Materials Chemistry and Physics 149-150 (2015) 34–42

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Synthesis and fabrication of Y_2O_3:Tb^{3+} and Y_2O_3:Eu^{3+} thin films for electroluminescent applications: Optical and structural characteristics

G. Alarcón-Flores [a, *], M. García-Hipólito [b], M. Aguilar-Frutis [a], S. Carmona-Téllez [c], R. Martinez-Martinez [e], M.P. Campos-Arias [a], E. Zaleta-Alejandre [f], C. Falcony [d]

[a] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, IPN, Legaría 694, Irrigación, C.P. 11500, México D.F., Mexico
[b] Instituto de Investigaciones en Materiales, UNAM, Apdo. Postal 70-360, Delegación Coyoacán, C.P. 04150, México D.F., Mexico
[c] Instituto de Física, UNAM, Coyoacán, C.P. 04150, México D.F., Mexico
[d] Departamento de Física, CINVESTAV, Apdo. Postal 14-470, Delegación Gustavo A. Madero, C.P. 07000, México D.F., Mexico
[e] Universidad Tecnológica de la Mixteca, Carretera Acatlima Km 2.5, Huajuapan de León Oaxaca, C.P. 69000, México, Mexico
[f] Universidad Autónoma del Estado de Hidalgo-Escuela Superior de Apan, Carretera Apan-Calpulalpan Km. 8, C.P. 43920, Apan, Hidalgo, Mexico

HIGHLIGHTS

- Terbium, europium and yttrium β diketonates have been synthesized.
- Luminescent thin films of Y_2O_3:Tb^{3+} and Y_2O_3:Eu^{3+} were obtained.
- Optical and structural characteristics of these thin films are presented.
- The films had a refractive index (1.81) and low average surface roughness (~62 Å).

ARTICLE INFO

Article history:
Received 28 March 2014
Received in revised form
29 July 2014
Accepted 22 September 2014
Available online 8 October 2014

Keywords:
Polycrystalline films
Spray pyrolysis
Photoluminescence
Cathodoluminescence

ABSTRACT

Terbium, europium and yttrium β diketonates have been synthesized from acetylacetone and inorganic metal salts and used as precursors for the deposition of Tb^{3+} or Eu^{3+} doped Y_2O_3 polycrystalline films by the ultrasonic spray pyrolysis technique. The films were deposited on c-Si substrates at temperatures in the 400–550 °C range. The optical and structural characterization of these films as a function of substrate temperature and Tb^{3+} and Eu^{3+} concentration was carried out by means of photoluminescence (PL), cathodoluminescence (CL), infrared (IR), ellipsometry, and UV–visible spectroscopy and atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and X ray diffraction (XRD) measurements respectively. The PL intensity from these films was found to depend on deposition temperature. Films deposited above 450 °C exhibited the characteristic PL peaks associated with either Tb^{3+} or Eu^{3+} intra electronic energy levels transitions. The most intense PL emission was found for dopant concentration of 10 at% for Tb^{3+} and at 8 at% for Eu^{3+} ions into precursor solution. In both cases concentration quenching of the PL emission was observed for concentrations above these values. The films had a refractive index (1.81), low average surface roughness (~62 Å) and a UV–Vis. transmission of the order of 90 %T.

1. Introduction

Metalorganic complexes such as metal β diketonates also called acetylacetonates are of great interest as precursors on chemically based deposition processes because of their excellent chemical and physical properties such as their high volatility and low decomposition temperature. The β diketonates have been used for metallic particle synthesis [1], as well as metalorganic vapor sources for deposition of metal oxide thin films [2,3]. The use of metalorganic precursors results in most film deposition methods in low surface roughness, better adhesion to the substrate, dense and relatively clean films, with better thermal stability and higher lateral resolution [4]. One of these methods is the ultrasonic spray pyrolysis (USP) technique that compared to others, chemical vapor deposition, sputtering deposition, pulsed laser deposition, for instance [5], has advantages like relatively low cost and industrial

* Corresponding author.
E-mail address: alar_fbeto@yahoo.com (G. Alarcón-Flores).

http://dx.doi.org/10.1016/j.matchemphys.2014.09.020
0254-0584/

scalability to large-area deposition of these films. On the other hand, wide band-gap metal oxides such as: Al_2O_3 (gap = 5.8 eV) [6], HfO_2 (gap = 5.4 eV) [7], Y_2O_3 (gap = 5.5 eV) [8] are often used as host lattice to incorporate optical activator ions, because of their high chemical and thermal stability, high resistance to cathode rays, among others. Yttria (Y_2O_3), in particular, is a cubic crystalline material with high melting temperature (2410 °C), large UV–Vis-IR transmittance (from 280 nm to 8 μm [9]), wide bandgap (5.5 eV) and high crystalline stability [8]. It has been used as host lattice for the manufacture of scintillators, lasers, optical fiber used in communications as well as nanocrystalline phosphors (luminescent properties of nanocrystalline phosphors might be quite different from their bulk counterpart and so their properties can be improved to expand their applications). Due to its high dielectric constant, yttria may be used in devices for flat panel displays applications (FED and PD), using electric fields much lower than those applied in the normal display devices [10]. Nanocrystalline phosphors generally have a higher efficiency which can be achieved with low voltages; therefore, they are ideal candidates for flat display devices [11]. In addition, application such as high definition televisions (HDTV) requires phosphors with small particle size, distribution size uniformity and high light intensity output without saturation [10]. Yttria films are in general, relevant for applications in field emission displays (FEDs) [12], Eu^{3+} doped Y_2O_3 is a red phosphor mainly used for FEDs. In this work the synthesis of β diketonates and their use as precursors to obtain Y_2O_3:Tb^{3+} and Y_2O_3:Eu^{3+} films by the USP method, is described. Additionally, the optical and structural characteristics of these resulting films as a function of deposition substrate temperature, and Tb^{3+} and Eu^{3+} concentration are presented as well.

2. Experimental

2.1. Synthesis of yttrium β diketonate [Y(acac)$_3$]

A solution of 3.83 g of $Y(NO)_3$ in 15 ml of bi-distilled water and 10 ml of methanol was placed in an ice bath, and then 3 ml of acetylacetone and 3 ml of propylene oxide were added. The pH was increased to 7 by adding, drop wise, concentrated NH_4OH, stirring for 45 min, until a light yellow precipitate was formed and then it was vacuum filtered. The powder obtained was then dried at 80 °C for four hours as described by W. Sheng-Yue, and T. E. Banach [13,14]. The synthetized compound was identified as yttrium β diketonate by means of proton nuclear magnetic resonance ^{1}H NMR (Bruker-Avance System 300 MHz instrument), Mass Spectrometry MS (Jeol AX505HA spectrophotometer), infrared spectroscopy IR (Perkin Elmer spectrum one). Its spectroscopic data and structural formula are:

^{1}H NMR (p.p.m): 1.74 (6H, s), 5.21 (1H, s).

MS (m/z): M^+ 386 (44.6%), 371 (3.1%) (M^+–15), 287 (100%) (M^+–99).

IR νmax (cm^{-1}) 1570 ν (C=O) and ν (C=C), 525 ν (C=C) and ν (C=O), 535 (MO).

2.2. Synthesis of terbium and europium β diketonates [Tb(acac)$_3$ and Eu(acac)$_3$]

Synthesis of terbium and europium β diketonates was carried out using terbium and europium chloride as raw precursor materials, respectively, following a similar procedure as the one used in the synthesis of yttrium β diketonate, described above. Spectroscopic data of IR and ^{1}H NMR of terbium and Europium β diketonate are similar to the yttrium β diketonate. However the MS were different because of the terbium and europium β diketonates molecular ion (M^+) are equal to 456 and 449 respectively. The molecular fragmentations are similar to yttrium β diketonate [4].

2.3. Synthesis of Y_2O_3:Tb^{3+} and Y_2O_3:Eu^{3+} thin films

To obtain Ln^{3+} doped films, yttrium β diketonate terbium and europium β diketonates, synthetized as described above, were used as precursors dissolved in N, N-dimethylformamide (DMF) [C_3H_7ON, JT Baker and purity of 99.96%]. For Y_2O_3:Tb^{3+} thin films, a 0.03 M solution of Y(acac)$_3$ was prepared (dissolving 1.16 g in 100 ml of DMF) and Tb(acac)$_3$ was added at different atomic percentages: 0, 2, 5, 10 and 15 at%. In the case of Y_2O_3:Eu^{3+} films, a solution 0.06 M of Y(acac)$_3$ was prepared by dissolving 2.32 g in 100 ml of DMF and Eu(acac)$_3$ was added at different atomic percentages: 0, 2, 5, 8, 10 and 12 at%. The films were deposited using the ultrasonic spray pyrolysis technique on crystalline silicon substrates of 1.5 × 1.5 cm at temperatures in the 400–550 °C range, for 15 min.

2.4. Optical and structural characterization

PL spectra were obtained with a SPEX Fluoro-Max-P spectrofluorimeter. CL measurements were performed in a stainless steel vacuum chamber with a cold cathode electron gun (Luminoscope, model ELM-2 MCA, RELION Co.). The diameter of the electron beam spot on the film was approximately 3 mm. The emitted light was collected by an optical fiber and fed into the SPEX Fluoro-Max-P spectrofluorimeter. The applied current of electron beam was 0.05 mA with an accelerating voltage in the range of 3–10 kV. All the luminescence measurements were performed at room temperature. Index of refraction and thickness of the deposited films were measured by ellipsometry (Gaertner LSE stokes ellipsometer), at 632 nm. A Siemens D-5000 X-ray diffraction system with CuK_α radiation (λ = 1.5406 Å) was used for the determination of the crystalline structure. Nanocrystalline sizes of films were estimated using the equation (1) (Scherrer's formula) [15].

$$T = \frac{0.9\lambda}{BCos\theta_B} \tag{1}$$

Where:

T = Crystallite size.
λ = Wavelength of CuK_α radiation.
B = Corrected half width of the diffraction peak.
θ_B = The Bragg's angle in radians.

Optical transmission spectra were obtained from films deposited on quartz substrates. An UV–vis spectrophotometer (Cary 50) in the 200–900 nm range was used for this purpose. Surface morphology of the films was determined by Atomic Force Microscope (Veeco CP research). The average roughness as well as the statistical analysis of the images is performed with the AFM Software. The average roughness is calculated using the following expression (Eq. (2)) over the analyzed area.

$$R_{ave} = \sum_{n=1}^{N} \frac{|z_n - \bar{z}|}{N} \tag{2}$$

Where:

R_{ave} = Average roughness.
$\bar{z}$ = mean z height.