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Microstructure, porosity and roughness of RF sputtered oxide thin films: Characterization and modelization

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ABSTRACT

Spinel $CoMnFeO_4$ thin films are stable materials useful to study the influence of radio-frequency (RF) sputtering experimental conditions on the microstructure of oxide films. It has been demonstrated by various techniques such as electronic and atomic force microscopy (AFM), gas adsorption techniques and ellipsometry, that films prepared with 0.5 Pa sputtering argon pressure and 5 cm target–substrate distance are very dense. On the other hand, the samples obtained under higher pressure and/or longer distances are microporous with a mean pore size generally lower than 2 nm. The specific surface areas of such films reach about 75 m^2/g.

According to the simple model proposed, the films are made of three layers. From the bottom to the top of the film, the first one at the interface with the substrate is 100% dense. The second layer is made of cylindrical rods set up according to a compact plane. Its porosity is due to the lattice interstices. Hemispheric domes covering each rod make up the third layer, which displays a degree of roughness related to the shape and the hexagonal arrangement of the domes. The surface enhancement factor (SEF), the porosity and roughness, calculated from the model, are in corroboration with the experimental values. The porosity factor is however slightly underestimated by the model for very porous samples.

1. Introduction

Radio-frequency (RF) sputtered thin films are generally made up of small crystallites which have developed closely in relation to each other, in such a manner that the pores in between can only be very small. It is then very difficult to precisely characterize the microstructure and the porosity of such films. Not only scanning and transmission electron microscopy (SEM, TEM) but also atomic force microscopy (AFM) is generally used to characterize the crystallite and grain size. But these techniques are not well suited to give quantitative information about open and close porosity.

For this reason, physical adsorption isotherms of nitrogen or krypton are sometimes used to determine the surface area of porous thin films, by the Brunauer, Emmet and Teller (BET) method [1]. However, this method is quite difficult to carry out because about 1 m^2 of an effective surface is required for the measurement using volumetric techniques. Only a few studies have been carried out so far for sputtered thin films [2–5]. Effective surfaces of less than 10 cm^2 can be measured using surface acoustic waves (SAWs) detection [6] in place of volumetric systems. Special interdigited electrodes however have to be deposited on the top of the films for these SAW measurements.

Ellipsometry is another interesting technique able to give precise information about the thin film porosity. The volume fraction of adsorbate molecule (nitrogen, ethanol, water, ...) inside the pores can be calculated from the measured change in optical characteristics of the porous film during adsorption/desorption at room temperature or liquid nitrogen temperature [7–9]. In air at room temperature, models for porous materials can also be used to determine the film porosity from the spectral variation of n and k optical indices, in the visible light range [10].

The purpose of this paper is to investigate the fine microstructure of thin films oxide prepared with different RF sputtering conditions and to build a microstructural model which is able to describe the architecture of the films on a nanometric scale. $CoMnFeO_4$ spinel oxide films were chosen for this study because $CoMnFeO_4$ displays a good structural stability and quite a low sensitivity to oxido-reduction phenomena [11]. Any significant change in the phase purity could not then be feared for the sputtering conditions used. Microscopy techniques such as, SEM, TEM and AFM, of course without forgetting conventional surface area measurements and spectral ellipsometry at room tempera-

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Table 1
Experimental conditions carried out for samples preparation

Argon flow rate (cm^3/min)	11	55
Argon pressure (Pa)	0.5	2
Target–substrate distance (cm)	5, 6.5, 8	5, 6.5, 8
Power density (W cm^{-2})	0.9	0.9
Film thickness (nm)	300	300

ture and grazing incidence X-ray diffraction (GIXRD) measurements were carried out to obtain precise microstructural information. From these experimental data a microstructural model could be proposed. The growth process of the film as a function of the elaboration conditions was also discussed in the light of this model.

2. Experimental

2.1. Films preparation

Mixed cobalt manganese ferrite thin films were deposited in an Alcatel A450 RF sputter system from a 10 cm in diameter $CoMnFeO_4$ target. The target was produced starting from commercial oxides with 99.999% purity. A mixture of Co_3O_4, Mn_2O_3 and Fe_3O_4 as required in a 1:3/2:1 proportion was used. The ceramic target, sintered at 1200 °C for 1 h, was made of pure $CoMnFeO_4$ spinel oxide. The Alcatel A450 RF sputter machine was equipped with a radio-frequency-generator (13.56 MHz) device as well as a pumping system (a mechanical pump coupled with a turbo molecular pump) which allows reaching a residual pressure down to 10^{-5} Pa, a gas flow controller, a water cooled target holder, a magnetron placed behind the target and two water cooled sample holders. The films were deposited on glass slides having an average arithmetic roughness lower than 0.5 nm. A residual vacuum of 5×10^{-5} Pa was reached in the sputtering chamber before introducing the deposition gas (argon). In order to obtain various microstructures, different distances and argon pressures were used. For each experimental condition, the target was sputtered for 20 min before starting the film deposition on the glass substrate. The whole experimental conditions used to prepare 300 nm thick films, are summarized in Table 1. In the next part of this publication, the samples will be named "Pxdy", with *x* the value of argon pressure in Pascal, and *y* the sample target distance in centimeter.

3. Characterizations

Film thicknesses were measured using a Dektak 3030ST profilometer. Structural characterizations of films were performed by grazing angle X-ray diffraction (GIRXD) on a Siemens D 5000 diffractometer. The apparent crystallite size determined in θ–2θ mode from the full width at half maximum (FWHM) of (3 1 1) spinel peaks, applying pseudo distribution for the peak broadening, and using the Sherrer formula below, to deduce the apparent crystallite size:

$$\mathrm{FWHM} = \frac{k\lambda}{L\cos\theta}$$

where FWHM is size broadening corrected by the instrumental contribution and k is a constant, in this calculation $k = 0.9$, λ is the radiation wavelength ($\lambda = 1.5406$ Å for Cu Kα_1), L is apparent crystallite size and θ is Bragg angle.

Microscopic studies were carried out with a Veeco Dimension 3000 AFM equipped with a super sharp TESP-SS Nanoworld© tip (nominal resonance frequency 320 kHz, nominal radius curvature 2 nm), a JEOL JSM 6700F field emission gun (SEM) and JEOL USF 2700 transmission electron microscope (TEM).

The surface area measurements were done on freshly prepared samples with a Micromeritics ASAP 2010 operating with Krypton at liquid nitrogen temperature. Several (1.3 cm × 1.3 cm) square samples covered on each side by 300 nm thick oxide films were placed in the Micromeritics ASAP 2010 cell for each experiment. Prior to measurements, the samples were heated under vacuum at 300 °C for 16 h to clean their surfaces [6].

Ellipsometry was also carried out with a spectroscopic ellipsometer Horiba Jobin-Yvon UVISEL™ apparatus in the whole visible spectral range of (350–800 nm), all ellipsometric data were recorded at an incidence angle of 70.4° and were analysed using the Delta-Psi software Version 2.0. The fitting of ellipsometric data, Is($\sin 2\Psi \cdot \sin \Delta$) and Ic($\sin 2\Psi \cdot \cos \Delta$) for the glass substrate and the oxide thin film, was first modelled with the Tauc-Lorentz (TL) dispersion relations [12–14]. A sample stack structure (Fig. 1a), glass/film/surface layer, was employed to extract the optical constants (n and k) of thin films. The glass thickness substrate is fixed at 1 mm and the thickness of film and surface layer are equally fitted.

Most of the films studied are porous and the optical constants measured are related to the properties of both $CoMnFeO_4$ and voids. Some samples however, are almost 100% dense, as demonstrated by surface area measurements and the high values of the refractive and absorptive indices. The real optical constants of dense $CoMnFeO_4$ can then be obtained from these samples. To determine the porosity and to study the evolution of the films, a second model is adopted considering a glass substrate of $L_1 = 1$ mm thickness, covered by the oxide film made itself by two layers L_2 and L_3 (Fig. 1b). The first one called (L_2), in contact with the substrate, is completely dense, its thickness is L_2 nanometers and its optical constants are those previously determined for dense $CoMnFeO_4$. The second layer (L_3) of L_3 nanometers, displays a porosity of p_3 percent. The upper part (L_4) of the film is made of a 50% porous layer having a thickness of L_4 nanometers. Surface roughness and porous layers were modelled with the Bruggeman effective medium approximation (BEMA) [15], where the layers are constituted of a mixture of dense $CoMnFeO_4$ and void.

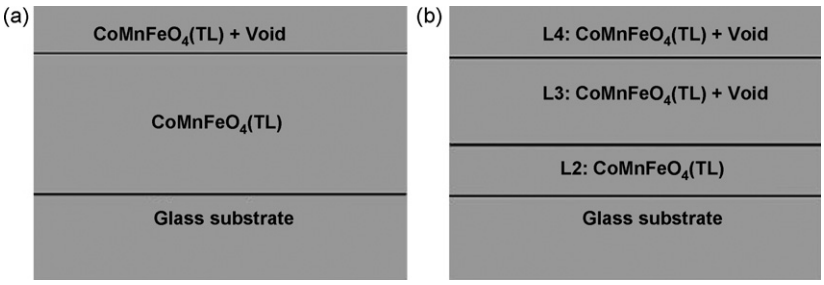

Fig. 1. The layer structure for ellipsometric data analysis (a) EMA model to extract refractive indices (b) EMA model of porous $CoMnFeO_4$ film.