Characterization of erbium oxide sol–gel films and devices by grazing incidence X-ray reflectivity

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Abstract

Recently, a significant amount of studies have been carried out on sol–gel films for optical applications, mostly motivated by the quickness and low cost of the film preparation process. Overcoating films of different density and thickness can produce waveguides for visible light as well as for X-rays. In order to preserve the coherence properties of the guided light, improvements in the current quality of the films are necessary as well as an appropriate technique for structural characterization and quality control. X-ray specular reflectivity can be such a technique, but it is limited by the complexity of the internal nanostructure of the films. In this work, we have developed a procedure to fit the specular reflectivity and extract the exact density profile of sol–gel films. It is applied to analyze a single compound film produced from a sol–gel of Er₂O₃ nanoparticles. It correlates the density variations and roughness with the steps of the preparation process. Moreover, we have also characterized an X-ray waveguide of Er₂O₃/TiO₂/Er₂O₃ and theoretically optimized its structure to demonstrate the effects of density floating and roughness on the waveguidance efficiency.

Keywords: Sol–gel films; X-ray reflectivity; Data fitting; Genetic algorithm; X-ray waveguide

1. Introduction

Sol–gel films have been widely investigated for optical applications due to their very low cost and fast preparation process [1,2]. Layered films of different density and thickness can easily produce waveguides for visible light [3–7] as well as for hard X-rays [8]. In high-brilliance synchrotron radiation sources, X-ray waveguides have become an important optical device that can lead to new developments in X-ray microscopy [9] and in characterization techniques with submicro-scale resolution [10]. Waveguides are basically a film composed of a light material onto a heavier one, whose waveguidance efficiency is strongly enhanced by overcoating the film with a very thin layer as dense as the bottom one. For most applications, coherence of the guided X-rays is crucial. Interface roughness does generate incoherent scattering that compromises the coherence of the beam exiting the waveguide and, at values above a few nanometers, the roughness can destroy the waveguidance.

The detailed structure of sol–gel films, i.e. films prepared by coating from a sol–gel solution, is still under investigation [11]. The dynamics of nanoparticles coalescence during firing, or heat treatment, can generate abrupt density variations and porosity inside a single film. Both features contribute to reduce the lateral coherence length and give rise to a sort of internal roughness that, in terms of incoherent scattering, is exactly the same as interface roughness. Then, at the present status of film preparation, it is evident that a characterization tool is needed for analyzing the structure of the films in a nanometer scale. It would provide the necessary information to improve the procedures for producing high quality sol–gel films. Density profile and internal roughness, besides thickness, are the most important parameters to be extracted and correlated to the variables of the preparation procedure, such as coating speed and firing temperature.

X-ray specular reflectivity is a non-destructive characterization method applied to a large variety of thin film materials. For laterally uniform films, grazing incidence reflectivity measurements can be applied equally effectively to single crystal, polycrystalline or amorphous films. The specular scattering in the region just above the critical angle contains information not only on the longitudinal
electron density and thickness of sub-micron films, but also surface and interface roughness on the atomic scale. Since a simple inverse transformation of the scattered intensity to obtain all the film parameters is not possible, the adopted approach for the interpretation of reflectivity data has been the simulation of the scattering from a model structure and adjustment of parameters until a good fit is obtained. In spite of all difficulties involved in this last step, i.e. in the adjustment of parameters, the technique is limited by the previous knowledge of the structure of the films. Exceptions are single layers with uniform density and thickness, which are extracted directly from the curves. Otherwise, the best possible fit will be satisfactory only when the correct model has been assumed, the model that has a number of adjustable parameters for which there is a set of values that describe the actual structure of the film. For sol–gel films, the uniform one-layer model is useful only to estimate the thickness and average (or apparent) density [11].

In this article, we describe some adjustable model structures able to extract, from the X-ray specular curve, the longitudinal density profile and roughness of sol–gel films. In the models, the heavy duty of adjusting the parameters, until the reflectivity simulation program [12] generates the best fit for the scattering data, is carried out by the differential evolution algorithm (DEA) [13]. Evolutionary algorithms, one particular class of genetic algorithms, apply some of the known mechanisms of evolution to solve optimization problems. Through simple mutation, recombination and selection schemes, the DEA finds the parameter vectors that yield the smallest value of the error function, where each \( n \)-dimensional parameter vector contains a set of values for all \( n \) adjustable parameters of the models. Mutation is an operation that makes small random changes in the population of vectors, and it is critical for maintaining the diversity in the population. This scheme allows the DEA to reach the global minimum of the error function instead of getting stuck on a local minimum. However, the accessible space of parameter values is defined by the user’s guess at the structure, when the range of allowed values for each adjustable parameter is imposed. Therefore, the global minimum for a given model will always be found by the DEA if it falls into the guessed accessible space, and if this space is narrow enough to allow the evolution to be concluded in a reasonably short period of time.

2. Experimental

A single compound film (Er\(_2\)O\(_3\) film) was prepared by three dip-coatings of a glass plate (2.475±0.025 g/cm\(^3\)) in a sol–gel of Er\(_2\)O\(_3\) nanoparticles. Each dip was followed by firing at 500 °C for a few minutes in order to eliminate the gel and the organic cap of the nanoparticles. The detailed process for producing such sol–gels has been described elsewhere [14]. Using this sol–gel and a second one of TiO\(_2\) particles, produced by the same process, a multilayered film (WG film) was also prepared. It has five layers; the odd layers (1\(^{st}\), 3\(^{rd}\) and 5\(^{th}\)) were coated by just one dip in the sol–gel of Er\(_2\)O\(_3\), and the even layers by two dips in the sol–gel of TiO\(_2\).

The grazing incidence X-ray reflectivity measurements were performed in a high-resolution X-ray diffractometer (Philips X’Pert-MRD) equipped with a Cu X-ray tube in the line focus. The primary optics (for the incident beam) was composed of a Soller slit, a 1/32° divergence slit and an attenuator, and for the secondary optics (reflected beam) we used, before the detector, a parallel beam collimator, a 0.1 mm anti-scatter slit and a flat crystal graphite monochromator. Before starting measuring, the sample height and the goniometer zero points (2θ=0 and ω=0) were precisely adjusted. The reflectivity spectra were recorded by a longitudinal scan in the reciprocal space, ω/2θ scan. The attenuator is used for angles lower than a pre-defined angle to avoid the detector damage due to a very intense incident radiation. The attenuator factor is automatically computed during the measurement, allowing a dynamical scale of eight orders of magnitude.

3. Results

Fig. 1 shows the experimental reflectivity curves (open circles) of the Er\(_2\)O\(_3\) film (a) and the WG film (b). In order to fit the first experimental curve three possible models for the structure of the films were considered at the beginning: the one-layer model, the multi-slab model and the multi-slab model with roughness at the interfaces of each slab (hereafter named MSr). The adjustment of the parameters was carried out by the DEA and the improvement of the fitting is driven by mean-absolute error of the log-transformed data. In the Parratt’s recursion-relation formalism [15] employed by the simulation program, the effects of roughness is taken into account by reducing the Fresnel reflection amplitude, \( r_\parallel \), of each interface. The expression for such reduction at the \( j \)th interface, between slabs \( j \) and \( j+1 \), is given [16] by \( r(j)=r_\parallel(j)\exp[-2(k_{\parallel j}k_{\parallel j+1})^{1/2}\sigma_j] \), where \( \sigma_j \) stands for the Gaussian width of the interface due to roughness, and \( k_{\parallel j} \) is the longitudinal component of the wavevector in the slab \( j \). Note that, \( \sigma_j \) also accounts for reduction in the lateral coherence length of the interfaces besides the physical roughness. Then, it is possible to have a value of \( \sigma_j \) larger than the thickness of its respective slab. The attenuation of the X-ray beam is also included in the reflectivity simulation program by means of a complex refractive index of the materials [12].

In the case of the Er\(_2\)O\(_3\) film, although the one-layer model as well as the multi-slab model with adjustable density can provide an estimation of the thickness (~24 nm) and of the average density (6.93 g/cm\(^3\)), none of them are able to fit the experimental curve. The remarkably good
Fig. 1. X-ray specular reflectivity curves from the erbium oxide sol–gel film (a) and the multilayered \( \text{Er}_2\text{O}_3/\text{TiO}_2 \) film, the WG film (b). The experimental curves—open circles—are compared to the best fitting curves—straight lines—obtained with the respective MSr models. An illustration of the models are shown in the insets, where the \( \text{Er}_2\text{O}_3 \) film is divided into eight slabs plus a cover layer, and each TiO layer in the WG film was divided into three slabs. The parameter values extracted with these MSr models are given in Fig. 2.

fitting shown in Fig. 1a could only be achieved when roughness is allowed at the interfaces of the adjacent slabs. The exact structure of the film determined with this MSr model is shown in Fig. 2a. It was necessary to divide the film thickness into eight slabs, seven slabs of 3 nm plus one top slab of adjustable thickness. A cover layer of H:1C:2N:5O, which might be present due to air contamination, have been added to the model, and it has significantly improved the quality of the fitting. Then, for this model there were 21 parameters adjusted by the DEA. With the density values of all slabs limited in the range from 4 to 9 g/cm\(^3\), their best-fit values do not differ from those in the figure by more than 2.5%. In the accessible space defined by this range, the values in the initial parameter vector do affect the evolution time required by the DEA for minimization of the error function. On the other hand, the sensitivity of the fit with the roughness depends on the density difference throughout each interface. The highest and lowest sensitivities are for the roughness at \( z=0 \) and \( z=12 \) nm, respectively. Changes of 2% and 32% in the roughness values at these interfaces would produce the same fit deviation of 5%.

For fitting the scattering data from the WG film, we also have to use the MSr model. However, in this case, the thickness of the slabs would have to be adjusted, besides their densities and interface roughness. Then, the DEA had to handle the adjustment of seven more extra parameters—standing for the thickness of the slabs—than in the case of the single compound film. The final MSr model structure responsible for the good fit shown in Fig. 1b is given in Fig. 2b. Each TiO layer was divided into three slabs with a total thickness of 6.62 nm and 10.53 nm for the first and...
second layers, respectively. Internal roughness and a density are observed only in the first layer, whose average density is much smaller than the nominal value (4.12 g/cm³) of the TiO₂ compound. High values of roughness were found at both interfaces of the Er₂O₃ layer at the middle of the structure. The assumption of a cover layer did not improve the fit quality. The small discrepancy of the fit observed around \( q_z = 1.8 \times 10^{-3} \text{ Å}^{-1} \), might arise due to some density profile in the Er₂O₃ layers, which could not be satisfactorily resolved by our nine-slab model. Although the DEA never stop the auto fitting, unless required to, 28 adjustable parameters is about the limit of its practical efficiency.

4. Discussions

The most important physical feature in the MSr model is that by introducing roughness at the interfaces of adjacent slabs, the model was able to simulate the effects of the internal roughness present in a single compound layer. Since this internal roughness stands for the reflectivity reduction, it demonstrates that some amount of diffuse scattering is generated inside the film. Otherwise, the multi-slab models without internal roughness would have succeeded in fitting the experimental curve and extracting the longitudinal density profile, which were more complex than just the average density for the Er₂O₃ film. The two minima of the density profile observed in Fig. 2a, around 4.5 and 12 nm, are correlated to the number of dips (three in this case) used to prepare the film. After each dip, the fired layer has a lower density towards the surface, and subsequent overcoating and heating did not restore the density of the previous surface. The first dip seems to provide a near 6 nm thick layer and each subsequent dip has added approximately 9 nm to the total thickness. Then, a length scale resolution of 3 nm—the slab thickness—was necessary to resolve the profile. The presence of the low-density cover layer has been observed in other sol–gel films [11]. And, although its thickness (2.3±0.5 nm) is still larger than the one expected for a contamination layer due to absorption of air species, it should be mentioned that this value was significantly reduced regarding the value (4.8±1.0 nm) estimated by using the one-layer model.

Reliability of the parameters obtained by the evolutionary algorithm, the DEA, is a very complicated issue, as it is in any other X-ray analysis based on curve fitting. It depends fundamentally on one factor: the quality of the final fit. The perfect fit would be the one where the minimum value of the error function is exclusively due to the statistical noise on X-ray generation and detection—calculated by a Poisson distribution. That will be the case when the structure of the sample is accurately described by the model, there are no errors associated with the simulation of the X-ray scattering, and there are no systematic errors present in the experimental data. Materials analysis by X-ray data fitting works assuming that there is only one model able to produce the perfect fit, and when it is obtained, the model responsible for such fit is taken as an accurate description of the sample. The problem, however, resides in the fact that in general there is not a model able to reproduce all features existential in the real samples. Therefore, the best-fit parameter values for a given model may carry some intrinsic errors due to a deficiency in the model, which can not be estimated. For instance, the 50% variation (or error) in the thickness of the cover layer in the Er₂O₃ film extracted by the one-layer model in comparison to the one obtained by the MSr model. When a reasonably good fit is archived, although not the perfect one, we expect that the deficiencies of the model do not significantly affect the best-fit parameter values, at least not to the point where there is change to any physical interpretation of the structure of the sample. In order to be very specific, the MSr models are very efficient for sol–gel films because they allow the necessary degree of freedom for the models to take into account the reduction in the specular reflected intensity by density gradients as well as by diffuse scattering due to internal roughness. Their deficiency is the finite number of slabs used to represent the density profile of the films. In the WG film, several more slabs would be necessary to obtain a really good fit of the experimental data—it is stated because the fit quality improves with the number of slabs in which the two TiO₂ layers have been divided into. However, it will not change the fact that there is an accentuated gradient in the density profile around \( z = 6 \text{ nm} \). Fig. 2b, neither the order of magnitude of the thicknesses, or the existence of roughness at the interface of the layers with different composition.

The value of roughness at the final surface of a film can be critical for waveguides of sol–gel films because it will be the interface between two compounds of very different densities. For this reason, the WG film was prepared in order to observe the level of roughness present at the interface of a dense (Er₂O₃) and a lighter (TiO₂) layer, and how it would affect the intensity of the possible guide modes. In the specular reflectivity curve, the guidance of the X-rays are characterized by a strong reduction in the reflectivity at some incidence angles below the critical angle, \( \theta_c \), of the dense layer. At these angles, a standing wave is formed inside the structure and the energy flow is parallel to the surface. The first dip observed in the specular curve of the WG film, Fig. 1b, is below \( \theta_c \) (≈1214°) of the Er₂O₃ film—for the measured density of 7.36 g/cm³. The simulation program used before is also useful to theoretically explore the effects of the features founded in the WG film that seem to have destroyed the guidance of this mode.

The thickness of the Er₂O₃ layer at the bottom of the

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1 Error estimated by fit deviation bouncing 5%.
It takes into account the diffuse scattering generated inside the film, which is evidence of the presence of porosity. The density profiles extracted by the appropriated models allow us to conclude that the shrinkage during firing introduces some sort of ‘rifts’ at the intradip surfaces, as schematized in the insets of Fig. 2. The decreasing density gradient towards the surface due to the rifts seems to affect more the guided intensity than the internal roughness, which is also a consequence of the rifts.

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References