Journal of Alloys and Compounds 509 (2011) 3160–3165

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Blue-yellow photoluminescence from $Ce^{3+} \rightarrow Dy^{3+}$ energy transfer in $HfO_2:Ce^{3+}:Dy^{3+}$ films deposited by ultrasonic spray pyrolysis

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ARTICLE INFO

Article history:
Received 20 July 2010
Received in revised form
25 November 2010
Accepted 25 November 2010
Available online 13 December 2010

PACS:
78.66.Nk
81.15.Rs
78.55.Hx

Keywords:
HfO_2
Ce^{3+}
Dy^{3+}
Films
Spray pyrolysis
Photoluminescence
Nonradiative energy transfer
Energy transfer efficiency

ABSTRACT

HfO_2 films codoped with Ce^{3+} and several concentrations of Dy^{3+} have been processed by the ultrasonic spray pyrolysis technique. Emissions from Dy^{3+} ions centred at 480 and 575 nm associated with the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively, have been observed upon UV excitation via a non-radiative energy transfer from Ce^{3+} to Dy^{3+} ions. Such energy transfer via an electric dipole–quadrupole interaction appears to be the most probable transfer mechanism. The efficiency of this transfer increases up to $86 \pm 3\%$ for the film with the highest Dy^{3+} content (1.9 ± 0.1 at.% as measured from EDS). The possibility of achieving the coordinates of ideal white light with increasing the concentration of dysprosium is demonstrated.

1. Introduction

Nowadays, the processing of white light emitting materials is of relevant interest to the optoelectronic industry. Several devices like plasma display panels [1], high brightness white light led technology based lighting systems, upconversion lasers and fiber amplifiers for optical communication [2] have been promoted using the photoluminescence properties of rare earth and transition metal ion-doped phosphors. The white light generation can be achieved by mixing of blue, green, yellow and red emissions from phosphors containing rare earth and transition metal ions [3]. Recently white light emission upon UV excitation was reported in $CeCl_3/TbCl_3/MnCl_2$ doped hafnium oxide films through an efficient sensitization of Tb^{3+} and Mn^{2+} ions by Ce^{3+} ions [4]. White light emission has been also attained in $Ca_3Y_2Si_3O_{12}$ [5] and Li_2CaGeO_4 [6] phosphors and oxyfluoride glass ceramics [7,8] codoped with Ce^{3+} and Dy^{3+} ions. In these materials white emission is originated from dysprosium through the mixture of its blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions, which are significantly enhanced through an efficient Dy^{3+} sensitization by Ce^{3+} ions excited at UV wavelengths. Ce^{3+} ions exhibit broad absorption bands in the UV, so that they can be easily excited by AlGaN/GaN-based LEDs [4]. The intense broad absorption band of Ce^{3+} ions is a consequence of their $4f \rightarrow 5d$ parity allowed electric dipole transitions, so that in co-doped materials such ions act as good sensitizers, transferring a part of their excitation energy to activator ions such as Tb^{3+} [4,9–11], Mn^{2+} [10–15] and Dy^{3+} [5–8,11].

The study of luminescent materials based on hafnium oxide (HfO_2) has attracted considerable attention, since it is a compound with a lot of possible technological applications because of its excellent physical and chemical properties, such as its high melting point

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doi:10.1016/j.jallcom.2010.11.203

and high chemical stability. Its high dielectric constant and insulating properties [16] allow its application as a dielectric material with relatively high refractive index and wide band gap, as well in the field of optical coatings and metal-oxide semiconductor devices of the next generation [17]. HfO_2 films have been used as sensors to detect CO gas [18], and sensing characteristics to propane of these films synthesized by the ultrasonic spray pyrolysis (USP) technique were recently studied [19]. HfO_2 can also be used for protective coatings due its thermal stability and hardness near to diamond in its tetragonal phase [20]. The large energy gap and low phonon frequencies of the HfO_2 [21] makes it appropriate as host material to incorporate rare earth ions, such as Ce^{3+} [22], Er^{3+}[23], Tb^{3+} [24] and Eu^{3+} [25], as well as Mn^{2+}[26] and Sm^{3+} [27] ions, which emit within their own energy levels.

According to all these perspectives above mentioned and the importance of finding efficient luminescent materials for the design of phosphors as white light sources based on hafnium oxide, in this investigation an exhaustive analysis of the blue-yellow photoluminescence of $HfO_2:Ce^{3+}:Dy^{3+}$ films synthesized by the UPS technique is presented. Moreover, this technique has demonstrated to be a very efficient way to synthesize luminescent films [13,15].

2. Experimental

Films of HfO_2 doped with only Dy^{3+} ions, and doubly doped with Ce^{3+} and Dy^{3+} ions were prepared using a low-cost process known as ultrasonic spray pyrolysis technique. In this technique, raw materials are mixed in a solvent, and then sprayed on a heated surface, where the constituents react to form a chemical compound. The detailed preparation of the spray solution is described elsewhere [10,13]. $HfO_2:Ce^{3+}$, $HfO_2:Dy^{3+}$ and $HfO_2:Ce^{3+}:Dy^{3+}$ films were deposited onto Corning 7059 glass slides used as substrates. The films were prepared using a spray solution of hafnium dichlororide oxide octahydrate (Aldrich Chemical Co, 99.99 + %) dissolved in deionised water (18 MΩ cm^{-1}). Cerium chloride heptahydrate and dysprosium chloride hexahydrate (Aldrich Chemical Co, 99.99 + %) were added as doping materials. The molar ratio of the spraying solution was 0.07. The substrate temperature during deposition was set at 300 °C. The carrier gas flow (filtered air) was 12 l min^{-1}. A 6 min deposition time was adjusted in order to obtain similar thicknesses for all the films studied. In the cerium or dysprosium singly doped films the $CeCl_3$ or $DyCl_3$ concentration in the spraying solution was 3 at.%. In the co-doped films the $CeCl_3$ concentration in the spraying solution was fixed at 3 at.%, varying only the $DyCl_3$ concentration (1.5, 3, 6 and 9 at.%). The crystalline structure of the films was analysed by X-ray diffractometry (XRD) using a 1.540 Å (Cu Kα) Siemens D5000 diffractometer, which was operated at 30 keV. The chemical composition of the films was measured using energy dispersive spectroscopy (EDS) with a Leica Cambridge Electron Microscope model Stereoscan 440 equipped with a beryllium window X-ray detector.

Photoluminescence and phosphorescence measurements were carried out using a Horiba Jobin–Yvon Fluorolog 3-22 spectrofluorometer.

The decay curves of the Ce^{3+} and Dy^{3+} emissions were recorded with 355 nm excitation of a pulsed YAG:Nd laser. A fiber optic probe was employed to collect the emission. The emitted light was dispersed by means of a half-meter monochromator equipped with a 150 lines/mm grating, and finally detected by a GaAs photomultiplier. The signal detected by the photomultiplier was then averaged and recorded by a digital oscilloscope. The very short decay times of the Ce^{3+} emission were obtained from the decay curves using a deconvolution procedure, which takes into account the shape and duration (about 8 ns) of the excitation pulse.

All the measurements were performed at room temperature.

3. Results and discussion

3.1. EDS and XRD measurements

The chemical composition of the studied films was determined by EDS. The values measured by EDS are listed in Table 1, which shows the relative atomic percentages of oxygen, chlorine, hafnium, cerium and dysprosium present in the films as a function of the $CeCl_3$ and $DyCl_3$ contents in the spraying solution. The studied films: $HfO_2:CeCl_3$(3 at.%), $HfO_2:DyCl_3$(3 at.%), $HfO_2:CeCl_3$(3 at.%):$DyCl_3$(1.5 at.%), $HfO_2:CeCl_3$(3 at.%):$DyCl_3$(3 at.%), $HfO_2:CeCl_3$(3 at.%):$DyCl_3$(6 at.%) and $HfO_2:CeCl_3$(3 at.%):$DyCl_3$ (9 at.%) will be referred to hereafter in terms of their Dy^{3+} concentration measured by EDS as HOC, HOD0.6, HOCD0.5, HOCD1.1, HOCD1.5 and HOCD1.9, respectively.

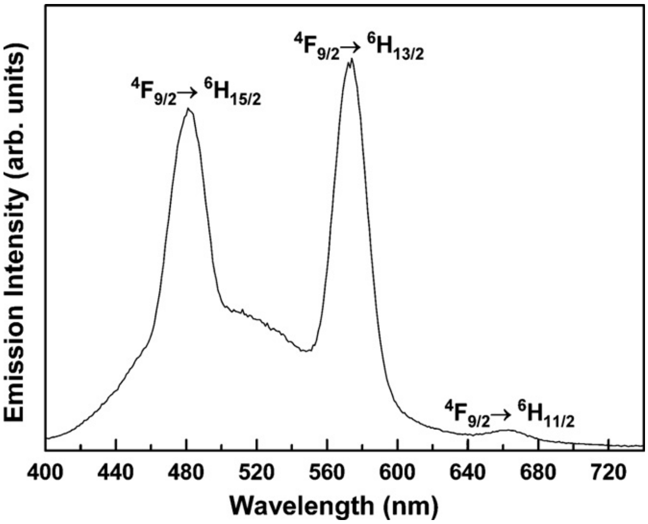

Fig. 1. Emission spectrum of the HOD0.6 film excited at 349 nm and recorded with a delay time of 0.01 ms.

X-ray diffraction patterns recorded for the films deposited at 300 °C exhibited a very broad band, and therefore they can be considered as predominantly amorphous.

An incorporation of chlorine ions might to be induced by the Ce^{3+} and/or Dy^{3+} ion substitution into Hf^{4+} cations in order to preserve the electrical neutrality in the trivalent ion doped HfO_2 film [22].

3.2. Photoluminescence of $HfO_2:Dy^{3+}$

The emission spectrum recorded for the HOD0.6 film excited at 349 nm, into the $^4M_{15/2},{}^6P_{7/2}$ absorption band of Dy^{3+}, exhibits several bands associated with transitions from the $^4F_{9/2}$ level to the $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ multiplets, which are centred at 480 nm (blue), 575 nm (yellow) and 663 nm (red), respectively (Fig. 1). This emission spectrum was recorded with a delay time of 0.01 ms, so that the intrinsic emission of the HfO_2 host is substantially eliminated. Major contribution to intense, bright, yellow emission comes from the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. No emissions from the $^4M_{15/2},{}^6P_{7/2}$ levels is observed, which suggests that Dy^{3+} ions depopulate nonradiatively from these levels to the $^4F_{9/2}$ emitting level. This level is separated from the next lower lying level ($^6F_{1/2}$) by about 7200 cm^{-1}, which makes the multiphonon relaxation negligible. It appears that only radiative transitions and relaxation by non-radiative energy transfer could be depopulating the $^4F_{9/2}$ level.

The excitation spectrum of the HOD0.6 film monitored at 575 nm, into the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission transition, consists of Dy^{3+} excitation bands corresponding to transitions from the $^6H_{15/2}(4f^9)$ ground state to higher energy states of the $4f^9$ configuration (Fig. 2), which are centred at 324 nm ($^6H_{15/2} \rightarrow {}^4L_{19/2}$), 350 nm ($^6H_{15/2} \rightarrow {}^4M_{15/2},{}^6P_{7/2}$), 364 nm ($^6H_{15/2} \rightarrow {}^4I_{11/2}$), 385 nm ($^6H_{15/2} \rightarrow {}^4K_{17/2},{}^4M_{19/2,21/2},{}^4I_{13/2},{}^4F_{7/2}$), 424 nm ($^6H_{15/2} \rightarrow {}^4G_{11/2}$), 450 nm ($^6H_{15/2} \rightarrow {}^4I_{15/2}$) and 467 nm ($^6H_{15/2} \rightarrow {}^4F_{9/2}$).

The decay curve of the ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) yellow emission of Dy^{3+} in the HOD0.6 film was recorded at 575 nm with Ce^{3+} excitation at 355 nm. It is non-exponential, so that its average decay time τ_{av} was obtained through the expression:

$$\tau_{av} = \frac{\int t\, I(t) \mathrm{d}t}{\int I(t) \mathrm{d}t} \tag{1}$$

where $I(t)$ is the emission intensity at time t. The τ_{av} value obtained for the Dy^{3+} yellow emission was 22 ± 1 μs, see Fig. 3.