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Variation of the refractive index by means of sulfate anion incorporation into nanoporous anodic aluminum oxide films

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ABSTRACT

The variation in the refractive index of nanoporous anodic aluminum oxide (AAO) films regarding the sulfur anion incorporation is studied in this work. For this purpose, different samples are grown under potentiostatic conditions at different voltages and concentrations of sulfuric acid in the electrolyte. The samples are analyzed by Rutherford backscattering spectroscopy and infrared spectrometry, confirming the presence of sulfate anions and water embedded into the nanoporous AAO films. The incorporation of sulfate ions into the alumina matrix varies from 6.3 up to 11.7% regarding aluminum content. We have studied Fabry–Pérot optical interferences by shining incident monochromatic light in specular reflectance conditions. The reflected monochromatic light waves interact in internal reflectivity generating constructive and destructive interferences known as Fabry–Pérot optical interferences. An iterative method based on the equation for constructive interferences conditions in thin films and Snell equations is developed in order to calculate the refractive index of the nanoporous AAO films as a function of the wavelength. The calculated refractive indices increase when the sulfur content of the nanoporous AAO films decreases. The variation of the calculated refractive index is 0.08 and remains constant in the wavelength range 400–1200 nm.

1. Introduction

Anodization of transition metals like titanium, copper, or tungsten is a cost-effective method to grow oxide nanostructures for energy applications [1–6]. Indeed, transition metal oxides are getting more and more popular in the field of materials for energy conversion and storage [7–9]. Significantly, since anodization of aluminum makes possible the fabrication of hexagonal ordered nanoporous [10], nanostructured anodic aluminum oxide (AAO) films have been used as a template to fabricate different nanostructures such as nanotubes [11,12], antidotes [13,14] or nanowires [15–17]. Moreover, nanoporous AAO films are being applied to multiple fields such as biosensors [18,19], optical sensors [20,21], magneto-thermoelectric and magneto-caloric materials [22–24] and to the study of magnetic properties of nanowires [25–27].

The enhancement of optical properties when light interacts with porous arrays at the nanoscale has attracted great interest [28–31]. Particularly, nanopore arrays fabricated on metal-dielectric structures are of particular interest due to surface plasmon improvement of the optical properties [32,33]. Nanoporous anodic alumina is playing a key role as a dielectric material, and it is of utmost importance to develop new methods to design novel forms of nanostructured AAO films by controlling their growth mechanism [34,35]. A recent study reports on enhanced reflectance fringe intensity in rationally controlled thin films of anodic alumina

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coated with a thin gold layer acting as a plasmonic nanostructure generating optical interferences [36]. These systems are also promising for biosensing applications because the enhanced reflectance fringe increases the sensitivity to biomolecules [37]. Nanoporous AAO membranes attached to the aluminum substrate improve metal-enhanced fluorescence of organic molecules in contact with aluminum [38]. Finally, reflectometry interference spectroscopy is also used to investigate molecular interactions on nanoporous AAO films [20,39,40].

Optical properties are closely related to the composition of the anodic alumina and are of primary importance to understand the growth mechanism of the nanopores [41–44]. In particular, the study of the anion incorporation into the alumina matrix is a fundamental issue and has been the focus of several important studies [45,46]. Rutherford backscattering spectrometry (RBS) is a key technique to study the behavior of the growth mechanisms of nanoporous AAO films [47–50]. During the anodization process, anionic impurities from the acidic electrolyte are incorporated into the nanoporous alumina layer. The concentration of these anions essentially depends on the anodization conditions, in particular the applied voltage and the electrolyte concentration [51,52]. The effective medium approximation describes the macroscopic properties of a composite material. This is of crucial importance to calculate the refractive index. An effective medium is considered when an embedded random unit cell is not detectable using an electromagnetic radiation confined to a specific wavelength range [53]. However, there are several alternatives as described by Aspnes et al. who developed an effective medium theory based on basic principles [54]. In a heterogeneous medium made of two components a and b, having dielectric functions ε_a and ε_b and volumetric fractions f_a and f_b, when a is a small fraction of b the Maxwell–Garnett effective medium model equation stands as:

$$\frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a} = f_b \frac{\varepsilon_b - \varepsilon_a}{\varepsilon_b + 2\varepsilon_a} \quad (1)$$

The refractive index is commonly measured by reflectance spectroscopy and calculations are based on the Maxwell–Garnett effective medium model [36,55–57].

In the present work, we study the variation of the refractive index of nanoporous AAO films as a function of the sulfate anion incorporation using optical interferences generated at the nanoporous AAO film. The calculation is based on an iterative method that combines Snell's law and the constructive interference conditions for thin films.

2. Experimental

Aluminum anodization is performed by a two-step potentiostatic process [58]. Aluminum foils (99.999% from Goodfellow) were cleaned and electro-polished before anodization process. Aluminum disks were anodized under potentiostatic conditions at 14, 17 and 20 V using a 3 wt% sulfuric acid aqueous solution as electrolyte and under 20 V using 10 and 20 wt% concentrations. The sample labels and experimental parameters are shown in Table 1. In both anodization steps, the electrolytes temperature is kept constant at 0.0 °C and the same stirring rates are applied. In all cases, the first anodization time is 16 h while the second anodization time for the A samples is 150 min and 20 min for B and C samples. The morphology of nanoporous AAO films is analyzed by scanning electron microscopy (SEM) using a Philips model XL-30, FEG-HRSEM microscope.

Rutherford Backscattering Spectrometry (RBS) experiments are carried out in a 5 MV tandem accelerator. Helium ions, He^+, at 3035 eV are used to receive the RBS spectra (oxygen resonance conditions). The spectra are simulated using the SIMNRA software [59].

Table 1
Sample labels as a function of acid concentration of the electrolyte and applied voltages during the anodization process.

	A14	A17	A20	B20	C20
$[H_2SO_4]$ (wt%)	3	3	3	10	20
V (V)	14	17	20	20	20

Infrared spectrometry is carried out in an FR-IR Bruker IFS66v spectrometer. The measurements are performed in the range 500–4000 cm^{-1}.

Reflectance spectra are performed in a Perkin Elmer spectrophotometer Lambda 950 with 45° incidence angle in the wavelength range 400–1200 nm. This experimental setup configuration slightly differs from usual ones. The use of a Perkin–Elmer universal reflectance accessory allows to increase the optical pathway through thin nanoporous AAO films and allows to extract data out of the interference regions. Data processing is carried out by using a simple iterative method for calculating the refractive index and the thickness of the AAO films.

3. Results and discussion

3.1. Morphological analysis

Cross-section SEM images of samples A14, A17, A20, B20 and C20 are showed in the left column of Fig. 1a. In all AAO film samples the nano-channels are parallel to each other. The diameter of the nano-channels varies from 14 to 25 nm depending on the experimental conditions. The thicknesses of the nanoporous AAO films as measured on the cross-section SEM images are presented in Table S1 (see Supplementary data). Top view SEM images show the nanopores arrangement (Fig. 1b). Self-ordering of the nanopores is qualitatively evaluated by self-correlation images (Fig. 1c) [60]. Self-correlation images show the evolution of self-ordering with the applied voltage for samples A14, A17 and A20 (Fig. 1c). An increase of the self-ordering arrangement is also observed samples A20, B20 and C20 (Fig. 1c).

3.2. Compositional and structural analysis

RBS spectra for samples A14, A17, A20, B20 and C20 are represented in Fig. 2. The signals of sulfur (labeled as *), aluminum (◇) and oxygen (▫) coming from the nanoporous AAO films have been detected. Aluminum nuclei coming from the substrate (○) have been detected for samples A14, A17 and B20 (Fig. 2a). The thickness of these samples is below 2.7 μm, which is the penetration depth of the He^+ ions into nanoporous AAO films under the experimental conditions. Fig. 2b shows the magnification of the signal corresponding to the sulfur nuclei incorporated into the anodic alumina matrix. In an electrolyte with a 3 wt% H_2SO_4 concentration, the intensity of the RBS sulfur signal increases with the applied voltage from 14 V to 20 V. A similar dependence is observed when varying the concentration of sulfuric acid in the electrolyte. Under an applied voltage of 20 V, the concentration of S-atoms increases as the H_2SO_4 concentration increases from 3 to 20 wt%. Simulations of the spectra fit to experimental results obtained by RBS (Fig. 2). The analysis of the RBS simulations allows quantifying the amount of elements embedded within the nanoporous AAO film (Table S1).

Infrared spectra of all samples as measured by diffuse reflectance contain vibration modes corresponding to water molecules (Fig. 3). The broad band centered at 3440 cm^{-1} corresponds to the