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Synthesis and characterization of hafnium oxide films for thermo and photoluminescence applications

J. Guzmán Mendoza [a,*], M.A. Aguilar Frutis [a], G. Alarcón Flores [a], M. García Hipólito [b], A. Maciel Cerda [b], J. Azorín Nieto [c], T. Rivera Montalvo [a,c], C. Falcony [d]

[a] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Instituto Politécnico Nacional, Legaria # 694, Miguel Hidalgo, 11500 México D.F., Mexico
[b] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Coyoacán, 04510 México D.F., Mexico
[c] Universidad Autónoma Metropolitana- Iztapalapa, Av. San Rafael Atlixco # 186, Col Vicentina, 09340 México D.F., Mexico
[d] Departamento de Física, CINVESTAV-IPN, A.P. 14-740, 07000 México D.F., Mexico

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A B S T R A C T

Hafnium oxide (HfO_2) films were deposited by the ultrasonic spray pyrolysis process. The films were synthesized from hafnium chloride as raw material in deionized water as solvent and were deposited on corning glass substrates at temperatures from 300 to 600 °C. For substrate temperatures lower than 400 °C the deposited films were amorphous, while for substrate temperatures higher than 450 °C, the monoclinic phase of HfO_2 appeared. Scanning electron microscopy showed that the film's surface resulted rough with semi-spherical promontories. The films showed a chemical composition close to HfO_2, with an Hf/O ratio of about 0.5. UV radiation was used in order to achieve the thermoluminescent characterization of the films; the 240 nm wavelength induced the best response. In addition, preliminary photoluminescence spectra, as a function of the deposition temperatures, are shown.
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1. Introduction

The measurement of ionizing radiation is, at this moment, a great challenge due to the risk associated with the exposure to this kind of radiation as well as solar radiation in medical and scientific equipments. Many measurement programs on ultraviolet radiation (UVR) have been implemented due to the spoiling of the ozone layer. However, little efforts have been dedicated to generate new materials that could be used as meters of ultraviolet radiation. UVR measurement using thermoluminescence (TL) materials has been suggested in the past by several authors (Driscoll, 1966; Chang and Su, 1993; Colyott et al., 1999; Azorin et al., 1998). The advantages of this technique are the easy readout of the samples and the small size of these kinds of dosimeters. In this sense, the hafnium oxide (HfO_2) is a material with a wide range of possible technological applications because of its chemical and physical properties such as high melting point, high chemical stability, and hardness near to diamond in its tetragonal phase. These properties make HfO_2 an attractive compound to be used as gas sensors and along with many electronic and optical applications (Capone et al., 1998; Wilk et al., 2001; Niimistö et al., 2004; Zukic et al., 1990; Edlou et al., 1993). The large energy gap and low phonon frequencies of the HfO_2 makes it appropriate as host lattice for being doped with rare earth activators (Mignotte, 2001; Zhao and Vanderbilt, 2002). In the recent years the study of luminescent materials based on HfO_2 has been intensified. Some groups have studied the optical properties of doped and undoped HfO_2 (Lange et al., 2006; Ito et al., 2005). Hafnium oxide films have been deposited by a variety of techniques; these include atomic layer epitaxy (Ritala et al., 1994), chemical vapor deposition (Balog et al., 1977; Reicher et al., 2000), electron beam evaporation (Cho et al., 2002). Compared to powdered materials, luminescent coatings offer advantages such as good adhesion to the substrates, have no outgassing problems, better thermal stability, posses uniform properties across the covered area and higher resolution and contrast with lesser materials. Ultrasonic spray pyrolysis represents an alternative processing method that has been employed for deposition of a wide variety of thin films, coatings and several types of powder production. Among them we can highlight those with luminescent properties such as Al_2O_3, ZrO_2 and $ZnAl_2O_4$, doped with rare earth or transition elements (Mn) (Esparza-García et al., 2002; García-Hipólito et al., 2002, 2003).

In this work, preliminary thermoluminescence (TL) and photoluminescence (PL) features of non-doped HfO_2 coatings, synthesized by the ultrasonic spray pyrolysis technique, are studied. Also, the surface microstructure characteristics, the crystalline structu, are shown.

* Corresponding author. Tel.: +55 57 29 60 00x67772; fax: +55 53 95 67 38.
E-mail address: joguzman@ipn.mx (J.G. Mendoza).

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2. Experimental details

The HfO_2 films were grown using the ultrasonic spray pyrolysis technique; this deposition process has been described previously (Langlet and Joubert, 1993). In brief, the precursor solution is atomized by an ultrasonic nebulizer and directed (by a carrier gas) towards the "Corning 7059 glass" substrate which was previously heated by means of a tin bath. $HfCl_4$ dissolved in deionized water was the starting reagent to HfO_2 films deposition; the molar concentration of the spraying solution was 0.05 M. Substrates temperatures (Ts) were in the range from 300 to 600 °C. The flow rate of the carrier gas (dry air) was 10 l/min. The deposition time was 10 min for all the samples almost the same thickness of the films was reached. The films showed a deposition rate of about 1 μm/min. The surface morphology and elementary composition (recorded by means of EDS: electron dispersive spectroscopy) were studied on a Jeol scanning electron microscopy (SEM) model LV6300 with a Si–Li characteristic X-ray detector Oxford model INCA Energy+. The crystalline structure of films was analyzed by X-ray diffraction (XRD) in a Siemens D-5000 diffractometer with CuK_α radiation (λ=1.5406 Å). Before being exposed to UVR the HfO_2 films were annealed at 300 °C for 20 min in order to erase all the remaining information in them. The films were exposed under UV radiation from a Xenon lamp coupled to a monochromator. The heating rate of the TL analyzer was kept at 10 °C/s for all readings, and integrating the signal from 50 up to 350 °C. All TL measurements were made in nitrogen atmosphere in order to reduce the thermal noise from the heating plate of the TL reader. TL measurements were carried out by means of a Harshaw analyzer (model 4000). The photoluminescence measurements were carried out by means of a spectrofluorometer SPEX Fluoro-Max-P, at room temperature.

3. Results and discussion

The XRD spectra obtained in the HfO_2 films are shown in Fig. 1. Diffraction patterns for samples deposited at Ts from 300 to 600 °C are exhibited. At Ts lower than 400 °C, the hafnium oxide films resulted amorphous, but for higher *Ts*, these films show peaks which correspond to the polycrystalline hafnium oxide monoclinic stable phase (referenced JCPDS 431017). Sharper diffraction peaks at high Ts could indicate an increase in the size of the crystallites. The results of EDS measurements are represented in Table 1, where the relative atomic percentage of the oxygen, chlorine and hafnium present in the films is summarized as a function of the deposition temperature. Here, it is possible to observe an appreciable reduction in the relative content of chlorine as the substrate temperature is increased. Moreover, the oxygen, chlorine and hafnium content remains almost constant when the substrate temperature is higher than 400 °C, that is, when the films are polycrystalline.

Fig. 2 shows the surface morphology of the HfO_2 films deposited at (a) 300 °C and (b) 500 °C. It is possible to observe rough but continuous films with good adherence to the substrate. The surface morphology of the films is dependent on the deposition temperature. The layers deposited at temperatures lower than 500 °C present rough and porous surfaces constituted by a network of "veins". As the deposition temperature increases,

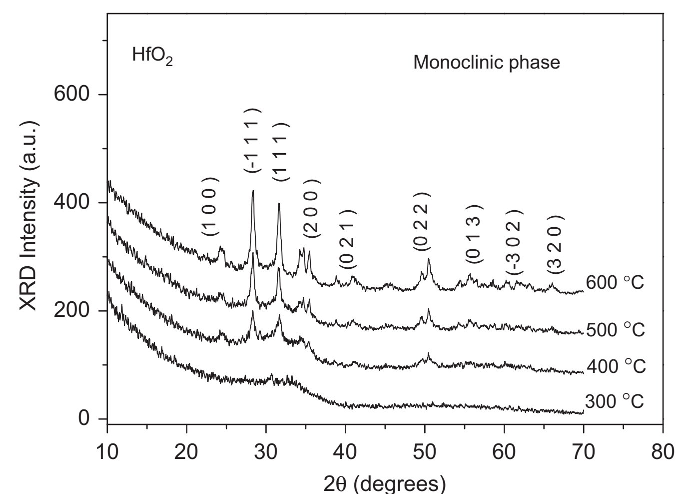
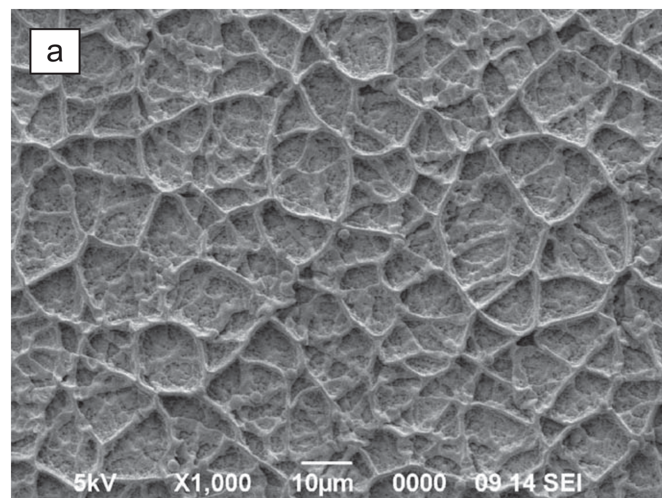


Fig. 1. XRD diffractograms for HfO_2 films grown at different *Ts*: 300, 400, 500 and 600 °C.

Table 1
Atomic percent content of the oxygen, chlorine and hafnium in the hafnium oxide (HfO_2) films as determined by EDS for different substrate temperatures.

Ts (°C)	O	Cl	Hf	Hf/O
300	63.89	8.88	27.23	0.4262
400	64.76	4.15	31.09	0.4801
500	65.75	3.71	30.53	0.4643
600	66.53	3.70	29.77	0.4481



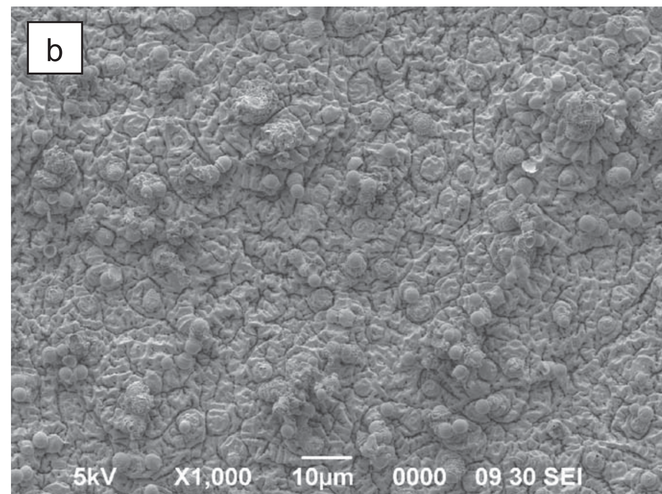


Fig. 2. SEM micrographs of the surface morphology for HfO_2 films deposited at (a) 300 °C and (b) 500 °C.

the network is closed, cracks-free, and apparently more compacted, although rough surfaces are also observed. Probably these characteristics are obtained because at higher substrate temperatures the deposited precursors have larger surface kinetic energy, which produces a more complete pyrolytic reaction of the reactant materials that result in a more compacted film. In the sample deposited at 500 °C it is possible to distinguish a rough and continuous surface finely granulated with some semi-spherical promontories upon the surface.

Fig. 3 shows the glow curve of HfO_2 films deposited at 500 °C. In this curve appears a single broadband centered at 175 °C. Samples grown at other temperatures had shown poor response. The TL emission observed in this film, yields a transient time dependent UV luminescence signal. Re-irradiation after annealing caused a reappearance of the luminescence. This effect confirms that the stimulated luminescence from irradiated samples is a result of the interaction of UV light with the matter. Dosimeter characteristics for this wavelength could be employed as a complementary thermoluminescent device with other TL phosphors as aluminum oxide.

The TL response of this film exposed to a spectral irradiance of 1500 μJ/cm^2 UV radiation as a function of the wavelength is shown in Fig. 4. As can be seen, the TL response of the HfO_2 film exposed to UV radiation of different wavelengths exhibit four maxima at about 240, 260, and 320 and 375 nm having the highest emission at 240 nm. TL response of HfO_2 exposed to visible light of different wavelengths were negligible compared with that obtained for the same spectral irradiance of UV radiation. Samples irradiated at diverse doses of gamma radiation did not exhibit any TL response. The TL response of HfO_2 exposed to 240 nm UV radiation as a function of spectral irradiance was linear in the range from 200 to 2500 μJ/cm^2 as shown in Fig. 5. Fading observed in this UV irradiated material was about 25% in the first month.

PL emission spectra, as a function of the substrate temperature (300, 400, 500, 600 °C), for hafnium oxide films are shown in Fig. 6. Here it is possible to distinguish three emission bands centered at 425, 512, and 650 nm when excited with a 254 nm wavelength. The results presented in this figure show that the amorphous films grown at 300 and 400 °C possess different photoluminescence characteristics compared with the crystalline samples containing monoclinic phase, 500 and 600 °C. The samples deposited at low substrate temperatures clearly show the band centered at 425 nm; the other bands (512 and 650 nm) appear in samples deposited at high substrate temperatures (500 and 600 °C). In the sample deposited at 600 °C, the band centered at 425 nm has a higher intensity.

All samples contain considerable amounts of chlorine (see Table 1), in particular the films deposited at 300 and 400 °C; the band centered in 425 is probably originated by the presence of these

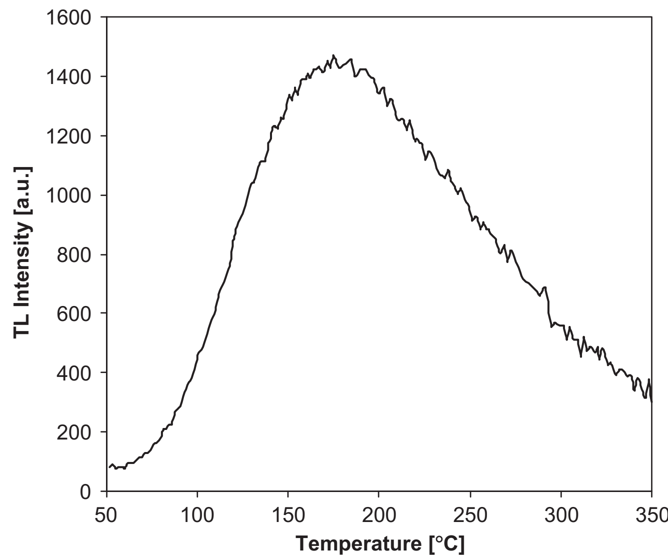


Fig. 3. Typical curve glow of HfO_2 film after a test UV radiation of 240 nm (1200 μJ/cm^2 spectral irradiance), using a heating rate of 10 °C/s.

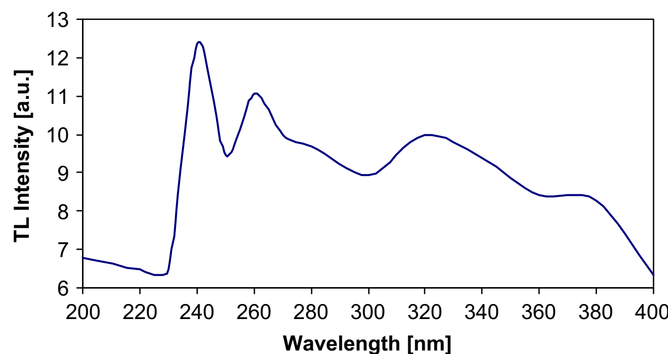


Fig. 4. TL response of the HfO_2 film deposited at 600 °C as a function of different wavelengths in the range from 200 to 400 nm.

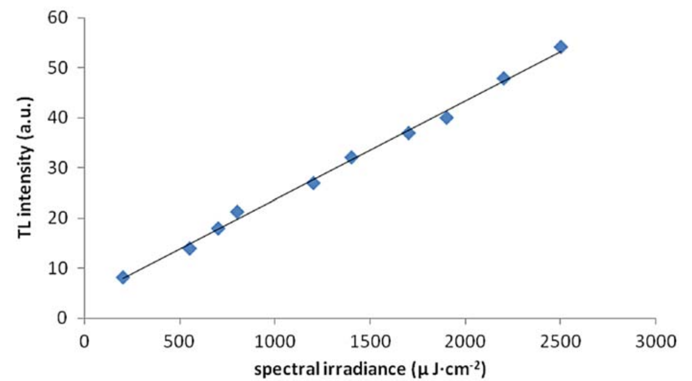


Fig. 5. TL response of the HfO_2 film as a function of spectral irradiance exposed to 240 nm UV radiation.

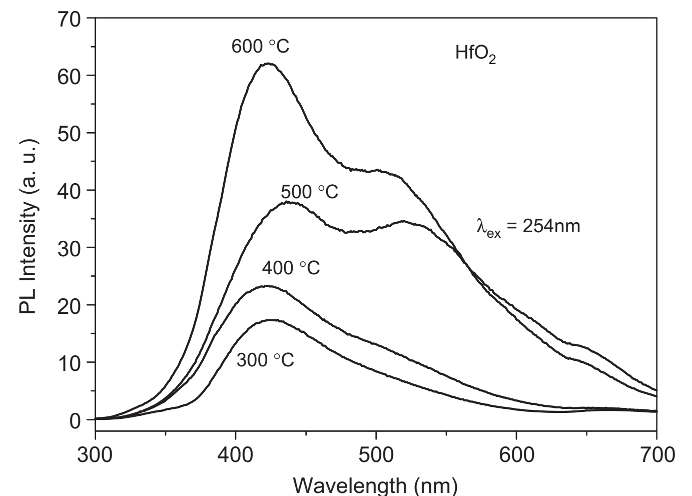


Fig. 6. PL emission spectra for HfO_2 films deposited at 300, 400, 500, 600 °C and excited with radiation of 254 nm.

chlorine ions. The relatively weak emission bands centered at 510 and 650 nm have probably an extrinsic origin arising from the radiative recombination at impurity and/or defect centers. For instance, deep levels related to oxygen vacancies might, in principle, contribute to the emission at these wavelengths. Obviously recombination of photo-excited electron–hole pairs (excitons) captured by those centers lead to the PL emission. Furthermore, the highest intensity of emission was obtained for 425 nm band, in the case of films grown at 600 °C and according to our XRD studies these samples possessed the most perfect structure. Hence, the band centered at 512 nm band (which diminishes, in this case) is likely related to defects. However, further studies are needed to clarify what kind of defects and/or impurities most significantly influence the PL properties of HfO_2 films.

4. Conclusions

This contribution reports on the structural, TL and PL characteristics of HfO_2 films synthesized by the ultrasonic spray pyrolysis process. These films show good adherence to the substrate and a high deposition rate up to 1 μm/min. The crystalline structure of the analyzed coatings depended on the substrate temperature; at low temperatures the films were amorphous and when the deposition temperature was increased they evolved mainly polycrystalline showing the monoclinic HfO_2 phase. Also, the coatings surface morphology depended on the substrate temperature. SEM micrographs showed that these films were rough but continuous as the deposition temperature was increased. The main feature of the results obtained by irradiating HfO_2 with UV radiation at different wavelengths is that the TL emission of HfO_2 as a function of the wavelength of the excitation spectrum covers the complete UV radiation spectrum with wavelengths from 100 to 290 nm (UVC), 280 to 315 nm (UVB), and 315 to 400 nm (UVA) range indicating an advantage over other ultraviolet dosimeters currently used. TL experimental results showed that HfO_2 could be useful in UV radiation dosimetry applications, using the thermoluminescence method mainly in the interval of 200–400 nm. The PL spectra showed emission bands centered at 425, 512 and 650 nm associated to impurities such as chlorine and/or structural defects. As the substrate temperature was raised, a higher intensity of the band centered at 425 nm was observed.

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