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Density, thickness and composition measurements of TiO_2–SiO_2 thin films by coupling X-ray reflectometry, ellipsometry and electron probe microanalysis-X

A. Hodroj [a,*], H. Roussel [a], A. Crisci [b], F. Robaut [b], U. Gottlieb [a], J.L. Deschanvres [a]

[a] *Laboratoire des Matériaux et du Génie Physique (UMR 5628 CNRS), Ecole Nationale Supérieure de Physique de Grenoble, Institut National Polytechnique de Grenoble, Minatec, 3 parvis Louis Néel, BP 257, 38016 Grenoble Cedex 1, France*

[b] *Consortium des Moyens Technologiques Communs, Institut National Polytechnique de Grenoble, BP 75, 38402 St. Martin d'Hères, France*

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Abstract

Mixed TiO_2–SiO_2 thin films were deposited by aerosol atmospheric CVD method by using di-acetoxi di-butoxi silane (DADBS) and Ti tetra-butoxide as precursors. By varying the deposition temperatures between 470 and 600 °C and the ratios between the Si and Ti precursors (Si/Ti) from 2 up to 16, films with different compositions and thicknesses were deposited. The coupled analysis of the results of different characterisation methods was used in order to determine the variation of the composition, the thickness and the density of the films. First EPMA measurements were performed at different acceleration voltages with a Cameca SX50 system. By analysing, with specific software, the evolution of the intensity ratio I_x/I_{std} versus the voltage, the composition and the mass thickness (product of density by the thickness) were determined. In order to measure independently the density, X-ray reflectometry experiments were performed. By analysing the value of the critical angle and the Kiessig fringes, the density and the thickness of the layers were determined. The refractive index and the thickness of the films were also measured by ellipsometry. By assuming a linear interpolation between the index value of the pure SiO_2 and TiO_2 films, the film composition was deduced from the refractive index value. XPS measurements were also performed in order to obtain an independent value of the composition. A good agreement between the ways to measure the density is obtained.

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Keywords: TiO_2–SiO_2; Ellipsometry; XPS measurements; X-ray reflectometry; EPMA

1. Introduction

TiO_2 and SiO_2 materials are commonly used as optical thin films in the visible and near-infrared wavelength ranges. TiO_2–SiO_2 films have a wide range of achievable refractive index due to the large difference in refractive index between TiO_2 and SiO_2. This property is useful for the preparation of several optical devices (antireflective coatings, passive or active waveguides). Titanium silicate thin films can also be used as dielectric materials due to a high dielectric constant, a high breakdown field and a low leakage current [1].

We deposited TiO_2–SiO_2 thin film with an atmospheric aerosol CVD reactor. This process is based on the pyrolysis on a heated substrate of on aerosol produced by ultrasonic spraying of a solution [2,3]. As starting solution, di-acetosi di-butoxi silane (DADBS) and Ti tetra-butoxide precursors are dissolved in organic solvent [4]. Cleaned IR transparent (1 0 0) oriented silicon wafers were used as substrates. The substrate temperature is varied from 470 to 600 °C. Related to the CVD conditions, the deposited films are adherent. As observed by scanning electron microscopy (SEM), the surface morphology is very flat and smooth. This fact is confirmed by atomic force microscopy (AFM) measurement (Fig. 1) which revealed a roughness ranging from 0.25 to 1 nm (RMS).

In order to determine the films thickness, their composition and the film density, we proposed a coupled analysis of the results of different characterisation techniques. This coupled analysis is described by approach (Fig. 2). The film density is deduced from X-ray reflectometry (XRR) at a first time. On the other hand, the measured values of electron probe

* Corresponding author. Tel.: +33 4 56 52 93 23; fax: +33 4 56 52 93 01.
E-mail address: abbas.hodroj@inpg.fr (A. Hodroj).

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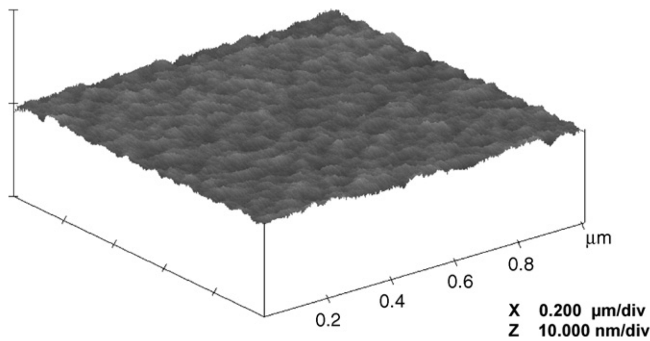

Fig. 1. AFM topography of TiO_2–SiO_2 films: the RMS roughness is about 0.28 nm.

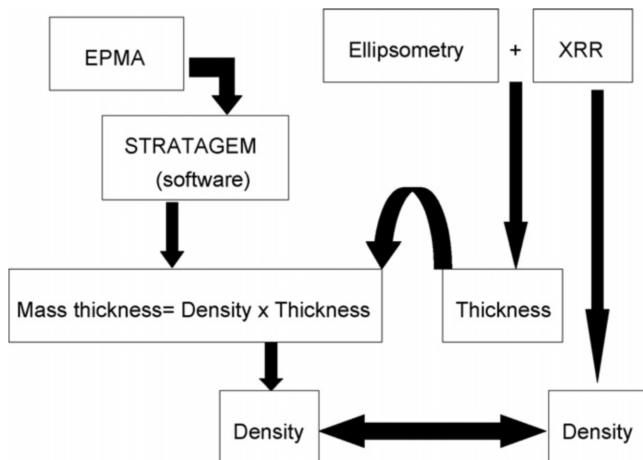

Fig. 2. Analysis scheme approach.

microanalysis-X (EPMA) treated by STRATAGEM software can give the mass thickness of the film. Using the thickness obtained by both ellipsometry and XRR techniques, we can deduce the density of the film at a second time. The two values of film density are then compared.

2. Experimental

The surface morphology of the deposited sample was observed with a Philips XL30 SEM equipped with a conventional thermoelectronic tungsten gun. Refraction index and thickness were measured on an Ellipsometer at 633 nm. We used a commercial atomic force microscopy from Nanoscope (Veeco 3100). X-ray reflectometry experiments were carried out on a Brucker D500 diffractometer equipped with Cu Kα radiation and a front monochromator. X-ray photoelectron spectroscopy (XPS) was studied with XR3E2 apparatus from vacuum generator in a UHV chamber (10^{-10} mbar), sample surfaces were irradiated with Mg Kα radiation (1253.6 eV). The ejected electrons were collected by a hemispherical analyser at constant pass energy of 30 eV. Analyses were carried out at the angle between the sample surface and the analyser, namely $\alpha = 90^{\circ}$. A xenon erosion (at beam energy 3 kV for 15 min) was used to eliminate the surface contamination. Electron probe X microanalysis (EPMA) was performed on a Cameca SX50 system.

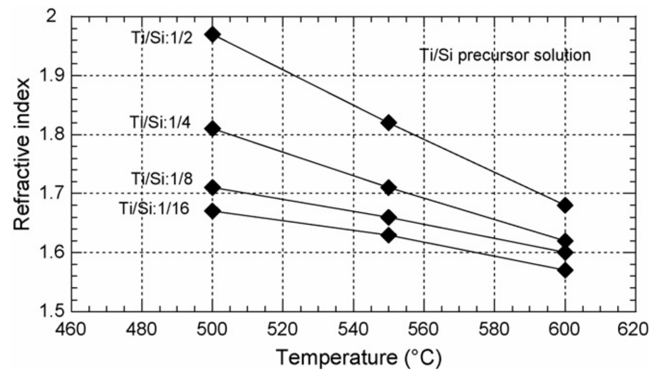

Fig. 3. Refractive index of TiO_2–SiO_2 films as a function of the deposition temperature for different Ti/Si ratios.

3. Results and discussion

The films were systematically characterised by ellipsometry at 633 nm; in order to explore the thickness and the refractive index *n*. The film thickness ranges from 80 to 120 nm, and the refractive index from 1.57 to 1.97.

In Fig. 3, the refractive index of the films is plotted, versus different deposition temperatures for different Ti/Si source ratios. For all solution, when the substrate temperature increases, the refractive index decreases. This result is related to an increase of the SiO_2 content in the film. In order to relate the measured values of refractive index of the films to their composition, we performed quantified XPS measurements on various films. As shown in Fig. 4, after erosion, the measured spectra were exempted of any contamination, except xenon line. For as-deposited films, the energy scale was calibrated with the C 1s line at 285.0 eV. Under this condition, the Ti $2p_{3/2}$ line is centred at 458.5 eV. After erosion, the energy was calibrated to keep the same value for Ti $2p_{3/2}$ line. The Si $2p_{3/2}$ and Ti $2p_{3/2}$ lines corresponded to single components with position and width values of 102.5/1.7 and 458.5/1.8 eV, which are ascribed to SiO_2 and TiO_2 contributions, respectively [5,6]. We obtained the film composition within uncertainty of 10% by using sensitivity factors of 0.17 and 1.1 relative to Si $2p_{3/2}$ and Ti $2p_{3/2}$ lines, respectively. In Fig. 5, we present the refractive index as a function of the percentage of SiO_2 relative to TiO_2 in the films. We can notice that, for more than 60% of SiO_2, the

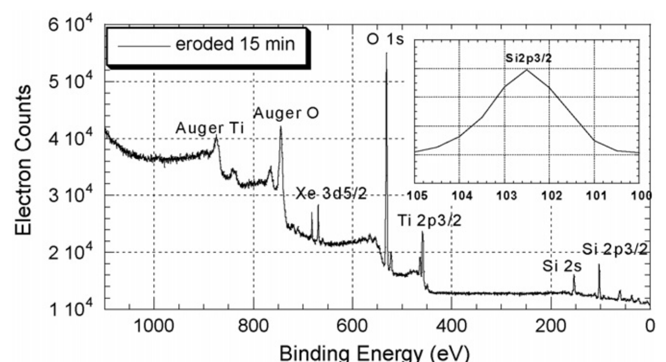

Fig. 4. XPS spectrum of TiO_2–SiO_2 films after xenon erosion. The Si $2p_{3/2}$ line is plotted in the inset.

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