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Residual stress study of nanostructured zirconia films obtained by MOCVD and by sol–gel routes

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ABSTRACT

The residual stress study of nanostructured zirconia films obtained by two deposition techniques, MOCVD and sol–gel used in this work, shows the advantages and limitations of each process. The MOCVD technique allows obtaining dense and thick zirconia films. Sol–gel deposition led to thinner zirconia films compared to those obtained by MOCVD, but the possible control of deposition parameters including multi-layers deposition is an advantage for the development of dense and homogeneous zirconia films. The crystalline structures and residual stress levels of nanostructured films have been studied by X-ray diffraction method; the film morphology has been analyzed by FEG-MEB.

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1. Introduction

Zirconia (ZrO_2) thin films are of considerable interest because of the variety of their uses in industrial applications. They exhibit special properties such as low electrical conductivity [1], good chemical inertness or low reactivity under oxygen [2], excellent permeability [3], good thermal shock resistance [4] and good biocompatibility [5], which makes them suitable for the design of advanced biomaterials. The deposition of zirconia films can be achieved using physical methods [6] or chemical methods [7]. However, using these deposition technologies it is sometimes difficult to succeed in realizing thin films with both a good homogeneity of the deposit and the desired thickness. Moreover, when deposited in the peculiar condition that promotes the targeted microstructure, the adhesion of the film is not yet fully mastered. In the present work, we will study a series of nanostructured undoped zirconia films deposited using two chemical processes. We will compare the films obtained by both sol–gel method and metal organic chemical vapor deposition (MOCVD) to identify the impact of the deposition parameters on the surface morphology, crystalline structure and residual stresses of the deposited films.

2. Experimental

Thin films were deposited on thick substrates so that the thickness of this deposit was greatly lower compared to the dimensions of the substrate. Therefore, the interface between the substrate and the oxide layer plays a primordial role on the structure and mechanical properties of the deposited film.

As this paper deals with a comparison between, ZrO_2 films obtained by two chemical routes the temperature process conditions of both, sol–gel (soft chemistry: low temperature) and MOCVD (high temperature) routes are given in Fig. 1.

According to this graph, the deposit of zirconia films takes place in two steps for the sol–gel route (i.e. Phase I at room temperature followed by a heat treatment during Phase II). On the other hand, in the MOCVD process, the heat treatment is performed simultaneously at the final substrate temperature without any further re-heating of the substrate.

2.1. Preparation of ZrO_2 films by the sol–gel method

2.1.1. Deposition step

The zirconia sol was prepared by progressive addition of 2.86 g of a zirconium n-propoxide (Zr $(OC_3H_7)_4$) (70% solution in n-propanol, Alfa Products) precursor solution in 8.9 ml of n-propanol. Acetyl acetone (acacH) was added to the solution of zirconium n-propoxide (0.8 M) in order to form acetyl acetonate complexes

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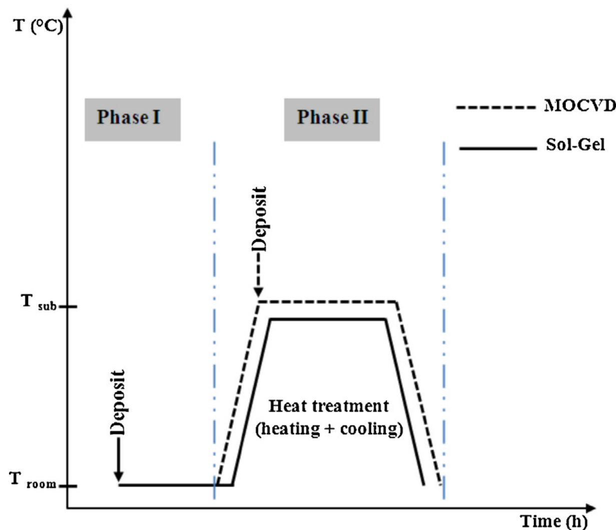

Fig. 1. Sol–gel and MOCVD deposition processes.

Table 1
Physical characteristics of Alumina and Silicon substrates.

	Alumina (96%)	Silicon Si (1 0 0)
Dimensions (mm^3)	15 × 10 × 1.5	10 × 10 × 0.5
Roughness (μm)	0.6	0.2
Young modulus (GPa)	380 [8]	129.5 [9]
Thermal expansion coefficient (10^{-6} K^{-1}) 25–1000 °C	8 [10]	3.4 [11]
Maximum operating temperature (°C)	1700 [12]	1400 [13]

and thus to avoid the formation of zirconium hydroxide. Then, the modified alkoxide was hydrolyzed by addition of water.

The solution was homogenized with a magnetic stirrer for 1 h at room temperature and under atmospheric pressure until getting a yellow and transparent sol. No precipitation or turbulence was observed, even after one month.

The deposition of ZrO_2 films on silicon Si (1 0 0) and alumina substrates (see Table 1 for physical characteristics of the mentioned substrates) [8–13] is carried out by spin coating using a DELTA 6 RC Spin Coater. After a month of aging, the zirconia sol was deposited on the substrates with a rotation speed of 600 rpm, and then dried for 24 h at room temperature and atmospheric pressure before carrying out the heat treatment.

2.1.2. Heat treatment

After drying, the samples are firstly heat-treated at 80 °C for 5 h and then heated at 380 °C for 3 h. According to thermogravimetric and thermodifferential analysis data (TGA/TDA); temperature of 80 °C corresponds to the removal of water and organic solvents, while the temperature of 380 °C enables the decomposition of all organic components in the film. Finally, the deposits were calcined in a muffle furnace (with temperature varying from 450 °C to 950 °C) with a heating rate of 5 °C/min for 10 h and deposited using two deposition modes M1 and M2.

2.1.3. Deposition mode

Two deposition modes were used called M1 and M2 in the following. They are described below.

2.1.3.1. M1 deposition mode. Each layer of zirconia deposited on the substrate is dried at room temperature for 24 h, and then heat treated at 80 °C and 380 °C. The set of "*n*" deposited layers will be treated to the final temperature T_f (see Fig. 2).

2.1.3.2. M2 deposition mode. After drying at room temperature and calcining at 80 °C and 380 °C, the deposited zirconia layer is heat treated at the final temperature T_f. This process was repeated for each deposited layer (Fig. 3) so that the thin film is obtained by duplexing "*n*" times the same process.

2.2. Preparation of ZrO_2 films by MOCVD

Under a relatively low total pressure (i.e. 100 Pa) and a low partial oxygen pressure of 23 Pa, two kinds of samples of ZrO_2 were deposited on silicon substrates Si (1 0 0) using a cold wall reactor [8] at various substrate temperatures, from 450 °C to 950 °C. The detailed experimental set-up and conditions are widely described in a previous work [14]. The precursor ($Zr_2(OP^ir)_6(thd)_2$), dissolved in cyclohexane was injected with a injection frequency of 2 Hz for 30 min, in a vaporization chamber at 200 °C. After spraying, the precursor was carried by preheated nitrogen to the reaction chamber and mixed with the preheated oxygen. Thus, this reactive atmosphere could react with the heated substrate and promote the layer growth.

3. Characterizations

The surface morphology and the thickness (estimated using the cross-section observation of the samples) of ZrO_2 thin films were characterized using a field emission gun-scanning electron microscope (FEG-SEM) (HITACHI S-4800-2 model).

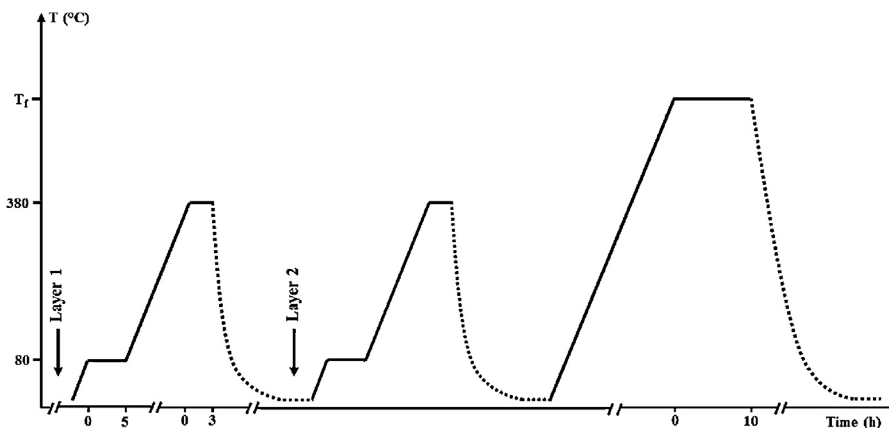

Fig. 2. Thermal treatment process of the M1 deposition mode by sol–gel.

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