Microstructural Characterization of Hierarchical Structured Surfaces by Atomic Force Microscopy

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Abstract. In this work, we evaluate the hierarchical surface topography of reactively sputtered nanocrystalline Pb(Zr,Ti)O3 and TiO2 thin films as well as plasma-treated antireflective PET films by means of determining the fractal dimension and power spectral density (PSD) of surface topography recorded by atomic force microscopy (AFM). Local fractal dimension was obtained using the triangulation method. The PSDs of all samples were fitted to the k-correlation model (also called ABC model) valid for a self-affine surface topography. Fractal analysis of AFM images was shown to be an appropriate and easy to use tool for the characterization of hierarchical nanostructures.

1. Introduction

A large number of modern electronic device applications are based on hierarchical micrometer- and nanometer-sized building blocks, for instance, metal oxide gas sensors, catalytic electrodes and electrolytes of solid oxide fuel cells, dye-sensitized solar cells, antireflective solar cell and display coatings, mesoporous films of biosensors, and others. Hierarchical meso- and nanoporous structures provide an effective liquid or gas transport via well aligned mesoporous structures and a large surface area for catalytic reactions [1]. Optical applications of hierarchical surface structures include the huge market of antireflective touch-screen and mobile phone coatings.

The structural characterization of hierarchical structures composed of lower dimensional building blocks requires application of different measurement techniques to cover a wide range of sizes being present within the microstructure. By taking advantage of the scaling property of many physical systems [2], hierarchical structures might be adequately characterized by atomic force microscopy with resolution from about 10 nm to the micrometer range. The advantage of AFM is that it already provides a digitized image suitable for numerical analysis.

Surface topography is usually described in terms of surface roughness which is by definition solely a function of height, i.e., it provides no information about the lateral spacing of surface features. Consequently, two surfaces can have the same root mean square roughness, but very different topographies [3]. The root mean square method of roughness evaluation is most applicable to surfaces which are well represented by a Gaussian height distribution [4]. On the other hand, higher dimensional structures composed of many; lower dimensional building blocks make a single surface roughness value not very instructive.

In general, fractal models provide a more realistic description of many natural surfaces such as craters, mountain ranges, clouds and others which cannot be described by usual geometric objects (spheres, cones, cubes, cylinders etc.) [2]. With regard to the finite numbers of pixels of an AFM image, the triangulation method provides a more reliable value of fractal dimension D in the range 2.1 < D < 2.5 while the cube counting underestimates the real value [5].

When a surface is well represented by a superposition of sinusoidal relations, the description by power spectral density (PSD) is most appropriate [4]. The PSD describes how the power of the Fourier transform of the surface height is distributed with wave-numbers of the spatial frequency in reciprocal space, i.e., it identifies wavelengths of features that contribute to the surface topography. A one-
dimensional PSD of a self-affine surface is well described using the k-correlation model (also called ABC model) assuming perfectly isotropic surfaces [6]:

$$PSD = \frac{A}{(1 + B^2 k^2)^{C/2}}.$$  \hspace{1cm} (1)

The fit to a model PSD allows getting rid of algorithmic procedure artifacts related to finite bandwidth, discrete spatial frequencies and fluctuations [6]. The parameter $A$ describes the low-frequency limit of the spectrum. The physical meaning of the flat part of this curve at low frequencies is that - across these dimensions in real space, - there is no significant deviation in the height value. Therefore, the parameter $B$ defines a correlation length beyond which the surface height fluctuations are not correlated. Hence, $B$ represents a mean grain size. The parameter $C$ depends on the growth mechanism [7]. The integration of the PSD yields the RMS roughness $\sigma$ of the surface.

$$\sigma_{r-D}^2 = \int_{f_{min}}^{f_{max}} PSD_{r-D}(k) \cdot dk.$$ \hspace{1cm} (2)

Recently, we have characterized the hierarchical surface topography of sol-gel derived SiO$_2$-SnO$_2$ nanocomposite films [8] and of solid oxide fuel cell Ce$_{0.01}$Sc$_{0.10}$Zr$_{0.89}$O$_{2-x}$ electrolytes and 60 wt% Ce$_{0.01}$Sc$_{0.10}$Zr$_{0.89}$O$_{2-x}$-40 wt% NiO anodes [9] by evaluating fractal dimension and fitting the PSD to the k-correlation model.

In this work, we extend and generalize this approach by investigating reactively sputtered nanocrystalline Pb(Zr,Ti)O$_3$ and TiO$_2$ thin films as well as plasma-treated antireflective PET films.

2. Experimental

Lead-zirconium-titanium oxide thin films were deposited by reactive sputtering from 8-inch Zr, Ti and Pb targets in an oxygen/argon atmosphere onto not intentionally heated, copper-coated Kapton® HN films by means of a LS730S multi-target sputtering system (Von Ardenne Anlagentechnik, Dresden) [10]. The base of the Pb target is directly connected with the RF (13.56 MHz) generator (PFG 1600 RF, Hütttinger). A unit for pulsed DC (30 kHz, duty cycle ~ 90 %) and arc suppression (Pinnacle$^{TM}$ plus, Advanced Energy) was connected between the power supply and the Ti target. High-power-pulse sputtering (5 kHz, duty cycle 50-85 %) was performed by connecting a switching unit (USB-C2, Fraunhofer Institute for Electron Beam and Plasma Technology, Dresden) between the DC power supply (PFG 5000 DC; Hütttinger) and the Zr-Target. In some experiments, the pulse frequency was increased to 50 kHz. Preliminary experiments were performed using the same pulsed DC unit as for the Ti target but at frequencies of 100 to 300 kHz and a duty cycle of 50%. The film composition was in rhombohedral range near the morphotropic phase boundary of the PZT phase diagram, e.g. at ratios $Zr/(Zr+Ti) > 0.52$ [11]. XRD revealed a nanocrystallite mixture of lead, zirconium and titanium oxides in the as-deposited films which can be transferred into perovskite Pb(Zr,Ti)O$_3$ by rapid temperature annealing. The value of the XRD Scherrer coherence length of PZT amounted to 36 nm, i.e. it is in the order of the domain width of PZT thin films and well above the size-limit for ferroelectricity.

TiO$_2$ thin films were deposited by reactive pulsed magnetron sputtering in the transition mode between the metal and the oxide mode onto glass substrates using a pulse packet mode. Processing in the transition mode was stabilized by means of closed loop control of oxygen flow referencing to a Ti emission line (500 nm) in the low pressure plasma. Details of the deposition process are described elsewhere [12]. Samples consisting of different phases were selected for this investigation.

Polyethylene-terephthalate (PET Melinex®400 by Dupont Teijin Films) films were subjected to low-pressure plasma surface treatment in an argon-oxygen atmosphere as described in [13]. Stable self-organized nanostructures were created on these polymer substrates by using an ECR plasma source or a dual magnetron as an ion source driven in pure oxygen.
Microstructure of the samples was investigated by atomic force microscopy using an NTEGRA Therma scanning probe microscope (NT-MDT, Zelenograd, Russia). Tapping mode imaging was performed in air using silicon cantilevers (Type NSG01, NDT-MDT, Zelenograd, Russia). The fractal dimension analysis was performed by means of the Open Source Software Gwyddion 2.21 supporting the triangulation method [14]. To calculate the one-dimensional PSD, the two-dimensional AFM image was averaged over the profiles traced in the fast scan direction using the same computer code. This allows reducing noise due to instrument drift which is more pronounced in the slow scan direction. Moreover, a PSD calculated from only a few profile measurements is exceedingly noisy and non-reproducible. On the other hand, the averaging over 256 scans is approximately equivalent to the integration of the two-dimensional PSD over the slow scan direction [15].

3. Results and discussion

Figure 1 shows the surface texture of reactive sputtered PZT thin films and the corresponding power spectral densities. The low-frequency region of the PSD is not very well reproduced by the simplified model of eq. (1). On the one hand, this is attributed to not enough data points available in the averaging procedures so that an adequate statistics cannot be obtained. On the other hand, periodic surfaces produce peaks in the PSD spectrum. The frequency value at the center of the peak is related to the real space value of the wavelengths that define this periodic surface. The occurrence of a periodic superstructure is described by adding Gaussian functions with its peak-maximum shifted to a non-zero spatial frequency [16]

$$PSD_g = \sqrt{\pi} \delta^2 \sigma \cdot \exp \left[ -\frac{\sigma^2(k-k_0)^2}{4} \right],$$

(3)

to the k-correlation model PSD where $\delta$ and $\sigma$ are the height and the correlation length of the superstructure, respectively. In our case, there is a pronounced feature size of $\sigma = 0.55$-0.80 $\mu$m attributed to warpage since the substrate was a polymer film. The thereby produced sample waviness gives an additional contribution to the PSD which is not accounted in the model.

Table 1 summarizes the root mean square (RMS) roughness, the fractal dimension and the k-correlation model parameters of the PSD of the PZT film surfaces. The PSD and fractal dimension of reactive sputtered PZT thin films are strongly affected by processing conditions. Fractal dimensions are higher for films deposited under enhanced ion bombardment compared to standard films and lead-enriched ones.

The three TiO$_2$ samples selected for this research represent the rutile phase (substrate not intentionally heated during deposition), the anatase phase (substrate temperature during deposition − 350$^\circ$C) and a mixture of rutile and anatase phases (substrate temperature during deposition − 200$^\circ$C). As expected, the last sample exhibits the highest roughness and correspondingly larger PSD values (Fig. 2a and table 2). The obtained PSD model parameters are in the order of that obtained earlier for titanium oxide films deposited onto glass substrates at 270 to 480 $^\circ$C by d.c. magnetron-sputtering [17]. Here, water vapour was used as reactive gas and after deposition all samples were submitted to a thermal treatment. The thus deposited titanium oxide films had a polycrystalline, multiphase (anatase and/or rutile) structure. For pure rutile or anatase phases, we found a tendency to larger values $C > 4$ in this work giving evidence of shadowing and/or coarsening during film growth.

The PSD, fractal dimensions and ABC model parameters of virgin and plasma treated PET films are summarized in figure 2b and table 3. The initial waviness of PET films disappears after plasma treatment.

Generally, the self-affine k-correlation model eq. (1) describes a large number of different surfaces including Pb(Zr,Ti)O$_3$ and TiO$_2$ thin film, sol-gel derived SiO$_2$-SnO$_2$ nanocomposite films [8], nanocrystalline NiO$_x$ film on Al$_2$O$_3$ ceramic substrates [18], protective WC coatings on steel and silicon [18], Gd$_2$O$_3$ film deposited by electron beam evaporation on quartz substrates [19], Ce$_{0.01}$Sc$_{0.10}$Zr$_{0.89}$O$_{2-x}$-based ceramics [9], and plasma-treated PET films.
Figure 1. AFM-images of reactive sputtered PZT thin films and power spectral density of the images. The fit to the ABC model is shown by solid lines.
Table 1. RMS roughness, fractal dimensions and k-correlation (ABC) model parameters of PZT thin film surfaces.

| Sample                                           | RMS roughness (nm) | Fractal dimension | $A$ ($\mu m^3$) | $B$ ($\mu m$) | $C$ |
|--------------------------------------------------|---------------------|-------------------|------------------|--------------|-----|
| DC-pulsed, 100 kHz                               | 4.37                | 2.38              | $4 \cdot 10^{-7}$ | 0.11         | 3.7 |
| DC-pulsed, 300 kHz                               | 7.63                | 2.41              | $1 \cdot 10^{-6}$ | 0.11         | 3.8 |
| High power current pulse, standard technology     | 3.60                | 2.34              | $4.5 \cdot 10^{-7}$ | 0.08         | 5.5 |
| High power current pulse, increased Pb excess     | 4.86                | 2.32              | $1.2 \cdot 10^{-7}$ | 0.05         | 6   |
| High power current pulse, increased current pulse frequency | 3.31                | 2.48              | $2 \cdot 10^{-7}$  | 0.06         | 3.7 |

Figure 2. Power spectral density of TiO$_2$ (a) and PET (b) AFM images.

Table 2. RMS roughness, fractal dimensions and k-correlation (ABC) model parameters of TiO$_2$ surfaces.

| Sample            | RMS roughness (nm) | Fractal dimension | $A$ ($\mu m^3$) | $B$ ($\mu m$) | $C$  |
|-------------------|---------------------|-------------------|------------------|--------------|-----|
| Rutile            | 2.1                 | 2.4               | $9 \cdot 10^{-8}$ | 0.05         | (10) |
| Rutile+Anatase    | 7.1                 | 2.41              | $1.3 \cdot 10^{-6}$ | 0.11         | 3.6  |
| Anatase           | 5.2                 | 2.44              | $5.3 \cdot 10^{-7}$ | 0.08         | 4.7  |
Table 3. RMS roughness, fractal dimensions and k-correlation (ABC) model parameters of PET surfaces.

| Sample             | RMS roughness (nm) | Fractal dimension | $A$ ($\mu$m$^3$) | $B$ ($\mu$m) | $C$   |
|--------------------|-------------------|------------------|-----------------|-------------|-------|
| PET (virgin)       | 1.24              | 2.2              | $2.5 \times 10^{-8}$ | 0.08        | 3.6   |
| PET 01             | 4.18              | 2.4              | $3.7 \times 10^{-7}$ | 0.11        | 3.2   |
| PET 03             | 3.73              | 2.4              | $2.7 \times 10^{-7}$ | 0.10        | 3.2   |

Conclusions

In this work, we have demonstrated that fractal analysis of AFM images is an appropriate and easy to use tool for the characterization of hierarchical nanostructures. Surface topography fractal dimension was found to be sensitive to PZT thin film processing conditions, to the appearance of TiO$_2$ phase mixtures and to technological parameters of oxygen plasma treatment of PET film surfaces. The PSD allows analysis of substrate waviness and film growth.

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