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A fractal analysis of TiO_2 sol-gel films treated under different atmospheres♣

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We report in this work a fractal analysis on TiO_2 films, treated under ammonia and oxygen atmospheres, in correlation with their surface morphology. Titanium dioxide films were deposited on fused silica substrates by a sol-gel and dipping method. The morphology of the five-layered TiO_2 films was investigated by atomic force microscopy (AFM). Furthermore, the AFM images from 4x4, 2x2 and 1x1 μm^2 scanning areas were analyzed by computing the fractal dimensions by applying both the correlation function method and the variable length scale method. It was found that all samples exhibited fractal behaviour in a large self-similarity domain. The sample surfaces were characterized by three different fractal dimensions, indicating three different superimposed structures on them. The short self-similarity range fractal dimension was higher in the case of NH_3 annealing, compared to those obtained for O_2 annealing, indicating a lower roughness at short distances. Samples annealed in a NH_3 flux and a higher temperature had higher fractal dimensions at short ranges, the three fractal dimensions having almost the same values. These results could be used in future work as a standard analysis method, and also in the preparation of materials with tailored nanostructural properties.

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1. Introduction

The necessity of a sensitive technique, capable of describing in a geometric way the complexity of the nature is the reason to use fractal theory [1]. Several experiments have confirmed that the surfaces and internal structures of many solid materials are fractal at molecular level [2-5].

If an object has a fractal behavior, it is possible to compute a quantity, named "the fractal dimension", capable of describing its irregular geometry. Characterizing the geometry of an object, at a molecular scale, by a number, the fractal dimension, will help us to correlate this quantity with the object history (preparation conditions). In this way, the fractal dimension will help us to classify and perhaps better understand some properties of fractal materials. Fractal analysis can simply describe disordered systems, by attaching to every structure a real, positive, number. Low fractal dimension values (2.0) indicate regularity and smoothness, while intermediate values indicate irregular surfaces and values close to 3 indicate highly irregular surfaces. When other geometric characteristics cannot provide information on amorphous or rather poor crystallized structures, fractal geometry is the instrument that can describe them.

There are a lot of methods to compute a fractal dimension. Direct methods usually analyze microscopic images (AFM, SEM, STM, TEM micrographs) using different algorithms, such as the "box-counting" method, the mass-radius relation, the correlation function method and the variable length scale method. Our goal is to compute the fractal dimensions of TiO_2 films, deposited by a sol-gel method and thermally treated under different conditions, by applying AFM micrographs and two methods from the above ones, namely the correlation function method and the variable length scale method.

2. Experimental

2.1 Film preparation

Multilayered TiO_2 films were deposited on quartz substrates by a sol-gel and dipping method. A complete description of the preparation procedure can be found in our recent paper [6]. The films with five layers were firstly

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treated at 450°C for 30 min in air. Afterwards, they were supplementarily treated for 2 h, either under an O_2 atmosphere at 500°C and 600°C (samples A and C, respectively), or under an NH_3 atmosphere at 500°C and 600°C (samples C and D).

2.2. AFM measurements

The AFM experiments were carried out in the intermittent contact mode, by an EasyScan 2 apparatus (Nanosurf® AG Switzerland) equipped with a high resolution scanner (z-axis resolution of 0.027 nm and an X-Y linearity mean error of less then 0.6 %). SiN tips having a square pyramidal profile with a radius of curvature of less than 10 nm and a half angle of 35° were used. The AFM investigations were performed on different scales from 8 μm down to the sub-micrometric scale (4x4, 2x2 and 1x1 μm^2 scanning areas), and these images were analyzed qualitatively and quantitatively.

2.3. Theoretical methods for computing the fractal dimension

A fractal is an object and its observed volume depends on the resolution (length scale) over several orders of magnitude and follows power law behaviour with a nontrivial exponent. The most important property of fractals is the self-similarity, which is the property for a part to look like the whole [1].

Self-similarity has a mathematical description; the number of boxes N(r) necessary to cover a fractal object depends on the box size r as:

$$N(r) \sim r^{-D} \quad , \tag{1}$$

where D is the fractal dimension. This equation can be used to compute D. This is named the "box-counting method" [1].

A fractal dimension can also be computed using more elaborated methods, such as the "height correlation function" [2-4]:

$$G(r) \equiv \left\langle C(\vec{x}, r) \right\rangle_x \tag{2}$$

where the symbol <…> denotes an average over $\boldsymbol{x}$, and $C(\boldsymbol{x},r)$ is defined as

$$C(\vec{x}, r) = \left[h(\vec{x}) - h(\vec{x} + \vec{r})\right]^2 \tag{3}$$

The scanned surface is described by the function $h(\boldsymbol{x})$, which gives the maximum height of the interface at a position $\boldsymbol{x}$. Thus, the height correlation function $G(r)$ obeys the following scaling relation [7]:

$$G(r) \propto r^{2\alpha}, r << L \tag{4}$$

where, for a surface embedded in a 3-dimensional Euclidean space with a fractal dimension D :

$$\alpha = 3 - D \tag{5}$$

The scaling range obeyed by Eq. (4) is defined by "cut-off" limits, and it indicates the range of self-affinity, in other words, the range where there are correlations between surface columns.

This method is applied for a narrow scale range, and it cannot be extended to a larger scale range because of the great amount of computations needed. To extend the scale range to larger values in order to investigate the fractal behaviour, a second method has been used: the variable length scale method. This was proposed by Chauvy et al. [8], and it involves computing the RMS deviation of the surface. The algorithm is the following: (i) an interval of length ε in the case of a profile (or a box of size $\varepsilon x \varepsilon$ in the case of a surface) is defined; (ii) a linear (or planar) least squares fit to the data within the interval is performed, and the roughness is calculated; (iii) the interval (box) is moved along the profile (surface) and step (ii) is repeated; (iv) the RMS deviation for multiple intervals is computed; (v) steps (ii)-(iv) are repeated for increasing lengths (box sizes).

The smallest size for an interval corresponds to 10 data points (10x10 points for 3-dimensional embedded objects) and its maximum size is the total length of the profile (size of the surface). The RMS deviation $R_{q\varepsilon}$, averaged over n_ε, the number of intervals of length ε, is defined as:

$$R_{q\varepsilon} = \frac{1}{n_\varepsilon} \sum_{i=1}^{n_s} \sqrt{\frac{1}{p_\varepsilon} \sum_{j=1}^{p_s} z_j^2} \tag{6}$$

where z_j is the j^{th} height variation from the best fit line within the interval i, and p_ε is the number of points in the interval ε.

A log-log plot of $R_{q\varepsilon}$ versus ε gives the Hurst or roughening exponent H, and the fractal dimension D can be calculated as

$$D = D_T - H \tag{7}$$

where D_T is the topological dimension of the embedding Euclidean space (D_T = 2 for profiles and D_T = 3 for surfaces). The variable length scale method is more suitable for higher scaling range than the correlation function method, because of the necessity to have enough points in an interval $\varepsilon x \varepsilon$ to compute the RMS deviation $R_{q\varepsilon}$ averaged over n_ε, meaning that ε must be high enough for good statistics.

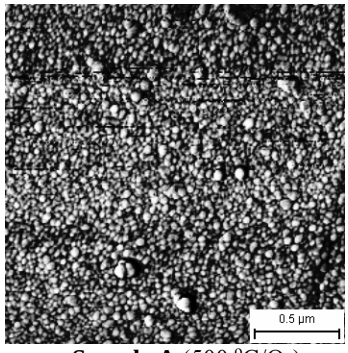
In the following, we shall use Eqs. (4) and (6) to compute the fractal dimensions of our samples.

3. Results and discussion

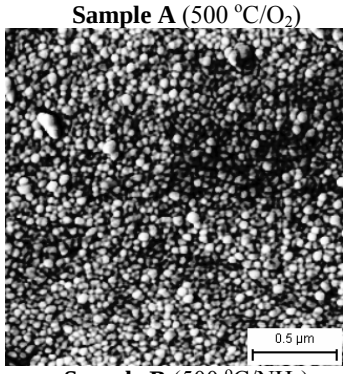
Fig. 1 presents AFM images for samples A, B, C and D at a scan scale of 2x2 μm^2, acquired in a phase contrast working mode with a scan rate around 1-2 Hz. Below each

image, the temperature and atmosphere used for annealing are indicated. These images, showing the formation of a grain structure, are found to be characteristic of the morphology of the sol-gel TiO_2 films treated at 500 and 600°C under oxygen or ammonia atmospheres. However, at 600°C, for both O_2 and NH_3 atmospheres, the surface morphology undergoes slight changes.

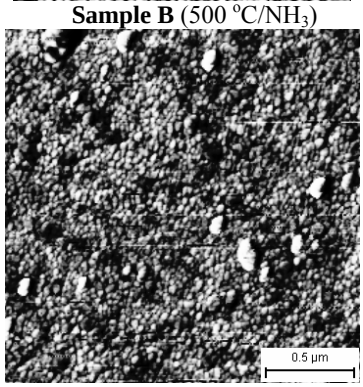
Both, the correlation function method and the variable length scale method were used to compute the fractal dimension of these AFM images. For every sample, three AFM images of different sizes (1x1 μm^2, 2x2 μm^2 and 4x4 μm^2) were analyzed. The results are summarized in Table 1.



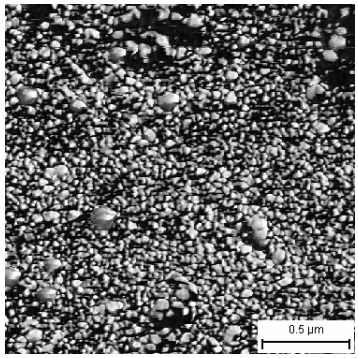
Sample A (500 °C/O_2)



Sample B (500 °C/NH_3)



Sample C (600 °C/O_2)



Sample D (600 °C/NH_3)

Fig. 1. Contrast phase AFM images of the samples A-D from 2x2 μm^2 scans.

The samples exhibited fractal behavior over large self-similarity limits, as is seen from Table 1. Depending on the atmosphere and temperature of the thermal treatment, we obtained different fractal dimensions. However, all samples showed three variation domains for the fractal dimensions, indicating three different superposed structures on the surfaces. While samples A and B had fractal dimensions spread on a large interval (2.38-2.91 and 2.44-2.88, respectively), sample C had fractal dimensions between 2.52 and 2.87. For sample D, the situation appears to be a little different; the three structures having fractal dimensions in the same range (2.60-2.87).
The short self-similarity range fractal dimension is higher in the case of NH_3 than that obtained for an O_2 annealing atmosphere (samples B and D compared with A and C, respectively), indicating a lower roughness at short distances.

Increasing the temperature of the thermal treatment (sample C compared with sample A and sample D compared with sample B) resulted in an increase in the short range fractal dimension. Thus, even samples C and D were characterized by three superposed fractal structures, and the three fractal dimensions did not differ much from each other.

Table 1. Fractal dimensions of samples A-D.

S	Size (μm^2)	Fractal dimension	Self-similarity limits (nm)	Method (Eqs.)
A	1	2.38±0.01 2.86±0.01	4-16 97-252	(4) (6)
	2	2.62±0.01 2.87±0.01	15-25 116-193	(4) (6)
	4	2.65±0.02 2.91±0.01	15-31 155-387	(4) (6)
B	1	2.45±0.01 2.56±0.04 2.82±0.01	4-23 38-96 96-232	(4) (6) (6)
	2	2.44±0.02 2.67±0.04 2.88±0.01	10-24 24-32 116-232	(4) (4) (6)
	4	2.54±0.01	15-242	(4)

C	1	2.56±0.01	4-34	(4)
		2.72±0.01	34-60	(4)
		2.56±0.02	38-155	(6)
	2	2.52±0.01	8-40	(4)
		2.82±0.01	40-67	(4)
		2.69±0.02	77-193	(6)
		2.87±0.01	193-503	(6)
	4	2.83±0.01	34-79	(4)
		2.83±0.01	155-465	(6)
D	1	2.62±0.01	11-38	(4)
		2.52±0.04	38-96	(6)
		2.77±0.01	96-213	(6)
	2	2.60±0.03	8-35	(4)
		2.85±0.02	35-56	(4)
		2.72±0.01	77-155	(6)
		2.86±0.01	155-232	(6)
	4	2.83±0.01	127-334	(4)
		2.87±0.01	232-775	(6)

4. Conclusions

Modified TiO_2 sol-gel coatings on quartz substrates were analyzed using fractal theory. AFM images of different sizes were used to compute the direct fractal dimensions. All samples showed fractal behaviour in a large self-similarity domain. The surfaces of the samples were characterized by three different fractal dimensions. Samples annealed in a NH_3 flux and higher temperatures had larger fractal dimensions at short ranges, and the three fractal dimensions had close values.

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