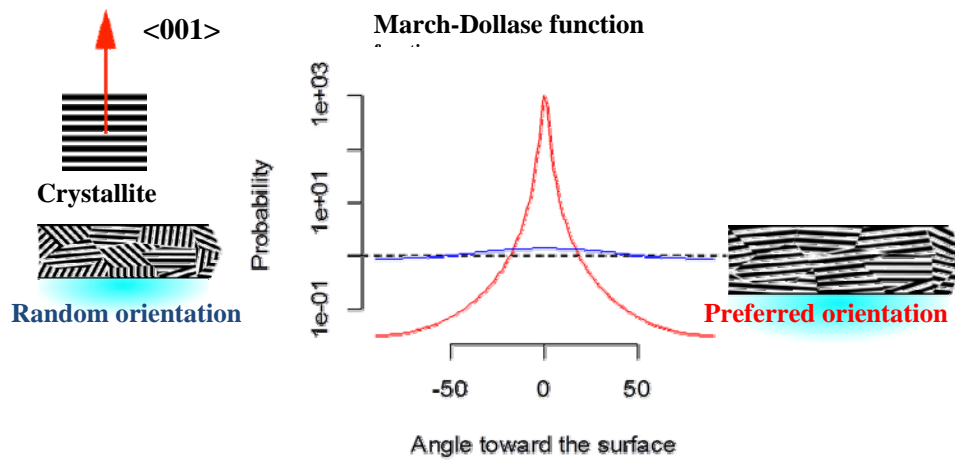
Figure 1. The March-Dollase function for crystallite orientation distribution. The insets represent two examples of films with random and preferred orientation.

We suggest that the introduction of non-stoichiometric growth sites induces crystallites with random growth leading to lower total amount of preferred orientation in the samples. The mean crystallite sizes were estimated to be between 25 and 18 nm, and inversely proportional to P_{O2}.
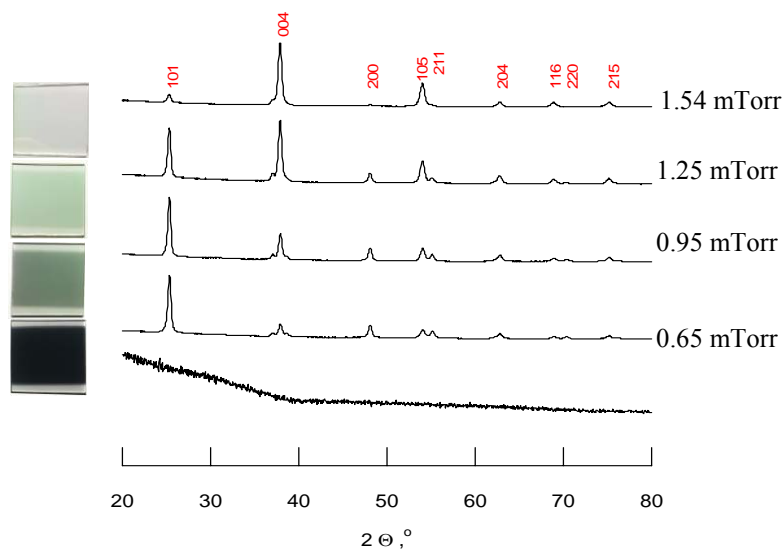

Figure 2. GI-XRD diffractograms for the post-heat treated samples, deposited at different P_{O2} pressures. The insets on the left represent the color of the as-deposited films, which were amorphous as visible by the lowermost diffractogram..

Analysis of AFM data shows that all films were equally smooth and dense regardless of P_{O2} with spherical surface features with sizes comparable with the mean crystalline size (figure 3). The root mean square roughness of the films was about 2.5 nm irrespectively of the sputtering conditions.
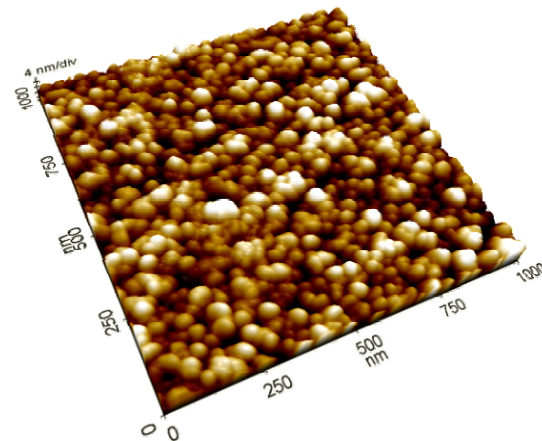
Figure 3. Example of the surface topology of a sputtered anatase TiO$_2$ film. R_{rms}
was found to be about 2.5 nm regardless of sputtering conditions.

The optical properties of the films including refractive index and optical bandgap were determined from UV-VIS spectrophotometry. The refractive index, estimated using the Swanepoel approach [10], decreased with increasing P$_{O2}$ from 2.23 to 1.96 (literature value is 2.56, see figure 4). The packing density was determined from the Pulker equation and it was found to be correlated to an increased porosity at higher P_{O2} of about 10% (which is not detectable by AFM). The optical bandgap was estimated according to the method suggested by Hong et al. [11] revealing an approximately constant bandgap with the experimental measurement error (see table 1).
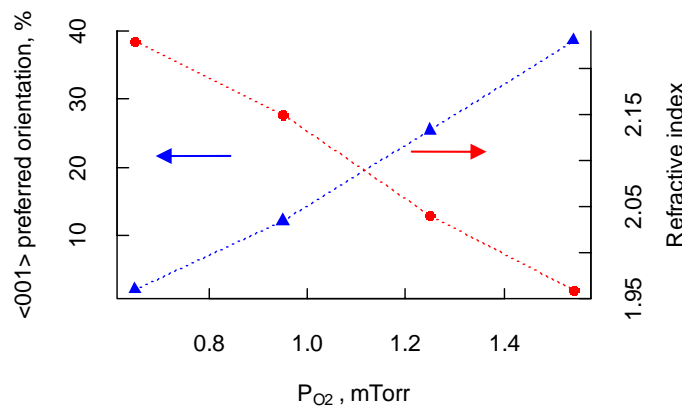

Figure 4. Dependence of <001> preferred orientation fraction and the refractive index of the samples by the oxygen partial pressure.

Table 2. Rate constant for methylene blue photodegradation for TiO$_2$ films with different η$_{<001>}$ [12].

P$_{O2}$, mTorr	$\eta_{<001>}$, %	r, min^{-1}
0.65	1.99	0.95
0.95	12.1	0.99
1.25	25.4	1.43
1.54	38.6	2.49

Table 2 shows the results from photodegradation of methylene blue for the various TiO_2 thin films used in this study, as described in detail elsewhere [12]. It is evident that the photodegradation rate increases as $\eta_{\langle 001 \rangle}$ increases, and that an approximately 262% increase of the rate constant is obtained at $\eta_{\langle 001 \rangle} = 39$ % compared with an almost randomly oriented film with $\eta_{\langle 001 \rangle} =$ **2 %**.

4. Conclusions

We have presented an approach to fine-tune and quantify the fraction of <001> oriented crystallites, $\eta_{<001>}$, in DC magnetron sputtered anatase TiO_2 films by means of controlling the partial O_2 pressure in the deposition atmosphere, P_{O2}. It was found that increasing P_{O2} leads to increased $\eta_{<001>}$, and porosity, and decreased n. Measurements of the photocatalytic degradation of methylene blue in aqueous solution show that $\eta_{<001>}$ scales with the degradation rate, and hence that photocatalytic reactive TiO_2 thin films can be prepared by purposefully increasing $\eta_{<001>}$ by adjusting sputtering conditions. Such films with controlled fraction of <001> orientation and optical properties might find applications in photocatalysis, as self-cleaning surfaces, or as optical coatings.

5. Acknowledgements

References

[1]　Hagfeldt A and Graetzel M 1995 *Chem. Rev.* **95** 49-68
[2]　Sério S, Melo Jorge M E, Maneira M J P and Nunes Y 2011 *Mater. Chem Phys* **126** 73-81
[3]　Howitt D G and Harker A B 1987 *J. Mater. Res* **2** 201-210
[4]　Hengerer R, Kavan L, Krtil P and Graetzel M 2000 *J. Electrochem. Soc.* **147** 1467
[5]　Deng H, Zhang H and Lu Z 2002 *Chem. Phys. Lett.* **363** 509-514
[6]　Zheng J-Y, Bao S-H, Guo Y and Jin P 2014 *ACS Appl. Mater. Interfaces* **6** 5940-5946
[7]　Kharrazi M, Azens A, Kullman L and Granqvist C G 1997 *Thin Solid Films* **295** 117-121
[8]　Kraus W and Nolze G 1996 *J. Appl. Crystallograph.* **29** 301-303
[9]　Dollase W A 1986 *J. Appl. Crystallograph.* **19** 267-272
[10]　Swanepoel R 1983 *J. Phys. E Sci. Instrum.* **16** 1214-1222
[11]　Hong S, Kim E, Kim D.-W., Sung T.-H. and No K 1997 *J. Non-Cryst. Solids* **221** 245-254
[12]　Stefanov B and Österlund L 2014 *Coatings* **4** 587-601