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# Preparation and characterization of ZrO<sub>2</sub>:Sm amorphous thin films by solid state photochemical deposition method

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#### ABSTRACT

Thin films of ZrO<sub>2</sub> loaded with 10, 30 and 50 mol% Sm were prepared by a photochemical method using thin films of metal acetylacetonate complexes as precursors. The photolysis of these films induces the fragmentation of the acetylacetonate ligand and the partial reduction of metal ion together with volatile organic compounds. When the metallic complex is exposed to air, the product of the reaction is metal oxide. The photoreactivity of these films was monitored by FT-IR spectroscopy, followed by a post-annealing treatment process. The obtained films were characterized by X-ray photoelectron spectroscopy and atomic force microscopy.

Photoluminescense studies of the films employed 400 nm radiation for excitation of the Sm ions present. The emission spectra showed signals arising from the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$  (J=3/2, 7/2, 9/2) transitions, where the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{3/2}$  transition has the highest intensity. The concentration dependence of the PL intensity was also studied. A maximum PL intensity was observed with 10 mol% Sm content but then diminished with higher Sm concentrations.

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# 1. Introduction

Zirconia-based oxide ceramics are attractive for a variety of applications in areas such as optoelectronics devices [1]. Several attributes influence the physical and chemical properties of these materials, including crystal and amorphous structure, type and level of dopant, surface morphology, composition, stoichiometry, as well as the methodology of preparation.

In these last decades, there has been a considerable interest in the lanthanide ions incorporated into host compounds due to their luminescence properties. However, when the number of non-radiative pathways increases, the fluorescence quantum efficiency decreases considerably. One of the most important non-radiative processes that every material has is the multiphonon relaxation by the vibration bands of the system. When the frequency of this vibration band increases, the non-radiative decay rate increases. Consequently, the quantum efficiency is reduced. The stretching frequency of  $ZrO_2$  is about  $470 \text{ cm}^{-1}$ , which is very small compared to that of other oxide hosts such as  $TiO_2$ ,  $Al_2O_3$  or  $SiO_2$  [2]. This low phonon energy opens up the possibility of more efficient luminescence of active ions incorporated into the  $ZrO_2$  matrix. Recently, a considerable amount of work has been reported on the properties of rare earth-doped  $ZrO_2$ , such as  $ZrO_2$ :Eu [3,4],  $ZrO_2$ :Er [5,6] and  $ZrO_2$ :Sm [1,7,8]. The lanthanide ions incorporation into Zirconia materials can achieve special optical properties due to structural modifications, thereby impacting the electronic structure of the lattice host material. In the present study, we report the formation of  $ZrO_2$ :Sm amorphous thin films, which were generated via a photochemical reaction. In this method, thin films of inorganic or organometallic precursors are irradiated, thereby converted to amorphous films of metals or oxides, depending on the reactions conditions. The development of this method requires that the precursor complexes form stable amorphous thin films upon spin-coating onto a suitable substrate and photolysis of these films results in photoextrusion of the ligands leaving the inorganic products on the surface (Eq. (1)).

$$M(acac)_{n(thin film)} \xrightarrow{h\nu} M^{n-1} + nHacac \xrightarrow{O_2} M_x O_{y(thin film)} + sub-products$$
(1)

where M=Zr or Sm; acac: acetylacetonate ligand.

The photochemistry of metal  $\beta$ -diketonate complexes has been widely investigated [9], because they absorb strongly at readily accessible parts of the UV spectrum (250–400 nm). In general, the irradiation of the complexes with UV light (254 nm) leads to the photoreduction of the complexes, upon LMCT (ligand-to-metal charge transfer) excitation to form metals.

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In the case of lanthanide  $\beta$ -diketonate complexes, the charge transfer process between the lanthanide ion and the ligands results when the easily oxidized ligand is bound to tervalent lanthanide(III) ion which can be reduced to the divalent state [10]. In the sense that the photo-deposition of the  $\beta$ -diketonate complexes with UV light generates a partial reduction of metal ion, which is finally oxidized under aerated conditions.

In the present work we report the preliminary results on the characterization of zirconium oxide thin films loaded with samarium, generated by a photochemical reaction.

## 2. Experimental

## 2.1. General procedure

Fourier Transform Infrared spectra (FT-IR) were obtained with  $4 \text{ cm}^{-1}$  resolution in a Perkin Elmer Model 1605 FT-IR spectro-photometer.

UV spectra were obtained with 1 nm resolution in a Perkin Elmer Model Lambda 25 UV-vis spectrophotometer.

X-ray photoelectron spectra (XPS) were recorded on an XPS–Auger Perkin Elmer electron spectrometer Model PHI 1257, which included an ultra-high vacuum chamber, a hemispherical electron energy analyzer and an X-ray source providing unfiltered K $\alpha$  radiation from its Al anode (hv=1486.6 eV). The pressure of the main spectrometer chamber during data acquisition was maintained at ca 10<sup>-7</sup> Pa. The binding energy (BE) scale was calibrated by using the peak of adventitious carbon, setting it to 284.8 eV. The accuracy of the BE scale was ± 0.1 eV.

Atomic force microscopy (AFM) was performed in a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in contact mode. Film thickness was determined using a Leica DMLB optical microscope with a Michelson interference attachment.

Solid state photolysis was carried out at room temperature under a low-pressure Hg lamp ( $\lambda$ =254 nm) equipped with two 6 W tubes in an air. Progress of the reactions was monitored by determining the FT-IR spectra at different time intervals, following the decrease in IR absorption of the complexes.

The substrates for deposition of films were borosilicate glass microslides (Fischer,  $2 \times 2 \text{ cm}^2$ ) and n-type silicon (100) wafers ( $1 \times 1 \text{ cm}^2$ ) obtained from Wafer World Inc, Florida, USA.

Photoluminescense (PL) emission spectra measurements were carried out in a multifrequency phase fluorometer (K2, ISS Inc., Urbana, Champaign, IL, USA) with a L-type setup. Excitation was done with a 400 W UV Xe arc lamp, and the UV light passed through a monochromator set to 400 nm. The measurements were done at room temperature.

## 2.2. Preparation of amorphous thin films

The precursors Zr(IV) and Sm(III) acetylacetonate complexes were purchased from Aldrich Chemical Company and thin films were prepared by the following procedure: A silicon chip was placed on a spin coater and rotated at a speed of 1500 RPM. A portion (0.1 ml) of a solution of the precursor complex in  $CH_2Cl_2$ was dispensed onto the silicon chip and allowed to spread. The motor was then stopped after 30 s and a thin film of the complex remained on the chip. The quality of the films was examined by optical microscopy (1000 × magnification).

# 2.3. Photolysis of complexes as films on Si (100) surfaces

All photolysis experiments were done following the same procedure. A typical experiment was done as follows: A film of the

complex was deposited on n-type Si (100) by spin-coating from a CH<sub>2</sub>Cl<sub>2</sub> solution. This resulted in the formation of a smooth, uniform coating on the chip. The quality (uniformity, defects, etc.) of the precursor films was determined by optical microscopy  $(1000 \times)$ , while the thickness was monitored by interferometry. The FT-IR spectrum of the starting film was first obtained. The irradiation of the films was carried out at room temperature using two low-pressure Hg lamps (6 W, Rayonet RPR-2537A) in air, until the FT-IR spectrum showed no evidence of the starting material. Prior to analysis, the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface. In order to obtain films of a specific thickness, successive lavers of the precursors were deposited by spin-coating and irradiated as above. This process was repeated several times until the desired thickness was achieved. Post-annealing was carried out under a continuous flow of synthetic air at 750 °C for 2 h in a programmable Lindberg tube furnace.

# 3. Results and discussion

## 3.1. Photochemistry of Zr(IV) and Sm(III) acetylacetonate complexes

We have previously reported the solid state photochemistry of the  $Zr(acac)_4$  complex films. They were deposited on  $Si(1 \ 0 \ 0)$  by spin-coating and irradiated under air with a 254 nm UV source, obtaining thin films of  $ZrO_2$  [11]. In order to evaluate the photoreactivity of  $Sm(acac)_3$  complex, thin films of the  $Sm(acac)_3$  complex were irradiated and the photolysis was monitored by FT-IR spectroscopy (Fig. 1). It was observed that the band at 1515 cm<sup>-1</sup> approx. associated with the carbonyl group of the ligand, decreased in intensity and after 24 h of irradiation only minimal absorptions in the infrared spectrum remained. These results suggest that the diketonate groups on the precursor material are photodissociated on the surface, forming volatile products which are partially desorbed.

## 3.2. Characterization of ZrO<sub>2</sub>:Sm photodeposited thin films.

For the deposition of  $ZrO_2$ :Sm thin films, solutions of  $Zr(acac)_4$  with different proportions of the  $Sm(acac)_3$  complexes (10, 30 and 50 mol%) were spin-coated on the appropriate substrate and the



Fig. 1. FT-IR spectral changes associated with photolysis for 4 h of a  $Sm(acac)_3$  film deposited on Si (1 0 0).

thin films were irradiated until minimal absorptions in the infrared spectrum from the complexes were observed.

#### 3.2.1. XPS analysis

The elemental composition of the thin films was analyzed by XPS in order to investigate their chemical nature. Fig. 2 presents the XPS spectrum in the range of 0–1200 eV binding energy of asdeposited and annealed samples. This survey spectrum shows lines from Zr, O, and Sm, as well as a small amount of carbon, which can be attributed to an organic residue from organic raw precursors. After annealing at 750 °C it is found that a partial elimination of this residual carbon occurs.

Other authors, working with metal-organic chemical vapor deposition (MOCVD), have reported that metal  $\beta$ -diketonates such as Zr(acac)<sub>4</sub> require high substrate temperatures ( > 600 °C) for oxide growth and this may result in carbon incorporation [12,13]. On the other hand, Samarium  $\beta$ -diketonates complexes such as Sm(DPM)<sub>3</sub> (DPM=2,2,6,6-tetramethyl-3,5-heptanedionate) have been used as metal-organic precursors in aerosol-assisted metal-organic chemical vapor deposition method (AA-MOCVD). In this case, a small amount of carbon has been found on the surfaces due



Fig. 2. XPS survey spectrum of (a) an as-deposited and (b) annealed at 750  $^\circ\text{C}$  ZrO<sub>2</sub>:Sm thin films prepared by UV irradiation at 254 nm.

to contamination from the environment rather than organic residue from the organic raw materials [14].

The XPS spectra (Fig. 2) showed that the Zr 3d was composed of two peaks with binding energy of 182.0 eV (Zr  $3d_{5/2}$ ) and 185.5 eV (Zr  $3d_{3/2}$ ). The latter is usually disregarded, since almost all published data refers to the  $3d_{5/2}$  state. The observed binding energy of 182.1 eV for Zr  $3d_{5/2}$  can be assigned to ZrO<sub>2</sub> [15,16]. After annealing at 750 °C, the binding energy for Zr  $3d_{5/2}$  was 181.9 eV.

The O 1s peak positions are at about 530 eV. (Fig. 3a) The high resolution spectrum indicates that there are at least two chemical states, including lattice oxygen ( $O_L$  at 529.8 eV) and adsorbed oxygen ( $O_{ads}$  at 531.7 eV). The  $O_L$  1s is mainly attributed to the contribution of Zr–O bonds in the lattice and the  $O_{ads}$  1s is close to the O–H bonds from adsorbed water molecules [17]. The peak attributed to the hydroxyl group (OH) finally weakened significantly after annealing at 750 °C.

The Sm  $3d_{5/2}$  core level can be fitted with two subpeaks (Fig. 3b), centered at 1083.3 eV (67.4%) and 1079.2 eV (32.6%) for as-deposited films and 1083.0 eV (80.5%) and 1079.7 eV (19.6%) for annealed films. The Sm  $3d_{5/2}$  subpeak appearing at 1083 eV is assigned to the Sm<sup>3+</sup> states and the subpeak at 1079 eV is associated to the Sm<sup>2+</sup> states. Similar values have been reported by other authors [18–20]. In summary, our results show a mixture of two Sm oxidation states for as-deposited and annealed films.

#### 3.2.2. Film morphology

AFM was used to study the morphology of photodeposited films and the results are summarized in Table 1. Fig. 4 shows the AFM micrographs. The as-deposited films have a non-uniform rough surface without structural order, which is characteristic of an amorphous deposit, with rms values increasing slightly with the amount of Sm present in the films. After these films were annealed at 750 °C for 2 h, rms values decrease significantly and a more regular surface can be observed.

This reduction in roughness is due to the fact that a great part of the sub-products generated during photolysis are eliminated partially from the surface as a result of thermal treatment. This in turn produces a redistribution of the deposits on the surface generating a more compact and uniform film.

#### 3.3. Photoluminescence study of the ZrO<sub>2</sub>:Sm thin films

The Sm ions were excited using 400 nm radiation, which matches with the  ${}^{6}H_{5/2} \rightarrow {}^{4}K_{11/2}$  electronic transition in Sm ion



Fig. 3. High resolution spectra: (a) O 1s, where O<sub>L</sub> is lattice oxygen and O<sub>ads</sub> is adsorbed oxygen and (b) Sm 3d core level XPS spectra: fitted with two subpeaks of Sm<sup>3+</sup> and Sm<sup>2+</sup> states.

[21,22]. Similar values of excitation have been reported in other studies [21,23–25]. The excitation spectra (Fig. 5) were obtained by monitoring the emission related to the band at 532 nm. It can be seen that the spectra mainly consist of an intense and broadband in the interval range between 390 and 410 nm and another band situated at 380 nm. These bands indicate that the samarium ions are located in an amorphous matrix.

#### Table 1

AFM results for ZrO<sub>2</sub>:Sm thin films: Rms (nm) and maximum height (nm).

Thin Films	10 mol% Sm	30 mol% Sm	50 mol% Sm
As-deposited	34.13 (224.6)	45.18 (283.1)	50.22 (315.5)
Annealed at 750 °C	1.739 (21.54)	1.961 (17.67)	2.713 (18.79)

Values in parenthesis show  $R_{max}$  maximum height (nm).

Photoluminescence emission spectra were measured in the range of 450–800 nm. They are shown in Figs. 6 and 7. Three characteristic emission bands have been reported to be at 560 nm (green), 600 nm (orange) and 650 nm (red). They are assigned to the  ${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{J}$  transitions of the Sm<sup>3+</sup> ions, where J=5/2, 7/2 and 9/2, respectively [21,23,25].

The positions and intensity of the peaks correspond to different PL mechanisms. The three Sm emission bands have been frequently observed in various host matrices and have usually assigned to the transitions from the first excited level  ${}^{4}G_{5/2}$  to the ground state  ${}^{6}H_{J}$  levels. These three emission bands of Sm resulted following non-radiative energy transfers from the ZrO<sub>2</sub> host to the Sm ions which was followed by radiative Sm emission processes.

In our case, we have observed two broandbands centered at 533 and 600 nm and a shoulder at 646 nm. These signals can be assigned to the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{3/2}$  [26],  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  and  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$  transitions [21,27–29], respectively.



Fig. 4. AFM images of Sm loaded zirconium oxide films with: (a) as-deposited 10 mol% Sm, (b) annealed 10 mol% Sm, (c) as-deposited 30 mol% Sm, (d) annealed 30 mol%, (e) as-deposited 50 mol% Sm, and (f) annealed 50 mol% Sm.



Fig. 5. Excitation spectra of as-deposited and annealed  $\text{ZrO}_2$  loaded with 10 mol% Sm thin films.



Fig. 6. Photoluminescence spectra of as-deposited  $\rm ZrO_2$  loaded with Sm thin films, excited at 400 nm.



Fig. 7. Photoluminescence spectra of annealed  ${\rm ZrO}_2$  loaded with Sm thin films, excited at 400 nm.

The fine structure can be explained by taking into account that the  ${}^{6}\text{H}_{J}$  levels are split in the crystal field into 2J+1 sublevels, which clearly demonstrate that Sm<sup>3+</sup> ions are placed in a quite regular environment, contrary to the situation encountered in amorphous matrices, where displaced emissions can appear corresponding to another transition type, besides the commonly known types.

Fig. 6 shows the dependence of the PL spectra on samarium concentration of as-deposited  $ZrO_2$  thin films. It is possible to observe that the intensity at 533 nm reaches a maximum when the concentration is 10 mol% Sm and decreases rapidly with further increase in Sm concentration, probably due to concentration quenching (self-quenching) [27].

The PL spectra of ZrO<sub>2</sub>:Sm annealed at 750 °C are shown in Fig. 7. Two bands centered at 532 and 598 nm and a small shoulder at 646 nm can be observed. When the concentration of samarium increases, the emission intensity decreases. Besides, the emission signal of annealed samples is lower in comparison with the signal from as-deposited samples. A possible explanation of the lower intensity is the fact that surface reconstruction of the annealed films may cause the formation of some clusters of Sm<sup>3+</sup> ions, which leads to concentration quenching of Sm<sup>3+</sup> luminescence.

On the other hand, it has been reported [30] the annealing samples at high temperature decrease the excitation efficiency and corresponding emission due to the loss of water within the interlayer or surface of the films, due to the water molecules in the interlayer or surface of the films can act as "water-bridge" to enhance the bonding state of Sm<sup>3+</sup> ions with O–Zr of the material host and thus improve the energy transfer process. When the films are annealed, the host band gap excitation efficiency decreases because the "water-bridge" is destroyed. When the films are further annealed at 750 °C, the host band gap excitation suddenly disappears and the luminescence quenches. In our case the results for XPS confirm the presence of oxygen weakly adsorbed attributed to groups OH of water molecules that diminish significantly after annealing at 750 °C.

We think that the nature of defects centers in doped zirconia influence the optical properties of these films. For example, the excitation maximum (400 nm, 3.1 eV) appeared in our samples at a lower energy than the band gap reported for the zirconia matrix (~5.0 eV) [1,11]. The energy level of these defects is critical to the energy transfer process because if it is lower in energy than emitting state of the lanthanide ion, no sensitized luminescence can be observed. The energy level of the emitting state of samarium ( ${}^4G_{5/2}$ ) approximately 2.3 eV and this is the lower state than the energy level of defects of material host. It can, therefore, be proposed that the energy of zirconia defects is not below this value.

We propose a modified model based on the model given by Frindell et al. [31] and similar to the one proposed by other authors [32,33] for the energy transfer in this system, which involves relaxation from defect states on zirconia before the energy is transferred to the samarium ion. Fig. 8 shows: (1) an energy level diagram which shows light being absorbed by defects from  $ZrO_2$  host, (2) followed the non-radiative energy transfer process from  $ZrO_2$  defect to  $Sm^{3+}$  level and (3) the emission process of  $Sm^{3+}$  ion.

Another mechanism proposed is (1) the excitation energy at 400 nm produce absorption by light corresponding to the  ${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{K}_{11/2}$  transition of Sm<sup>3+</sup> ion, (2) and the electron state moves to the lowest excited energy level ( ${}^{4}\text{G}_{5/2}$ ) through relaxation, (3) and finally the emission due to transitions from one of the excited state  ${}^{4}\text{G}_{5/2}$  to the ground levels of  ${}^{6}\text{H}_{3/2}$  and  ${}^{6}\text{H}_{7/2}$  from Sm<sup>3+</sup>.

The emission spectra of divalent samarium ions, in the spectral range from 685 to 775 nm, that are mainly attributed to



**Fig. 8.** Proposed mechanism of photoluminescence process in  $ZrO_2$ :Sm thin films: (1) excitation process, (2) non-radiative energy transfer process and (3) emission process of  $Sm^{3+}$ .

intraconfigurational  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (*J*=0,1,2,3) [27,34]. We have not seen any emission signal in the range of 650–800 nm. Therefore, we assigned the observed emission signals mainly to Sm<sup>3+</sup> ions.

On the other hand, the percentage of Sm<sup>2+</sup> present in the samples only reached 32% and 20% for as-deposited and annealed films respectively, according to information provided by the XPS analysis, and that probably do not contribute to new lumines-cence emission.

Thus, the proposed mechanism for this case is the absorption of photons (400 nm) by the nature of defects centers of  $ZrO_2$  or by the absorption corresponding to the  ${}^{6}H_{5/2} \rightarrow {}^{4}K_{11/2}$  transition of  $Sm^{3+}$  ion, then the energy transfer from these levels to  ${}^{5}D_0$  level corresponding to  $Sm^{2+}$  ion, which essentially correspond to non-radiative transitions. (Fig. 8).

It has been reported that the incorporation of metal ions into ZrO<sub>2</sub> thin films produce impurity levels between the intrinsic bands, which subsequently generate new band gaps [35]. The effects that dopants have on the performance of ZrO<sub>2</sub> are mainly associated with modifying the microstructure as well as reducing the band gaps [35]. Depending on type and chemical states of metal ions and of intrinsic defects of the material host, the energy levels in ZrO<sub>2</sub> varied. Various types of defect states have been shown to play an important role in energy transfers between other materials such as the semiconductors III–V and Si and rare earth ions [31]. In this way, the efficiency of these emissions are strongly dependent on the characteristics of the material host, which determine a variety of parameters such as energy levels, energy transfer and non-radiative relaxation process and also by the active lanthanide ion concentration, aspects that deserve a subsequent study.

#### 4. Conclusions

In this work, we demonstrated that the solid state photoreactions of  $Zr(acac)_4$  and  $Sm(acac)_3$  complexes on silicon substrates lead to production of amorphous  $ZrO_2$ :Sm thin films. These films contain low concentrations of OH groups and show carbon contamination attributed to the organic residue from organic raw precursors, which can be eliminated or reduced by submitting the deposits to a heat treatment, according to the information we obtained from XPS. The surface characterization of these thin films was performed using AFM, revealing that as-deposited  $ZrO_2$ :Sm films have a rougher and irregular surface than thermally treated films. Photoluminescent properties have been studied in Zr:Sm films and the observed emission bands have been assigned to  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$  transitions of the Sm<sup>3+</sup> ions. A maximum PL intensity is observed at low Sm concentrations, about 10 mol%, and then the intensity falls with increasing concentration. A more detailed study is required to determine photoluminescent properties of the obtained films to further explore this energy transfer system and elucidate the mechanism for the apparent concentration quenching, as well as verify the proposed mechanism, which involves light absorption and emission by matrix defects.

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