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MgO and CaO stabilized ZrO_2 thin films obtained by Metal Organic Chemical Vapor Deposition

Giovanni Carta [a,*], Naida El Habra [a], Gilberto Rossetto [a], Pierino Zanella [a], Maurizio Casarin [b], Davide Barreca [c], Cinzia Maragno [b], Eugenio Tondello [b]

[a] CNR-ICIS, Corso Stati Uniti, 4,35127 Padova, Italy
[b] Dipartimento di Scienze Chimiche e INSTM, Università di Padova, Via Marzolo,1, 35131 Padova, Italy
[c] CNR-ISTM e INSTM, Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo, 1, 35131 Padova, Italy

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Abstract

Metal Organic Chemical Vapor Deposition of cubic stabilized zirconia was investigated by the addiction of the alkaline-earth oxides MgO and CaO. While Cp_2ZrMe_2 [(Cp=–C_5H_5, Me=–CH_3)] was used as precursor for ZrO_2, two different Mg compounds were tested for the MgO deposition, namely bis-(η^5-methylcyclopentadienyl)Mg(II) [(Mg(Cp-Me)$_2$] and bis-(2,2,6,6-tetramethyl-3,5-heptanedionate)(tetramethylethylenediamine)Mg(II) [Mg(tmhd)$_2$·tmeda]. Bis-(2,2,6,6-tetramethyl-3,5-heptanedionate)(triethyleneglycoldimethylether)Ca(II) [Ca(tmhd)$_2$·triglyme] was used for CaO growth. Depositions were carried out on fused quartz at 500 °C, yielding colorless and crack-free films well adherent to the substrates. A thorough characterization of their microstructure and chemical composition was obtained by the combined use of XRD (X-ray Diffraction), XPS (X-ray Photoelectron Spectroscopy) and EDXS (Energy Dispersive X-Ray Spectroscopy). The obtained results indicated a complete stabilization of zirconia in its cubic-fluorite phase when the magnesium and calcium content ranged from 12 to 30 at.% and from 17 to 38 at.%, respectively.

Keywords: MOCVD; CaO-stabilized zirconia; MgO-stabilized zirconia; Cubic ZrO_2

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1. Introduction

In the last decade, ZrO_2 has been widely investigated for the preparation of heterogeneous catalysts and solid electrolytes used in Solid Oxide Fuel Cells (SOFCs), due to the anionic vacancies in its structure resulting in a high oxygen conductivity [1]. In order to obtain an efficient solid electrolyte, the high-temperature cubic-fluorite ZrO_2 is usually stabilized under ordinary conditions by adding different low-valent binary oxides such as CaO, MgO, Sc_2O_3 and Y_2O_3, yielding ultimately a system conductivity directly dependent on the nature and concentration of the used oxide [2]. It has been reported that a calcia content of 12–15 mol% is necessary to stabilized the cubic zirconia phase in bulk, but no data are reported for MgO [3].

The stabilization of zirconia with alkaline-earth oxides can be obtained by different methods, such as combustion synthesis [3], coprecipitation [4], thermal decomposition of metal alkoxides [5], hydrothermal routes [6] and powder mixing [7]. Recently, these mixed oxide systems have been conveniently obtained in the form of thin films by Metal Organic Chemical Vapor Deposition (MOCVD), thanks to the possibility of controlling their structure and composition in view of eventual functional applications, by using two independent metal sources. The low-pressure MOCVD of yttria-stabilized ZrO_2 (YSZ) using Zr(tmhd)$_4$ and Y(tmhd)$_3$ (tmhd=2,2,6,6-tetramethyl-3,5-heptandionate) as source materials, has already been successfully performed [8]. Nevertheless, to the best of our knowledge, no literature studies concerning the MOCVD preparation of ZrO_2–MgO and ZrO_2–CaO films are available up to date.

In this work we report preliminary results on the MOCVD of cubic zirconia thin films stabilized with MgO and CaO using

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* Corresponding author. Tel.: +39 049 8295942; fax: +39 049 8295951.
E-mail address: carta@icis.cnr.it (G. Carta).

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Cp_2ZrMe_2, Mg(Cp-Me)$_2$ (**1**) Mg(tmhd)$_2$·tmeda (**2**) and Ca (tmhd)$_2$·triglyme as precursors. The use of Cp_2ZrMe_2 as precursor was made for its good volatility at relatively low temperatures (95 °C), while the more available β-diketonate compounds require appreciably higher temperatures for an efficient vaporization. Moreover, the chosen compound offers a better thermal match with Mg(Cp-Me)$_2$, as they can be effectively decomposed into the corresponding oxides at deposition temperatures of 500 °C.

Several depositions were carried out on fused quartz substrates, with a particular attention to the optimization of the process conditions aimed at the stabilization of the cubic ZrO_2 phase.

2. Experimental

All the reactions for the precursors synthesis were carried out in dry-box under a nitrogen atmosphere, as reported in literature [9].

The ZrO_2–MgO and ZrO_2–CaO thin films were co-deposited in a low-pressure hot wall MOCVD reactor equipped with a Pyrex tube heated by a tubular furnace. Concerning ZrO_2–MgO coatings, the Zr and Mg precursors were put in two different evaporators, thermostatically set to a temperature suitable for an efficient vaporization free from thermal decomposition. In a different way, ZrO_2–CaO thin films were obtained by vaporizing Ca(tmhd)$_2$·triglyme in a crucible placed in close proximity to the entrance of the reactor chamber, due to the low volatility of Ca precursor. For both systems the carrier gas was N_2, while the reactant gas (O_2+H_2O) was introduced in the main flow very close to the reaction zone, with a flow rate of 100 sccm. More specifically, water vapor was introduced by bubbling oxygen into a 500 cm^3 flask containing 250 cm^3 of distilled water kept at 30 °C. The amount of released water was constant (10 g/h) for all the depositions. During all the experiments, the total pressure and the growth temperature were fixed at 3 Torr and 500 °C, respectively. Fused quartz, suitably cleaned with hot trichloroethylene and rinsed with acetone prior to each experiment, was used as substrate.

XRD patterns, recorded at grazing angle ($\omega=2°$), were obtained by means of an X'Pert PW 3710 Philips instrument with a graphite monochromator and a proportional counter using the Cu K_α radiation. A parallel plate collimator was used in front of the detector. Phase identification was performed with the support of standard ICDD files.

A Perkin Elmer Φ 5600ci spectrometer with a non-monochromatized AlK_α (1486.6 eV) source was used for the X-ray Photoelectron Spectroscopy (XPS) analysis, at a working pressure lower than 5×10^{-9} Pa. The spectrometer was calibrated by fixing the Binding Energy (BE) of the Au4f$_{7/2}$ line at 84.0 eV with respect to the Fermi level. The reported BEs (standard deviation $=\pm$ 0.2 eV) were corrected for charging effects, assigning to the C1s line of adventitious carbon a position of 284.8 eV [10]. The atomic compositions were evaluated by employing sensitivity factors provided by Φ V5.4A software supplied by Perkin Elmer. In-depth analyses were carried out by Ar$^+$ sputtering at 3.0 keV, with an argon partial pressure of $\approx4\times10^{-8}$ Pa.

Compositional analysis was carried out by an analytical system working in energy dispersion (EDS-EDAX DX PRIME) in a Philips XL-40 scanning electron microscopy (SEM) equipped with a LaB_6 source.

Film thickness was determined by using a KLA Tencor Alpha-Step IQ surface profiler used to analyse the film height steps on partially masked samples.

3. Results and discussion

Thin films of ZrO_2–MgO and ZrO_2–CaO containing different amounts of the alkaline-earth oxides were grown in an atmosphere of O_2+H_2O. In fact, water vapor mixed with oxygen is usually employed in the CVD of oxide films for its beneficial effects on the precursors decomposition, since it favours a protolytic cleavage of the Metal-C bond yielding stable organic byproducts (as CpH) during the deposition process, thus reducing the carbon contamination within the films [9a]. The obtained layers were colorless and well adherent to the substrates, with an uniform and crack-free surface. The experimental conditions are reported in Table 1.

3.1. ZrO_2–MgO system

ZrO_2–MgO depositions were carried out using two different magnesium precursors at different source temperatures in order to change the magnesium concentration in the obtained films. As a general rule, a higher film growth rate was obtained starting from Mg(Cp-Me)$_2$ (**1**) with respect to Mg(tmhd)$_2$·tmeda (**2**), due to the higher volatility of (**1**).

The film microstructure was studied by XRD, with a particular attention for the obtained crystalline phases as a function of the magnesium contents. Fig. 1 shows the XRD patterns for films deposited on fused quartz from precursor (**1**) at three different Mg source temperatures. As it can be noted, both the tetragonal (ICDD pattern 00-014-0534) and cubic-

Table 1
Experimental growth conditions for ZrO_2–MgO and ZrO_2–CaO thin films

Precursor	Source temperature (°C)	Deposition time (min)	Flow rate N_2 (sccm)	Flow rate O_2+H_2O (sccm)	Thickness (nm)	Growth rate (nm/min)
Cp_2ZrMe_2	95	60 (Mg) 30 (Ca)	50	100	–	–
Mg (Cp-Me)$_2$ (**1**)	35, 40, 45	60	25	100	200, 200, 220	3.33, 3.33, 3.66
Mg(tmhd)$_2$·tmeda (**2**)	100, 110, 120	60	40	100	80, 90, 100	1.33, 1.5, 1.66
Ca(tmhd)$_2$·triglyme	180, 200, 220	30	50	100	80, 100, 120	2.66, 3.33, 4.0