Rapid Research Note

Characterization of HfO$_2$:Mn luminescent coatings deposited by spray pyrolysis

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Novel manganese doped hafnium oxide cathodoluminescent films have been synthesized by the Pyrosol technique. The material obtained is in an amorphous state up to 300 °C. For higher temperatures a polycrystalline material is obtained with a monoclinic hafnium oxide phase. The cathodoluminescence spectra show blue–green and red bands associated with the electronic transitions $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ of the Mn^{2+} ions. A dependence of the cathodoluminescence, as a function of the doping concentration, substrate temperature and electron accelerating voltage is observed. In addition, preliminary results indicate that the chlorine relative content inside the processed films has been found to have an important role on the luminescent emission intensity of the studied materials.

1 Introduction   The Pyrosol (ultrasonic spray pyrolysis) process has proved to be very efficient to synthesize luminescent powders and films [1]. This technique has advantages such as: low cost, a high deposition rate, ease of operation and capacity to deposit layers on big areas. At the moment, research on hafnium oxide (HfO$_2$) has attracted considerable attention due to its excellent chemical and physical properties such as its high dielectric constant and insulating characteristics [2]. Also, HfO$_2$ can be used for gas sensors [3], and for protective coatings due to its thermal stability and hardness [4, 5]. The most important application of this oxide is probably as dielectric material with a relatively high dielectric constant, refractive index and wide band gap. These properties make it a good candidate for applications as optical coatings and metal−oxide semiconductor (MOS) devices of the next generation [6, 7]. However, systematic studies on the luminescent properties of doped HfO$_2$ are very scarce. Only a few studies on Tb and Eu doped hafnium oxide have been recently reported [8, 9]. Mn ions (3d^5 configuration) participate actively in order to create very efficient luminescence centers in a great variety of host lattices; also, they are important activators of luminescence in many commercial phosphors [10]. The emissions of this ion can be situated in the blue, green, yellow−orange or red regions depending on the influence of host lattices and co-activator ions [11]. The luminescent materials can be used for color plasma display panels, fluorescent lamps, electroluminescent flat panel displays, cathode ray tubes, etc.

The potential of manganese activated HfO$_2$ coatings to produce efficient luminescent materials is explored in this work. The structural and cathodoluminescent (CL) characteristics of HfO$_2$:Mn layers deposited by the ultrasonic spray pyrolysis technique were studied. In particular the luminescent characteristics of Mn doped hafnium oxide have not been reported before, to the best of the authors' knowledge.

2 Experimental   The details of the ultrasonic spray pyrolysis process have been presented elsewhere [1]. The starting reagents to deposit HfO$_2$:Mn films were HfCl$_4$ and MnCl$_2 \cdot$4H$_2$O (Aldrich Chemical

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Co.). The molar concentration of the spraying solution was 0.2M and the solvent was de-ionized water. Substrate temperatures (T_s) during deposition was in the range from 300 °C to 500 °C. The carrier gas flow (air) was 10 l/min. MnCl$_2 \cdot$4H$_2$O concentration in the spraying solution (C_{Mn}) was in the range from 1 to 20 atomic percent (a/o) in relation to the Hf content. These doping conditions result in Mn concentrations incorporated in the film in the range from 0.19 a/o to 3.47 a/o which is a common characteristic of the spray deposition technique. Corning 7059 glass slides were used as substrates for all the experimental results presented in this work. However, in order to avoid the contribution of the oxygen from the glass substrate, the determination of the chemical composition by EDS was performed on films deposited on silicon wafers with a (100) crystalline orientation. The deposition time was adjusted (5–6 min) in order to obtain similar thickness of all samples studied. This thickness was approximately 5 μm as measured by a Sloan Dektak IIA profilometer (within ±0.03 μm). CL measurements were performed in a vacuum chamber with a cold cathode electron gun (Luminoscope, model ELM-2 MCA, RELION Co.). The electron accelerating voltage (V_{ac}) was varied in the range 4–15 kV. The emitted light from the samples was coupled into an optical fiber bundle leading to a Perkin-Elmer LS50B fluorescence spectrophotometer. All CL measurements were carried out at room temperature. The chemical composition of the films was measured using Energy Dispersive Spectroscopy (EDS) using a Oxford Pentafet, with a beryllium window, X-ray detector integrated in a Leica-Cambridge electron microscope model Stereoscan 440. The crystalline structure of the studied films was analyzed by means of X-ray diffraction (XRD), using a Siemens D-5000 diffractometer ($\lambda = 1.5406$ Å, CuK$_\alpha$).

3 Results and discussion   XRD measurements carried out on HfO$_2$:Mn ($C_{Mn} = 5$ a/o) films are shown in Fig. 1. Diffraction patterns for samples deposited at T_s from 300 °C to 500 °C are exhibited. The hafnium oxide coatings have poor crystallinity at low deposition temperatures (300 °C), but 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 ($\bar{1}$11) orientation of HfO$_2$ normal to the film surface. At high deposition temperatures, a small diffraction peak at $2\theta = 30.32°$, related with the (111) orientation of the orthorhombic HfO$_2$ phase is present.

CL emission spectra of HfO$_2$:Mn coatings, grown at $T_s = 300$ °C and $V_{ac} = 8$ kV, as a function of the doping concentration, are shown in Fig. 2(a). Wide bands centered at 620 nm (red emission) corresponding to the $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ electronic transition of Mn^{2+} ions are observed. The CL emission intensity presents a maximum for $C_{Mn} = 0.81$ a/o as measured by EDS (5 a/o in the start solution), higher or lower C_{Mn} results in less intense CL emission. The concentration quenching of the CL is due to the excess of activators, which, in this condition, interact with each other, generating clusters (pairs or triples of Mn ions) which favors the dissipation of the excitation energy by non-radiative processes [12].

Figure 2(b) shows the CL spectra of HfO$_2$:Mn (5 a/o) films deposited at 300 °C, as a function of V_{ac}. Again, wide bands centered at 620 nm are appreciated. It is possible to observe that accelerating voltages higher than 8 kV originate a substantial reduction of the 620 nm CL emission intensity. Probably $V_{ac} > 8$ kV produce changes in the center responsible for red emission, which could lead to this effect. A similar behavior has been observed in ZrO$_2$ films activated with manganese [13]. More work is in progress to obtain additional information regarding this point.
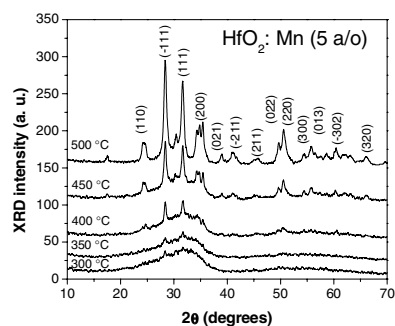

Fig. 1   XRD patterns for HfO$_2$:Mn (5 a/o) films grown at five different T_s: 300 °C, 350 °C, 400 °C, 450 °C and 500 °C.
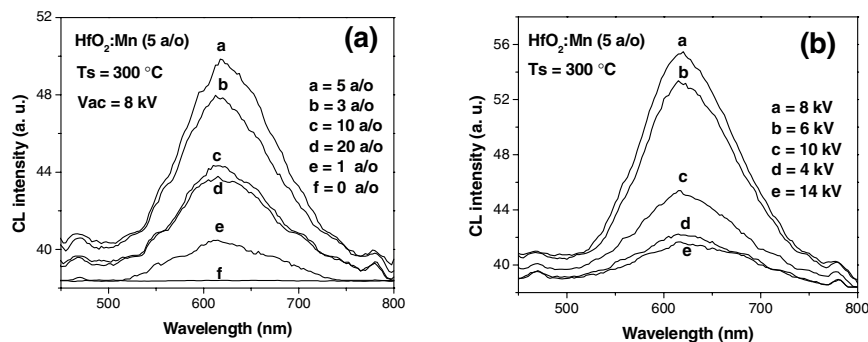
Fig. 2 CL spectra for HfO$_2$:Mn films deposited at T_s = 300 °C: (a) as a function of C_{Mn} and (b) as a function of V_{ac}.

Figure 3 shows the 620 nm CL emission intensity (V_{ac} = 8 kV) behavior of HfO$_2$:Mn (5 a/o) layers, as well as the dependence of the chlorine concentration inside the films as a function of the deposition temperature. Both the chlorine concentration and the CL emission intensity decrease as the T_s is increased up to 500 °C. It should be noted that C_{Mn} remains approximately constant according to the limits of sensibility of the detection technique (EDS). The quenching effect observed could be associated with the decrease of the chlorine (Cl) remaining in the films. This correlation could indicate some dependence between the CL intensity and the Cl concentration inside the films. Probably Cl acts as a co-activator to Mn in order to produce the red emission. Another possibility is that the manganese chloride molecule or some other compound involving Mn and Cl ions could be responsible for the red CL observed. It is known that an influence of Cl on the Mn luminescent properties exists. In general, it has been reported that increases in either the Cl or the Mn concentration cause the peak position of the Mn^{2+} emission band to shift to longer wavelength [14]. More studies are required, in our case, to elucidate this point.

CL spectra for HfO$_2$:Mn films deposited at 500 °C and irradiated under 15 kV electron accelerating voltage, as a function of the activator concentration, are presented in Fig. 4(a). In this case, wide bands centered at 475 nm are observed which correspond to blue–green emission arising from $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ (d–d) transition of the tetrahedrally coordinated Mn^{2+} ion (weak crystal-field) [15]. Here, again a concentration quenching is observed. C_{Mn}= 0.65 a/o as measured by EDS (5 a/o in the spraying solution) originated the maximum CL emission intensity.

Figure 4(b) presents CL spectra for HfO$_2$:Mn (5 a/o) films deposited at 500 °C, as a function of the electron accelerating voltage. We can observe wide bands peaked at 475–480 nm corresponding to blue–green emission from Mn^{2+} ions. No saturation effect is observed in the voltage range studied (12–15 kV). In addition, it should be pointed out that, for samples deposited at 500 °C, no CL emissions were observed for electron accelerating voltages lower than 12 kV. These samples have a relative minor amount of Cl and consequently the red emissions are not present and instead the blue–green emissions appear. It is also possible that the better resolved crystalline structure observed in these films might play a role on the observed emission changes.
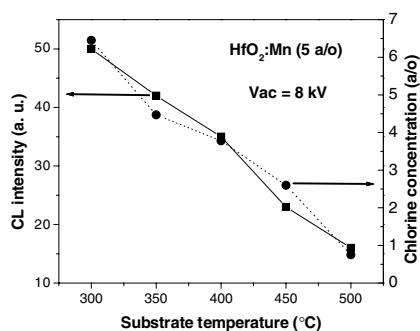

Fig. 3 Behavior of the 620 nm CL emission intensity and the relative chlorine content for HfO$_2$:Mn films as a function of T_s. C_{Mn} = 5 a/o and V_{ac} = 8 kV. The solid and dotted lines are only to guide the eye.
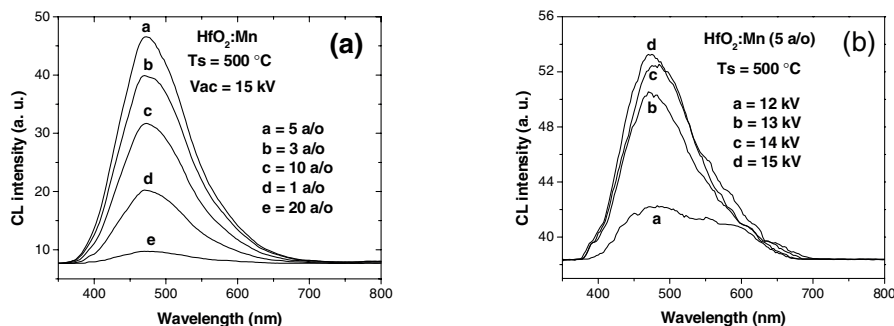
Fig. 4 CL spectra for HfO$_2$:Mn films deposited at T_s = 500 °C: (a) as a function of C_{Mn} and (b) as a function of V_{ac}.

4 Concluding remarks In summary, the present investigation has shown that good-quality cathodoluminescent HfO$_2$:Mn films have been deposited by the spray pyrolysis process. The crystalline structure of the analyzed coatings depended on T_s. A high deposition rate up to 1 μm per minute was observed. The CL emission intensities depended on T_s, C_{Mn} and V_{ac}. Concentration quenching of CL occurred at activator concentrations greater than 0.81 a/o for the red emission and 0.65 a/o for the blue–green emission, respectively. Apparently the presence of Cl inside the films is necessary to generate the red emission in the samples deposited at low substrate temperatures. A blue–green CL emission was obtained for samples deposited at 500 °C and electron accelerating potentials ≥ 12 kV. The results presented in this work indicate that amorphous and polycrystalline hafnium oxide make efficient and interesting hosts for Mn^{2+} ions. HfO$_2$:Mn films emitting in blue–green and red colors have been synthesized for the first time to our best knowledge.

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