

Violet–blue luminescence from hafnium oxide layers doped with CeCl₃ prepared by the spray pyrolysis process

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HfO₂:CeCl₃ coatings were deposited by the spray pyrolysis method employing hafnium dichloride oxide and CeCl₃ dissolved in deionized water (18 MΩ/cm). The room temperature photoluminescence characteristics of the HfO₂:CeCl₃ films were studied as a function of the deposition parameters such as doping concentrations and substrate temperature. The presence of two different Ce³⁺ centres in HfO₂ is detected from photoluminescence measurements. A reduction of the luminescence intensity is observed with an increase of both the CeCl₃ concentration and the deposition temperature. X-ray diffraction measurements of these films showed that the crystalline structure depends on the substrate temperature. For substrate temperatures less than 350 °C the deposited films are almost amorphous, while substrate temperatures higher than 400 °C produce diffraction peaks corresponding to the monoclinic phase of HfO₂. The chemical composition of the films as determined by energy dispersive spectroscopy is also reported. Furthermore, the surface morphology characteristics of the coatings, as a function of the deposition temperature, are also presented.

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1 Introduction

Nowadays, research on hafnium oxide (HfO₂) has attracted considerable attention due to its excellent chemical and physical properties such as its high dielectric constant and insulating characteristics [1]. Also, HfO₂ can be used for gas sensors [2], and for protective coatings due its thermal stability and hardness [3, 4]. The most important application of this oxide is probably as dielectric material with a relatively high dielectric constant and refractive index and wide band gap. These properties make it a good candidate for applications as optical coatings and metal-oxide semiconductor devices of the next generation [5, 6]. However, systematic studies of the luminescent properties of doped hafnium oxide are scarce [7]. Some groups have studied the optical properties of doped and undoped HfO₂ [7–9]. A few studies on Tb-, Eu- and Mn-doped HfO₂ have also been recently reported [10–12]. Luminescent materials doped with Ce³⁺ present light emissions related to radiative transitions between the 5d and 4f electronic energy levels of this ion that change significantly when it is inserted in different host materials due the fact that the 5d orbitals are very sensitive to the local environment [13]. Because of this characteristic, ultraviolet, violet, blue and green emissions have been observed from different luminescent materials doped with trivalent cerium [14, 15]. Up to now, however, it has been difficult to obtain efficient blue emitting mate-

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rials. Investigation of these materials has continued to grow in the last few years. The luminescent materials can be used for electroluminescent flat panel displays, colour plasma display panels, cathode ray tubes, fluorescent lamps, etc. The ultrasonic spray pyrolysis technique has proved to be very efficient for synthesizing luminescent powders and films [16]. This deposition process has advantages such as low cost, a high deposition rate, ease of operation and capacity to deposit films on large areas.

In the work reported in this contribution the photoluminescent characteristics of HfO₂:CeCl₃ coatings deposited by the ultrasonic spray pyrolysis technique were studied. In addition, the characteristics of the surface morphology, the chemical composition and the crystalline structure of the films, as a function of the deposition parameters, are discussed. To the best of the authors' knowledge, information on the luminescent characteristics of CeCl₃-doped hafnium oxide has not been reported before.

2 Experimental

The starting reagents to deposit HfO₂:CeCl₃ films were HfCl₂O·8H₂O and CeCl₃·7H₂O. The concentration of the spraying solution was 0.07 M and the solvent was deionized water. Substrate temperatures (T_s) during deposition were in the range 300–500 °C. The carrier gas flow (filtered air) was 12 l/min. The CeCl₃·7H₂O concentration in the spraying solution was in the range 1–15 atomic percent (a/o) in relation to the Hf content; these doping conditions result in Ce concentrations incorporated in the film in the range 0.67–6.47 a/o which is a common characteristic of the spray deposition technique. Corning 7059 glass slides were used as substrates for all the experiments presented in this work. The deposition time was adjusted (5–6 min) in order to obtain similar thickness of all samples studied. This thickness was approximately 5 μm (±0.03 μm) as measured using a Sloan Dektak IIA profilometer. The crystalline structure of the studied films was analyzed by means of X-ray diffraction (XRD), using a Siemens D-5000 diffractometer ($\lambda = 1.5406 \text{ \AA}$, Cu K_α radiation).

The chemical composition of the films was measured using energy dispersive spectroscopy (EDS) with an Oxford Pentafet, with a beryllium window, and an X-ray detector integrated in a Leica-Cambridge electron microscope model Stereoscan 440. (This microscope was used to obtain scanning electron microscopy (SEM) images.) The photoluminescence (PL) measurements were carried out using a Perkin–Elmer LS50B fluorescence spectrophotometer. All PL measurements were carried out at room temperature.

3 Results and discussion

In Fig. 1, the results of XRD measurements carried out on HfO₂:CeCl₃ (3 a/o) films are shown. Diffraction patterns for samples deposited at T_s from 300 to 500 °C are exhibited. The hafnium oxide coatings have poor crystallinity, which can be considered as almost amorphous and/or nanocrystalline layers at low deposition temperatures (300 °C); for higher T_s , these films show peaks which correspond to the hafnium oxide monoclinic phase (referenced JCPDS 431017). Sharper diffraction peaks at high T_s could indicate an increase in the crystallite size. The XRD spectra revealed a preferential (111) orientation of HfO₂ normal to the film surface. At high deposition temperatures, a small diffraction peak appeared at $2\theta = 30.32^\circ$, related to either the orthorhombic or the tetragonal HfO₂ phase [17, 18].

The results of EDS measurements are summarized in Tables 1 and 2. Table 1 gives the relative atomic percentages of the oxygen, hafnium, cerium and chlorine present in the films as a function of the content of the cerium trichloride in the spraying solution. A reduction of the relative content of hafnium and oxygen and an increase in the relative contents of cerium and chlorine are observed when the doping concentration is increased. The substrate temperature, in this case, was 300 °C. If the trivalent cerium ions substitute hafnium ions, the incorporated chlorine ions could act as charge compensators to preserve the electrical neutrality.

Table 2 shows similar results to those in Table 1 but as a function of the deposition temperature, keeping constant the doping concentration (CeCl₃, 3 a/o) in the starting solution. Here, we observe that the

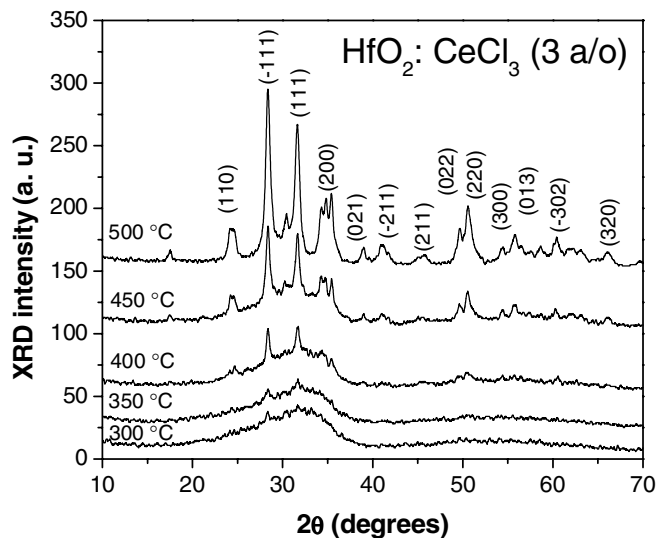


Fig. 1 XRD patterns for $\text{HfO}_2:\text{CeCl}_3$ (3 a/o) films grown at different T_s , as indicated.

relative content of oxygen and hafnium are slightly increased and there is an appreciable reduction in the relative content of cerium and chlorine as the substrate temperature increases.

Figure 2 shows the SEM surface morphology of $\text{HfO}_2:\text{CeCl}_3$ (3 a/o) coatings. It is possible to observe rough but continuous films with good adherence to the substrate. SEM micrographs of samples deposited at 300 °C (Fig. 2a), 400 °C (Fig. 2b) and 500 °C (Fig. 2c) are shown. It is also observed that the surface morphology of the films depends on the substrate temperature. Layers deposited at 300 °C show an open network formed by 'veins', probably in this case the thermal energy is not enough to process the material completely and to form a closed and compact surface. With increasing substrate temperature (400 and 500 °C), some cracks are seen but the morphology of the films is closed and apparently more compacted. Probably these characteristics are obtained because at higher deposition temperature the deposited precursors have larger surface kinetic energy, which produces a more complete pyrolytic reaction of the reactant materials that results in a more compacted film. In addition, for the sample deposited at 500 °C it is possible to distinguish a rough and continuous surface but more finely granulated.

PL measurements of $\text{HfO}_2:\text{CeCl}_3$ (3 a/o) coatings are shown in Fig. 3, as well as the emission from an undoped film (deposited at 300 °C) used as a reference. A marked decrease of the luminescence intensity is observed as the deposition temperature is increased. The maximum emission intensity was reached for

Table 1 Atomic percent content of oxygen, hafnium, cerium and chlorine in the cerium-doped hafnium oxide films as measured by EDS for different CeCl_3 concentrations in the spraying solution. The substrate temperature was 300 °C.

CeCl_3 concentration in the spraying solution (a/o)	oxygen (a/o)	hafnium (a/o)	cerium (a/o)	chlorine (a/o)
0	64.0	31.9	00.00	4.1
1	63.1	30.6	00.7	05.6
3	61.4	29.9	01.9	06.6
7	59.3	29.1	03.6	08.0
9	58.6	27.2	04.3	09.7
13	58.0	26.2	05.2	10.5
15	56.4	24.6	06.4	12.5

Table 2 Atomic percent content of oxygen, hafnium, cerium and chlorine in the cerium-doped hafnium oxide films as determined by EDS for different substrate temperatures. The CeCl_3 concentration in the spraying solution was 3 a/o.

substrate temperature (°C)	oxygen (a/o)	hafnium (a/o)	cerium (a/o)	chlorine (a/o)
300	61.4	29.9	01.9	6.6
350	61.5	31.3	01.0	05.9
400	62.1	32.6	00.8	04.4
450	63.3	33.0	00.6	03.1
500	64.9	33.7	00.3	00.9

the sample deposited at 300 °C. Increasing the deposition temperature results in two competing effects for the luminescence intensity: on the one hand, the crystallinity of the films improves; on the other hand, there is a reduction of the relative cerium and chlorine content remaining in the film. Although the former effect could result in increased luminescence intensity, the later results in the opposite, since the active luminescent centre is related to CeCl_3 . EDS measurements indicate a decrease of both the chlorine and cerium concentrations as the deposition temperature is increased (Table 2). Therefore, it is difficult to infer a specific role for the chlorine atoms in this case, although previous reports on aluminium oxide doped with CeCl_3 suggest that the presence of chlorine is necessary to activate the cerium luminescence [19].

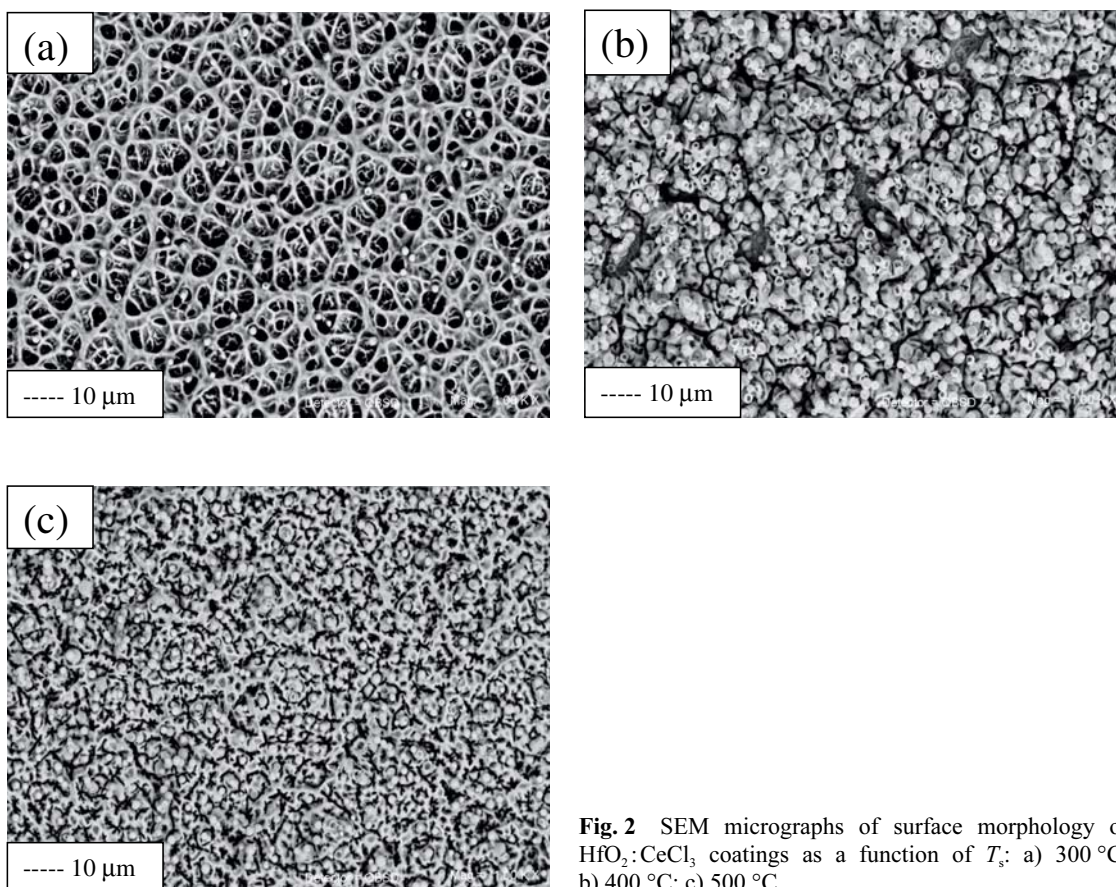


Fig. 2 SEM micrographs of surface morphology of $\text{HfO}_2:\text{CeCl}_3$ coatings as a function of T_s : a) 300 °C; b) 400 °C; c) 500 °C.

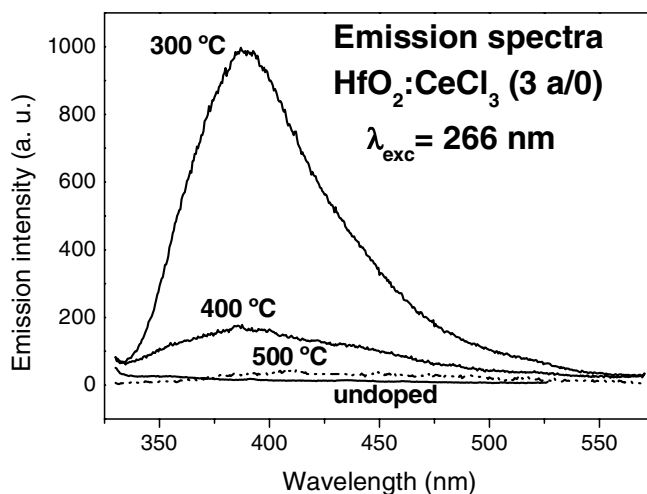


Fig. 3 PL emission intensity behaviour as a function of the wavelength for samples deposited at different values of the substrate temperature for $\text{HfO}_2:\text{CeCl}_3$ (3 a/o) coatings synthesized by the spray pyrolysis technique. Also, the emission spectrum from undoped HfO_2 film is shown.

Figure 4 displays the excitation and emission spectra of $\text{HfO}_2:\text{CeCl}_3$ films grown at 300 °C and with CeCl_3 concentrations of 3, 9 and 15 a/o. The emission spectra were obtained with 266 and 345 nm as excitation wavelengths. Two different blue emission bands associated with the Ce^{3+} 5d \rightarrow 4f transition can be detected for each excitation wavelength (bands A and B, respectively). At a low concentration of CeCl_3 (3 a/o) the first emission band (A; dashed thick curve) peaking at 385 nm is observed only under the higher excitation wavelength (266 nm). The second emission band (B; solid thick curve) peaking at 416 nm is observed under the lower excitation wavelength (345 nm). The energy difference between both non-symmetric bands is $\sim 1936 \text{ cm}^{-1}$, which is larger than that between the $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ doublets of

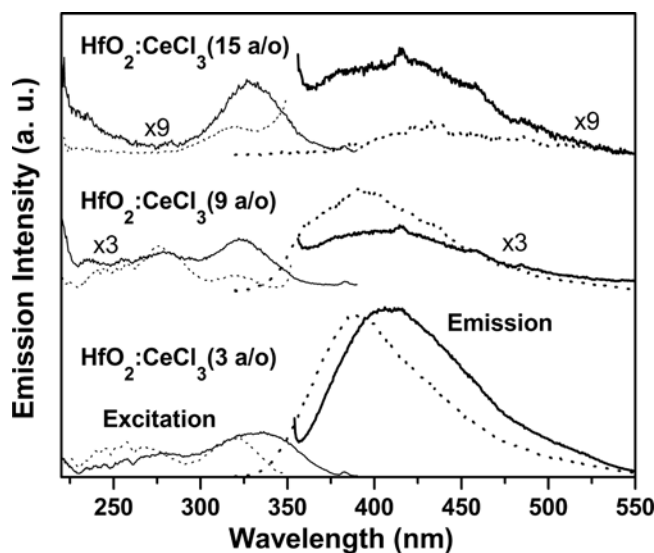


Fig. 4 Excitation and emission spectra of $\text{HfO}_2:\text{CeCl}_3$ films grown at 300 °C. The excitation spectra were recorded with $\lambda_{\text{em}} = 360 \text{ nm}$ (dashed thin curve) and $\lambda_{\text{em}} = 460 \text{ nm}$ (solid thin curve). The emission spectra were obtained with $\lambda_{\text{exc}} = 266 \text{ nm}$ (dashed thick curve) and $\lambda_{\text{exc}} = 345 \text{ nm}$ (solid thick curve). For clarity, the spectra are vertically shifted with respect to each other.

the 4f¹ ground state configuration of the Ce³⁺ ion. These results evidence the presence of two Ce³⁺ fluorescent centres at high energy (band A) and at low energy (band B), which might be associated with the molecular incorporation of the CeCl₃ into the HfO₂ film. Two similar centres have also been observed from PL spectra in LaMgB₅O₁₀:Ce³⁺ glasses [20]. In order to verify the two kinds of Ce³⁺ emission centres in the film, the excitation spectra of Ce³⁺ have also been analyzed (shown also in Fig. 4). The excitation spectra were recorded at 360 nm (within the A emission band) and at 460 nm (within the B emission band). The excitation spectra for the low concentration of CeCl₃ (3 and 9 a/o) consist of two bands whose peaks are at 280 and 324 nm, respectively (Fig. 4). Their energy difference is about 4850 cm⁻¹. This result is consistent with the possibility that there are two kinds of Ce³⁺-related emission centres.

As the cerium concentration increases both the A and B bands remain well localized at the same energy. At 9 a/o concentration of CeCl₃ both emissions appear slightly quenched. In the excitation spectrum recorded with $\lambda_{em} = 460$ nm the lower energy band associated with the B centre is more intense than the higher energy band associated with the A centre, whereas in the excitation spectrum recorded with $\lambda_{em} = 360$ nm the A centre band is more intense than the B centre one.

At high CeCl₃ concentration (15 a/o) the emissions are weaker. The excitation band associated with the A centre disappears, so that the excitation spectra exhibit only the lower energy band. Thus, the high-energy (A) emission band is quenched with an increase of Ce concentration, so that the film richest in cerium (excited at 266 or 345 nm) displays only the low-energy (B) emission band. The concentration quenching of the A centre luminescence suggests, hence, an energy migration from A to B centre [20].

4 Conclusions

The present article reports the luminescent characteristics of HfO₂:CeCl₃ coatings deposited by the spray pyrolysis process. These films show good adherence to the substrate with a violet–blue PL emission that can easily be seen with the naked eye in normal room light, when excited with a 4 W UV mercury lamp (254 and 366 nm). This gives an idea, if not quantitatively at least qualitatively, of the strength of the PL emission. PL spectra evidence the presence of two different Ce³⁺ centres in HfO₂. A complete concentration quenching of the luminescence of one of the two centres is observed at high concentration of CeCl₃ (15 a/o in the start solution), which suggests a fast energy transfer from the high-energy to the low-energy centres.

The samples synthesized at 300 °C show the highest PL emission intensity, and as the deposition temperature increases the PL emission intensity decreases. Simultaneously, as the substrate temperature increases the relative content of Ce and Cl decreases.

A high deposition rate up to 1 µm/min was observed. The crystalline structure of the analyzed coatings depends on T_s . At low temperatures the coatings are in an almost amorphous state and when the deposition temperature is increased they are transformed, mainly, to a polycrystalline monoclinic phase of the HfO₂. In addition, the surface morphology of the coatings also was dependent on T_s : SEM images showed that these films were rough but continuous as the deposition temperature was increased. Finally, it was confirmed that HfO₂ is an adequate host matrix for rare earth ions as active centres to generate strong violet–blue PL emissions; these HfO₂:CeCl₃ coatings emitting in the violet–blue have been synthesized for the first time to the best of our knowledge.

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