Evidence of local and global scaling regimes in thin films deposited by sputtering: An atomic force microscopy and electrochemical study

Tersio G. Souza Cruz, M. U. Kleinke, and A. Gorenstein

Citation: Applied Physics Letters 81, 4922 (2002); doi: 10.1063/1.1530739
View online: http://dx.doi.org/10.1063/1.1530739
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/81/26?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Optical waveguiding in magnetron-sputtered Na 0.5 K 0.5 NbO 3 thin films on sapphire substrates
Appl. Phys. Lett. 82, 439 (2003); 10.1063/1.1539295

Microstructural and electrochromic properties of sputter-deposited Ni oxide films grown at different working pressures
J. Appl. Phys. 92, 1268 (2002); 10.1063/1.1489717

Thickness-dependent microstructural and electrochromic properties of sputter-deposited Ni oxide films
J. Vac. Sci. Technol. A 20, 1468 (2002); 10.1116/1.1487871

Electrochromism of sputter deposited Ni–Cr oxide films
J. Appl. Phys. 84, 6454 (1998); 10.1063/1.368972

Magnetic measurements on electrochromic Ni-oxide-based films
J. Appl. Phys. 82, 1759 (1997); 10.1063/1.365977
Evidence of local and global scaling regimes in thin films deposited by sputtering: An atomic force microscopy and electrochemical study

Tersio G. Souza Cruz, M. U. Kleinke, and A. Gorenstein

Applied Physics Department, Gleb Wataghin Physics Institute, State University of Campinas, 13083-970 Campinas, São Paulo, Brazil

(Received 16 July 2002; accepted 24 October 2002)

The surface morphology of NiO thin films deposited by rf sputtering was studied by atomic force microscopy and by cyclic voltammetry. Linear relationships were observed in log–log plots of the interface width versus window length and in log–log plots of the peak current versus scan rate. Two different slopes were observed, by both techniques, indicating that distinct growth dynamics present in the system can be measured in different ways. Moreover, the calculated fractal dimensions are in excellent agreement: the local scaling regime corresponds to high scan rates and the global scaling regime corresponds to low scan rates, in accordance with the expected behavior for diffusion fronts.

Nickel oxide thin films are widely investigated materials, mainly due to their electrochromic properties. The electrochromic effect is promoted by an electrochemical process in which ions and electrons are inserted or extracted into and from the film. The insertion process promotes bleaching, and color is attained by reversing the process. Changes in transmittance as high as 70% can be attained, depending on the films’ physical properties.

Interaction with the electrolyte is through the surface, whose characteristics can influence performance of the materials. Roughness is the parameter commonly used to perform quantitative analysis of the surface. Since the roughness of thin film surfaces usually presents self-affine behavior, they can be described by scaling law concepts. The roughness exponent, associated with the fractal dimension value \( D_f \), is connected to the growth dynamics of the system. For polycrystalline films, different growth dynamics related to the intragrain and intergrain formation process (local and global dynamics, respectively) are expected, and, in fact, are observed.

Several experimental methods are available to evaluate the fractal dimension. In recent years, the evaluation of \( D_f \) by electrochemical methods has been revived. In the cyclic voltammetry (CV) technique, a controlled, triangular-shaped difference in potential is applied between two electrodes (the sample under analysis and a reference electrode, both immersed in an electrolyte), and the current that results is measured by an auxiliary electrode also immersed in the electrolyte. The ionic diffusion process is sensed in this method, and, in contrast with classical, flat electrodes, the electrode surface morphology influences the current/potential curve. The scaling behavior of the peak current \( (i_p) \) with respect to the scan rate \( (v) \),

\[
i_p \approx v^\xi,
\]

allows evaluation of the \( \xi \) exponent.

The fractal dimension is obtained from

\[
D_f = 2\xi + 1.
\]  

One of the most used techniques for analyzing the film surface morphology is atomic force microscopy (AFM). With this technique, the scaling behavior of the root mean square (rms) roughness \( W(L) \) (also called interface width) with regard to observation length \( L \),

\[
W(L) \approx L^\alpha,
\]

allows evaluation of the roughness exponent \( \alpha \), from which the fractal dimension is obtained using

\[
D_f = 3 - \alpha.
\]

In this work, the surface fractal dimension of nickel oxide thin films deposited by sputtering was investigated by both techniques (AFM and CV). We were able to provide evidence of the local and global dynamics of thin film growth, and the results obtained with these distinct techniques are in excellent agreement. To the best of our knowledge, this is the first report on evidence of two growth dynamics using both techniques.

The films were deposited by reactive rf sputtering in Ar+O\(_2\) atmosphere. The substrates were either 7059 Corning glass (in the AFM measurements) or SnO\(_2\)/glass (in the electrochemical measurements). The samples were deposited from a nickel target, under \( 7 \times 10^{-3} \) mbar total pressure. The other deposition conditions are shown in Table I.

X-ray diffraction (XRD) and Rutherford backscattering spectroscopy (RBS) analysis indicated that the films are stoichiometric nickel oxide (NiO\(_{0.96}\)) cubic in structure, texturized in the (111) direction.

TABLE I. Deposition conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen flow (sccm)</th>
<th>rf power (W)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.0</td>
<td>400</td>
<td>220</td>
</tr>
<tr>
<td>G</td>
<td>4.0</td>
<td>400</td>
<td>100</td>
</tr>
</tbody>
</table>

*Electronic mail: annette@ifi.unicamp.br*
The images were obtained with a Topometrix TS2000 scanning probe microscope (SPM), in AFM mode. Tips of high aspect ratio (sharpened pyramidal tip, angle of nearly 20°, Park Scientific Instruments) were used in order to minimize convolution effects. All images (300×300 pixels) were acquired at frequency of 2 Hz. The scan length was varied from 200 to 2000 nm. The topographic image data were analyzed by a posttreatment program based on both single- and multiple-image variography. The mean interface widths were estimated over nonoverlapping windows that covered the original micrographs.

The electrochemical experiments were performed using 0.1 M KOH as the electrolyte, Pt as the counterelectrode and a standard calomel reference electrode. The experiment was controlled by a potentiostat connected to a microcomputer.

Figure 1 shows AFM images of the morphology of the films at two distinct magnifications (500 and 2000 nm). Both films present a globular structure, but with distinct mean values of their globular dimensions (~50 nm for film C and ~150 nm for film G).

Figures 2a and 2c shows corresponding W(L) vs L log–log plots. For both films, two scaling regions (at short and medium ranges of the observation length L) before saturation of W(L) are apparent; the experimental roughness exponents are α_{local}=0.52 and α_{global}=0.19 for sample C and α_{local}=0.70 and α_{global}=0.32 for sample G. The crossover lengths (L_c) obtained from the value of observation length L at the intersection of the two different scaling regimes [Figs. 2a and 2c] are L_c=40 and 100 nm for samples C and G, respectively. The L_c values are clearly related to the value of the mean globular size obtained from the micrographs. Moreover, the average separation calculated from the first zero crossing of the circularly averaged autocorrelation function.

![FIG. 1. AFM micrographs at two different observation lengths L (500 nm × 500 nm, left side) and (2000 nm×2000 nm, right side), for samples C (upper line) and G (lower line). The vertical sizes of the micrographs are (a) 17, (b) 25, (c) 12, and (d) 26 nm.]

![FIG. 2. (a), (c) W(L) vs L log–log plots for samples C and G, respectively; (b), (d) the corresponding autocorrelation function.]

![FIG. 3. (a), (c) Cyclic voltammograms for samples C and G; (b), (d) the corresponding v vs i_p log–log plots.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>D_{local}</th>
<th>D_{global}</th>
<th>D_{slow}</th>
<th>D_{fast}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.48±0.06</td>
<td>2.81±0.04</td>
<td>2.82±0.04</td>
<td>2.36±0.04</td>
</tr>
<tr>
<td>G</td>
<td>2.30±0.05</td>
<td>2.68±0.05</td>
<td>2.72±0.04</td>
<td>2.32±0.06</td>
</tr>
</tbody>
</table>

TABLE II. Fractal dimensions obtained by atomic force microscopy (AFM) and from cyclic voltammetry (CV).
function\(^{12}\) [Figs. 2(b) and 2(d)] also presents values that are in good agreement with the mean global size (\(\sim 60 \text{ nm}\) for sample C and \(\sim 150 \text{ nm}\) for sample G). These results suggest that the growth dynamics of the sputtered film are described by two distinct processes, one related to the growth dynamic of each grain and the other to global correlations among grains. These observations have already been reported for other systems\(^{5,13}\). These two distinct dynamic processes are described by the fractal dimension values (\(D_{\text{local}}\) and \(D_{\text{global}}\)) presented in Table II.

Figures 3(a) and 3(c) present cyclic voltammograms at several scan rates (cathodic peaks). The corresponding \(i_p(\nu)\) vs \(\nu\) log–log plots [Figs. 3(b) and 3(d)] also present two scaling regions, one for slow scan rates and the other for fast scan rates. The associated \(\xi\) exponents are \(\xi_{\text{slow}} = 0.91\) and \(\xi_{\text{fast}} = 0.68\) for sample C and \(\xi_{\text{slow}} = 0.85\) and \(\xi_{\text{fast}} = 0.63\) for sample G. The fractal dimensions values (\(D_{\text{local}}\) and \(D_{\text{fast}}\)) calculated are also presented in Table II. From Table II it can be seen that the fractal dimension obtained from the AFM micrographs for \(L\) values in the short \(L\) ranges (\(D_{\text{local}}\)) is in good agreement with the value obtained by CV for fast scan rates (\(D_{\text{fast}}\)). The same observation is valid for the fractal dimension calculated at medium range \(L\) values (\(D_{\text{global}}\)) in comparison with the one obtained at slow scan rates (\(D_{\text{slow}}\)).

In cyclic voltammetry experiments, the extent of the diffusion layer can be considered the measuring scale. The diffusion layer depth is inversely proportional to the peak current, and higher (lower) peak currents are observed for faster (slower) scan rates. This means that at high \(\nu\), we are able to sense the fine, local details of the electrode’s morphology, since the diffusion process is restricted to a region close to the electrode; in an AFM experiment, these fine details are sensed at short \(L\). On the other hand, for slow \(\nu\), the global morphology of the electrode surface is predominant, like in AFM observations at large \(L\).

In conclusion, the fractal dimension of thin film surfaces was investigated with atomic force microscopy and cyclic voltammetry techniques. Both techniques allowed determination of the local and global characteristics of the samples. The calculated fractal dimensions measured by both techniques are in good agreement. The results demonstrate the possibility of assessing either the fine details or the global macrostructure using simple methods in carefully controlled experiments.

This work was supported by FAPESP, under Contract Nos. 98/00501-8 and 98/14769-2.

---