

Thermal evolution of CaO-doped HfO₂ films and powders

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Abstract. Solid solutions of ZrO₂ and HfO₂ are potential electrolyte materials for intermediate-temperature SOFC because both are oxygen-ion conductors. The main challenge for these compounds is to reduce the relatively high value of the activation energies vacancies diffusion, which is influenced by several factors. In this work the thermal evolution of CaO-HfO₂ materials have been investigated. (CaO)_y-Hf(1-y)O(2-y) (y = 0.06, 0.14 y 0.2) coatings and powders were synthesized by chemical solution deposition (CSD). Films were deposited onto alumina substrates by Dip Coating technique, the burning of organic waste was carried out at 500 °C under normal atmosphere and then the films were thermally treated at intervals of temperature rising to a maximum temperature of 1250 °C. By means Glazing Incidence X-ray Diffraction (φ -2 θ configuration) the phases were studied in the annealed films. On the other hand, the thermal evolution and crystallization process of powders were analyzed in-situ by HT-XRD. The phenomena crystallization occurred in films and powders were analyzed. The activation energies of diffusion of oxygen vacancies of HfO₂-14 mole% CaO and HfO₂-20 mole% CaO films were measured from the thermal evolution of the relaxation constant measured by Perturbed Angular Correlation Technique.

1. Introduction

The solid solutions based HfO₂ have taken very technological importance in recent years, not only for their applications as solid electrolyte in fuel cells and gas sensors, but also for its use as picture-Detectors high-energy particles (scintillation) [1]. Furthermore, due to the miniaturization of devices, the demand for functional materials in restricted dimensions, such as thin films, is imperative. The required properties of solid solutions based on HfO₂ for any of their applications, are dependent on the structures and the stability of cubic phases metaestables or tetragonal. The objective of this work is to study the evolution of phases in films and powders in the system CaO-HfO₂ prepared from the precursor solution.

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2. Experimental procedure

2.1. Samples preparation

CaO-HfO₂ precursor solutions were prepared by using Calcium acetate and Hafnium buthoxide (Hf(OC4H9)₄), as source materials, with buthanol as solvent. Acetoin (3-hydroxy-2-butanone, CH₃COCH(OH)CH₃) was used as chelating agent. Commercial starting materials were used in their as-received state from Aldrich. Acetoin was added to Hafnium buthoxide - buthanol solution (the molar ratio of the chelating agent to the alkoxide was R = 4). The compositions were Hf_{1-x}Ca_xO_{2-x} with x = 0,06; 0,14; 0,20. The solution was suitable for the deposition of uniform and crack-free layers by Dipping-coating, with a thickness of ~150 nm per layer deposited onto alumina substrates. After deposition, each layer was dried at 200 °C for 3 min and pyrolyzed at 500 °C for 6 min. Additional layers were dip-coated to build up the desired thickness. Several samples of multilayer coating was heat-treated by quickly placing it into a preheated furnace at temperatures ranged between 500 and 1250 °C for 60 minutes. To derive gel powders the parent solutions were kept overnight in an oven maintained at 60°C under 100 Pa of pressure. After solvent evaporation the residue was heating at 200 °C. The dried gel was crushed in a agate mortar to get fine amorphous powders.

2.2. X-ray diffraction

The structure of the films was measured using an X-ray diffractometer with Cu K_α radiation (Philips X-Pert Pro) and a graphite monochromator (the step size being of 2θ = 0.02° and a 1 second time per step). For annealed films, a grazing incidence configuration (GIXRD) was used for measuring at room temperature. High temperature in-situ X-ray diffraction (HT-XRD) patterns of powders were obtained in air atmosphere making use of an Anton-Paar HTK10 high-temperature chamber. The spectra were taken at nominal temperatures (temperature of heating filament) equal to the temperatures used in annealing treatment of films. In order to overcome partly uncertainty in the determination of temperatures, a second S-thermocouple was placed onto the sample to measure directly the temperature of the powders (TR). Diffraction spectra were exploited to calculate average crystallite sizes of the solid solution from the magnitude of the half-width of the main line for c-HfO₂ (2θ = 30°), instrumental broadening of 0.130°), using the Scherrer equation.

2.3. Thermal analyses

By means of a DTG-60H Shimadzu analyzer, simultaneous Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) measurements were carried out on the as-obtained powder gels from room temperature to 800°C in normal atmosphere. Alumina crucibles and α-alumina reference were used.

2.4. Oxygen vacancies movement

The activation energy of oxygen vacancies diffusion was measured by PAC experiment. The PAC method is a nuclear technique by which the hyperfine interaction between a radioactive nucleus acting as a probe and the internal fields of the solid in the nearest neighbourhood can be measured [2]. PAC experiment, gives the desired information about the electrical field gradient (EFG) produced by the surrounding ions at the probe nucleus via the determination of the four quantities, i.e., relative fraction, quadrupole frequency, asymmetry parameter, and frequency spread, associated with each unequivalent Hafnium lattice site. In fact, atomic or defect movements cause a further perturbation of the angular correlation which may be reflected in the PAC spin rotation curves by a damping in the amplitude obeying to a factor of the form $e^{-\lambda t}$ where λ is called the relaxation constant. In stabilized hafnias or zirconias, this situation appears with the onset of the thermally activated vacancy-hopping process. The jump frequency, ν obeys an Arrhenius law and the correlation time $\tau = 1/\nu$ can then be associated with the activation energy of the jump through the equation: $\tau = \tau_{\infty} e^{E_{ac}/kT}$ (1). It has already been reported that an exponential decrease of the relaxation constant with the reciprocal absolute temperature implies a slow diffusion movement for which the correlation time between two successive atomic

configurations is equal to λ^{-1} . By contrast, an exponential increase of λ with the reciprocal absolute temperature, generally found at higher temperatures, is typical of a fast relaxation regime, for which the correlation time is proportional to λ . Hence, considering equation (1), the activation energies for movement of the vacancies can be drawn from the slopes of the $\lambda (T^{-1})$ function [3].

3. Results and discussions.

3.1. Thermal evolution of as-prepared materials.

Figure 1 show DTA – TGA curves for CaO 20 mol% – HfO₂ powder (no substantial differences for other compositions). The TGA curve shows a weight loss assigned to the decomposition and burning of the residual organic groups and no weight loss at temperatures > 520°C is observed, so the thermal decomposition of the gel is completed at that temperature. The DTA curves display intense exothermic peaks, one at centered at 350 °C and another around 490 °C (488, 492 and 498 °C for 6, 14 and 20 mole% of CaO, respectively) that are attributed to burning of the residual organic groups and to removal of hydroxyls, with a simultaneous onset of the crystallization of the cubic/tetragonal phase, respectively.

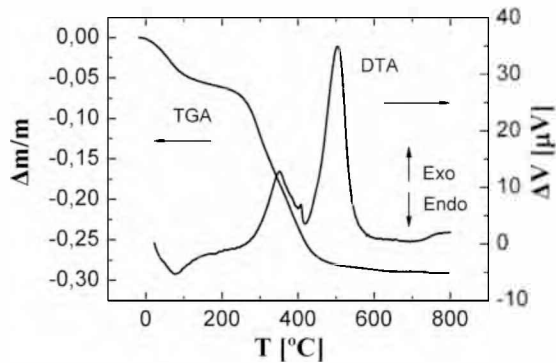


Figure 1. Thermogravimetric and Differential thermal analysis of powder CaO 20 mol% – HfO₂

3.2. Crystalline phases and metastable phase stabilization.

Figure 2 shows in-situ HT-XRD spectra of the CaO– HfO₂ powders that were taken at three temperatures for each composition: i) at 500 °C as nominal temperature, ii) at the highest temperature that the spectrum only exhibited diffraction peaks corresponding to cubic hafnia and iii) at the temperature that the monoclinic phase appears. The amorphous phase unambiguously transforms to cubic phase in the 14 and 20 mole% of CaO doped- HfO₂ powders. On the other hand, the metastable crystalline phase growth in the 6 mole% of CaO doped- HfO₂ powder could not be clearly identified as tetragonal phase or cubic phase due to its early destabilization by irruption of monoclinic phase at low temperature. The X-ray diffraction result follows the same trend that showed the DTA analysis, indicating that for increasing CaO content the crystallization temperature increases.

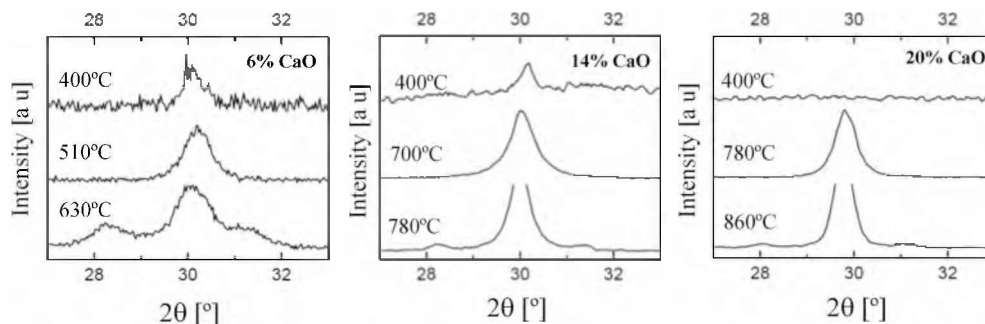


Figure 2. HT-XRD pattern of CaO - HfO₂ powders

Figure 3 shows ex-situ GI-XRD spectra of the CaO–HfO₂ films that were taken at room temperature on samples of annealed films at: i) 500 °C, ii) the highest temperature that the spectrum only exhibited diffraction peaks corresponding to cubic hafnia and iii) temperature that the monoclinic phase appears. The appearance of the monoclinic phase in the films occurred at higher temperatures than the ones in the powders; at 800 °C, 1000 °C and 1100 °C for the 6, 14 and 20 mole% of CaO doped- HfO₂ film, respectively.

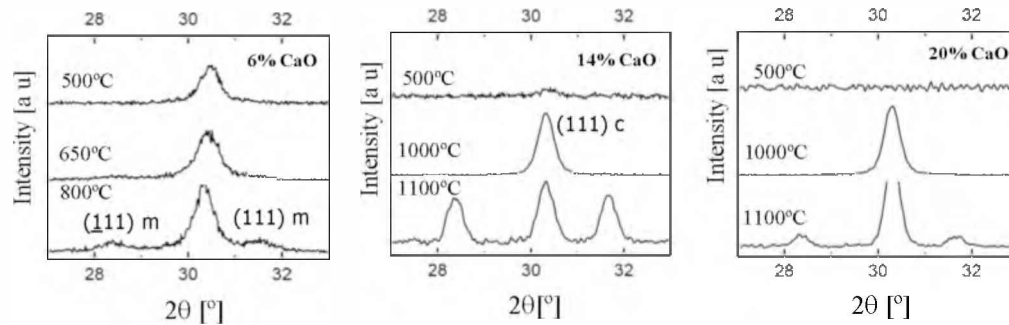


Figure 3. GI-XRD pattern of annealed for CaO - HfO₂ films

Table 1 shows the thermal evolution of fractions of cubic phase and monoclinic phase in annealed films and thermal treated powders of composition $x\text{CaO}-(1-x)\text{HfO}_2$ with $x = 0.06, 0.14$ and 0.2 .

Table 1. Thermal evolution phase fractions for CaO – HfO₂ materials

Comp.		Hf _{0.94} Ca _{0.06} O _{1.94}				Hf _{0.86} Ca _{0.14} O _{1.86}				Hf _{0.20} Ca _{0.20} O _{1.80}			
Temp. [°C]		Film		Powder		Film		Powder		Film		Powder	
T _N	T _R	c	m	c	m	c	m	c	m	c	m	c	m
500	400	100	0	100	0	100	0	100	0	¿?	¿?	¿?	¿?
650	510	94	06	100	0	100	0	100	0	100	0	100	0
800	630	79	21	72	28	100	0	100	0	100	0	100	0
900	700	64	36	40	60	100	0	100	0	100	0	100	0
1000	780	39	61	22	78	> 99	< 01	95	05	100	0	100	0
1100	860	0	100	17	83	36	64	71	29	79	21	98	02
1250	1130	0	100	21	79	0	100	61	39	75	25	87	13

The metastable tetragonal/cubic phases become unstable at increasing temperature of thermal treatment if the metastable–monoclinic transformation is not prevented. The Calcium cations are able to be substituted for Hf⁴⁺ ions in the cation lattice and consequently create vacancies in the oxygen sublattice in order to satisfy electroneutrality requirements. The oxygen vacancies increase the cubic phase stability due to the transformation of the Hf⁴⁺ surroundings from 8-folded oxygen coordination to 7-folded oxygen coordination. The question is to know the minimum dopant concentration for full cubic stabilization. Table 1 shows that the stability of the cubic phase increases for increasing CaO content for both films and powders. However, in the powders (TR) the irruption of monoclinic phase occurred at lower temperatures than in the films (TN). For thermal treatment at temperatures of 1000 °C, the cubic maintains as the unique phase in the 14 and 20 mole% of CaO doped-films.

This different behavior between films and powders has been already observed in the system Y₂O₃ doped-ZrO₂ [4]. The highly defective nature of the structure in the film coating, produced by presence of residual lattice strains and asymmetric grains, were been aiding the cubic phase stabilization.

The thermal evolution of the grain size vs. $1/kT(K)$ of the cubic phase in the HfO_2 - 20 mole% of CaO film and powder, make possible to infer that the mechanisms operated during the growth were dissimilar in each one of such materials (Figure 4). The change of slope at around 700 °C would indicate the starting of a recrystallization process during the thermal evolution of the powder, which would be indicating that in the powder the nucleation developed mainly by homogenous nucleation. Contrarily, the constant slope in the all temperature range and the low value of activation energy of the growing grain, it would evidence a heterogeneous nucleation in the film.

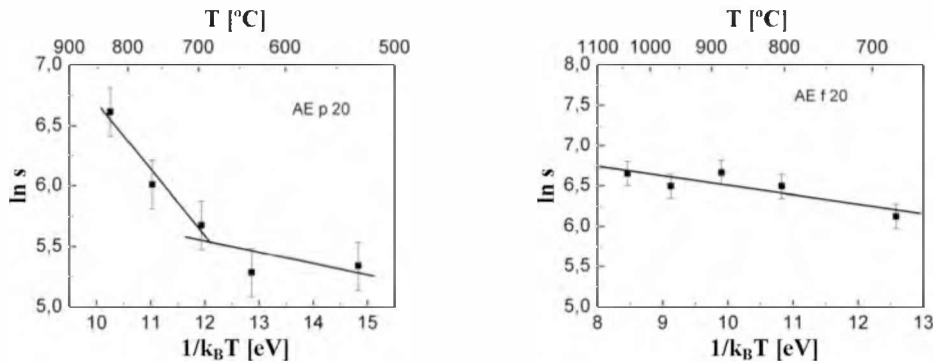


Figure 4. Thermal evolution of the size grain as function of $1/kT(K)$ of HfO_2 - 20 mole% of CaO

3.3. Oxygen vacancies diffusion.

Concerning the movement of oxygen vacancies, the $\lambda(T^{-1})$ function is plotted in figure 5. For both CaO 14 mole% doped- HfO_2 and 20 mole% CaO 20 mole% doped- HfO_2 films a slow-fast two regime behaviour can be observed. The movements at temperatures lower than 800°C correspond, according to the dynamic model assumed, to a slow diffusion ($\tau \propto \lambda^{-1}$) that is related to phenomena that are not linked to the oxygen vacancies diffusion. For temperatures higher than 800°C, in turn, the fast relaxation dynamical effect due to oxygen vacancies movement can be considered Arrhenius-like and an activation energies of 0.54 ± 0.04 eV and 0.70 ± 0.05 eV could be drawn from the $\lambda(T^{-1})$ slopes corresponding to HfO_2 -14 mole% CaO film and HfO_2 -20 mole% CaO film, respectively. Unexpectedly, the film that exhibits higher activation energy is the one where the CaO doping is higher, in which consequently the concentration of oxygen vacancies is higher also. This fact suggests that high levels of CaO content in the structure of the CaO doped- HfO_2 films performs a situation that impedes partly the oxygen movement. High CaO content would produce an increase of the $[V_o^{..}Ca^+]$ association or the growth of order nanophases formed by defective-oxygen compounds that were unappreciable in XRD [5].

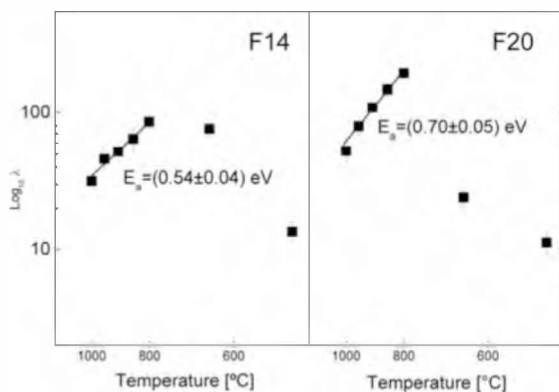


Figure 5. Activation energies deduced from the relaxation constants λ experienced by probes in the cubic solid solution.

4. Conclusions

Powders and coatings of metastable cubic hafnia have been successfully prepared by chemical solution deposition technique. The burning of residual organic groups, hydroxyls removal and onset of crystallization performed at temperatures lower than 500 °C.

The maximum temperature up to the stabilization is retained increases when CaO content increases in both powder and film. However, the irruption of monoclinic phase occurred at higher temperatures in the films. Films with 14 mole% doped- HfO₂ and 20 mole% CaO 20 mole% retained the cubic phase after annealing treatment at 1000 °C for 1 hour.

The determination of activation energies for oxygen vacancies movements allows to find that very high CaO content promotes the phenomena that impede partly the oxygen movement in the CaO – HfO₂ films.

References

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