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Application of photochemical method in the synthesis of Ga_2O_{3-X} thin films co-doped with terbium and europium

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ABSTRACT

Ga_2O_{3-X} thin films co-doped with terbium and europium have been prepared by photochemical metal-organic deposition. In this process, solutions containing Ga(III), Tb(III) and Eu(III) 2,2,6,6-tetramethyl-3,5-heptanedionate complexes were spin coated on silicon and quartz substrates. Upon irradiation, the photosensitive of the complexes precursors undergoes decomposition, leaving a gallium oxide amorphous thin film containing terbium and europium. The photo-reactivity of these films was monitored by UV vis and FT-IR spectroscopy. The obtained films were characterized by X-ray photoelectron spectroscopy and X-ray diffraction. Under UV light excitation (254 nm) the doped films (Ga_2O_{3-X}—Tb) show the characteristic emissions associated to $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions of terbium ion. However, these emissions decrease with the co-doped films (Ga_2O_{3-X}—Tb—Eu). Analysis suggests an energy transfer process among terbium and europium ions.

1. Introduction

The gallium oxide ceramic film has been extensively studied for its excellent opto-electronic and electrical properties. Gallium oxide is known as a nonstoichiometric n-type semiconductor with an adsorption edge of about 4.9 eV [1]. In general, gallium oxide exhibits different polymorphics phases such as rhombohedral (ɑ́), monoclinic (β), and cubic (ϒ and δ phases) [2]. Among these phases, β-Ga_2O_3 is a thermally and physically stable compound [3]. A large number of research works have been focused on the electrical properties of Ga_2O_3, especially for sensor and catalyst. However, only a small amount of these are devoted to the luminescence properties of Ga_2O_3, namely Ga_2O_3-based phosphors. It is known that the presence of structural defects, particularly the high concentration of oxygen vacancies is an efficient blue emitter when irradiated with UV light with energy higher than its band gap [4]. Recently, extensive attention has been paid to the properties of rare earth ion doped Ga_2O_3, the most frequency used europium and terbium ions as activators.
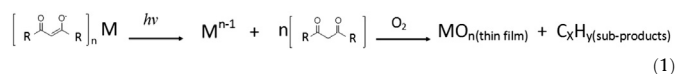
The composition, morphology, and size of these materials are important factors that dictate their characteristic properties. Therefore, the synthetic methods and precursors are very important in obtaining material of the desired properties. The photochemical synthesis of semiconductors and ceramics materials with light irradiation (both ultraviolet and visible) has been one of the most fruitful synthesis methods for obtaining new and unique structured inorganic compounds and materials [5]. Photochemical synthesis is different from other synthesis methods because it is selective. This selectively occurs because light absorption features of reactants determine their reaction products. Depending of photochemical system, the species generated by photon excitation or photolysis can by primary species for final products or precursors that react subsequently to form new species and then to final products. In this contribution, we report on the preparation by photochemical metal-organic deposition (PMOD) of thin films amorphous gallium oxide co-doped with terbium and europium and the study of their optical properties.

The method PMOD is a thin film deposition method that relies on the photodecomposition of the light-sensitive precursor complex in the solid state [6]. Thin amorphous films of the precursor are prepared by spin coating, and subsequently irradiated. The interaction of the precursor with the appropriate wavelength of light results in the loss of the organic ligands in the form of volatile by-products which are lost from the film. The metal remains on the

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surface and either gives rise to the formation of a metal film, or as in the case of concern to us here, reacts with oxygen in the air to produce an amorphous metal oxide film (Eq. (1)) [7,8].

$$\left[\begin{smallmatrix} & O & O \\ R & & R \end{smallmatrix} \right]_n M \xrightarrow{h\nu} M^{n-1} + n \left[\begin{smallmatrix} & O & O \\ R & & R \end{smallmatrix} \right] \xrightarrow{O_2} MO_{n(thin\ film)} + C_X H_{Y(sub\text{-}products)}$$

(1)

where: R = $-C(CH_3)$; M = Ga, Tb, Eu.

2. Experimental procedure

2.1. Preparation of amorphous thin films

The precursors Ga(III), Tb(III) and Eu(III) 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd) complexes were purchased from Aldrich Chemical Company. Thin films were prepared by the following procedure: A silicon chip was placed on a spin coater and rotated at a speed of 600 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 (500× magnification) and in some cases by SEM.

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

All photolysis experiments were done following the same procedure. The FT-IR spectrum of the starting film was first obtained. The chip was then placed under a UV-lamp setup equipped with two 254 nm 6 W tubes, in an air atmosphere. Progress of the reactions was monitored by determining the FT-IR spectra at different time intervals, following the decrease in the IR absorption of the complexes. After the FT-IR spectrum showed no evidence of the starting material, the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface, prior to analysis. In order to obtain films of a specific thickness, successive layers 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 900 °C for 2 h in a programmable Lindberg tube furnace.

2.3. Characterization of the thin films

The FT-IR spectra were obtained with 4 cm^{-1} resolution in a Jasco Serie 4100 FT-IR spectrophotometer. UV spectra were obtained with 1 nm resolution in a Perkin Elmer Model Lambda 25 UV–vis spectrophotometer. X-ray diffraction (XRD) patterns were obtained using a D8 Advance Bruker X-ray diffractometer, the X-ray source was Cu 40 kV/30 mA. X-relay 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 Kα radiation from its Al anode ($h\nu$ = 1486.6 eV). The pressure of the main spectrometer chamber during data acquisition was maintained at ca 10^{-7} Pa. The binding energy (BE) scale was calibrated by using the peak of adventitious carbon, setting it to 284.6 eV. The accuracy of the BE scale was ±0.1 eV.

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

complexes respectively. The substrates for deposition of films were quartz plates (2 × 2 cm^2) and p-type silicon (100) wafers (1 × 1 cm^2) obtained from wafer World Inc., Florida, USA.

Photoluminescense (PL) emission spectra measurements were carried out in an Ocean Optics Model QE65000-FL spectrometer with L type setup. Excitation was done with a PX-2 pulsed Xenon lamp (220–750 nm), and the UV light passed through a monochromator set to 254 nm. The measurements were done at room temperature.

3. Results and discussion

3.1. Photochemistry of the precursor complexes

The photo-reactivity in solution of gallium(III)-2,2,6,6-tetramethyl-3,5-heptanedionate [Ga(tmhd)$_3$] and gallium(III)-acetylacetonate [Ga(acac)$_3$] complexes has been extensively studied in our group [9]. It is known that these complexes absorb strongly at readily accessible parts of the UV spectrum (200–400 nm) and the irradiation of these complexes with UV light (254 nm) leads to the photo-reduction and the photo-fragmentation of these complexes. In this case no reports can be found in the literature concerning Tb(tmhd)$_3$ and Eu(tmhd)$_3$ complexes. We therefore carried out experiments to evaluate the photosensitivity of these complexes in solution as a film. When dichloromethane solutions of these complexes were photolyzed with 254 nm UV light, a gradual decrease in the absorption bands of the Tb(tmhd)$_3$ and Eu(tmhd)$_3$ complexes could be observed after 192 and 225 min of irradiation, respectively. Fig. 1 shows the profile of photo-reaction of both complexes, obtained by determining the UV spectra of samples taken at different time intervals. Both cases exhibit a single band at 276 nm, attributable to ligand transition of a $\pi-\pi^*$ electronic transition similar to the complex. These results demonstrate that these complexes are highly photo-reactive in solution; the excitation at 254 nm light generates a series of intermediaries or sub-products that facilitate the photochemical reduction of metal species present in the complexes.

In order to investigate the solid-state photochemistry, thin films of Tb(tmhd)$_3$ and Eu(tmhd)$_3$ were prepared by spin-coating dichloromethane solutions of the complexes on Si(100) chips. The FT-IR spectra were similar to those obtained for crystalline samples.

Irradiation of thin films (~400 nm thickness) of both complexes under air atmosphere, led to the disappearance of the absorptions associated with the ligand, as shown by FT-IR monitoring of the reaction (Figs. 2 and 3). During the photoreaction the films decreased in thickness to approximately 50–60% of its original thickness. At the end of the photolysis there are no detectable absorptions in the infrared spectrum. These results suggest that the diketonate groups on the precursors are photodissociated on the surface forming volatile products which are readily desorbed from the surface.

FT-IR spectroscopy was also used to characterize the photo-deposited films. Fig. 2a shows the FT-IR spectrum of a 400 nm films deposited on a polished Si wafer from Ga(tmhd)$_3$ precursor. These films show two peaks at 1578 and 1528 cm^{-1}. These bands are attributed to the stretching vibration of carbonyl groups of β-diketonate complexes. After 24 h of photolysis, these bands decreased in intensity, indicating that the β-diketonate ligands are lost upon photolysis (Fig. 2b). Careful examination of the 1100–400 cm^{-1} region in the FT-IR of the films annealed at 900 °C for 2 h (Fig. 2c) showed the growth of two bands centered between 1050 and 500 cm^{-1}. These absorptions were assigned to ν Ga–O and ν Ga–O–Ga vibrations, respectively. These results are in agreement with values reported by other authors [10].
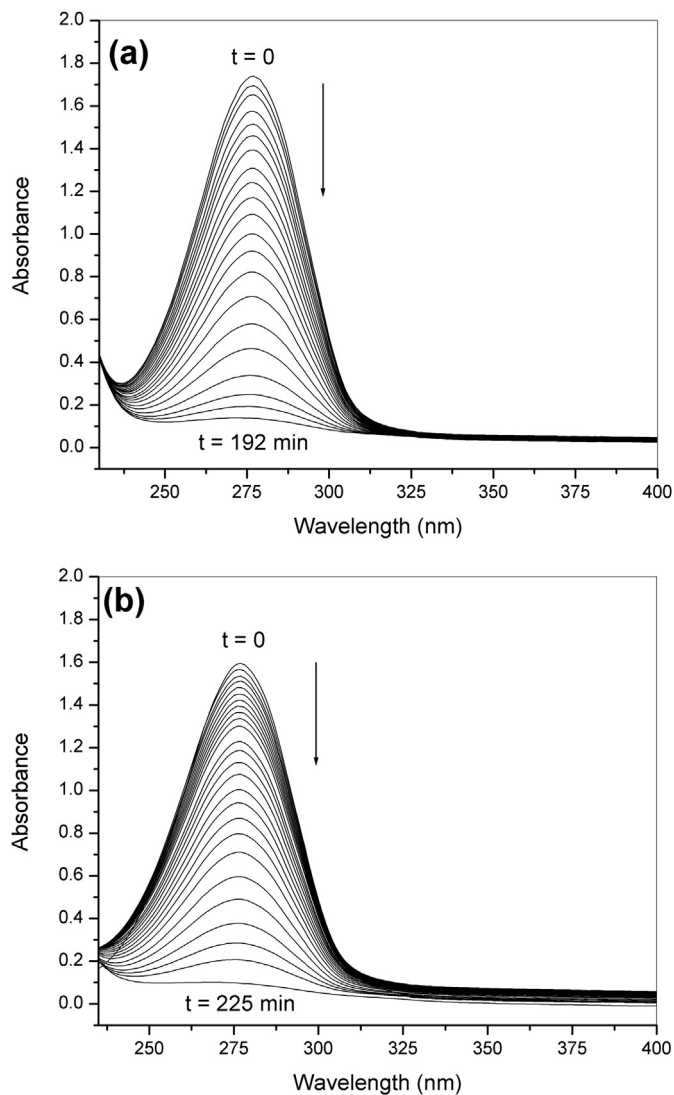
Fig. 1. Changes in the UV spectrum of a solution of (a) Tb(tmhd)$_3$ (4.51 × 10^{-5} M in CH$_2$Cl$_2$) upon 192 min irradiation and (b) Eu(tmhd)$_3$ (4.56 × 10^{-5} M in CH$_2$Cl$_2$) upon 225 min irradiation with 254 nm light.
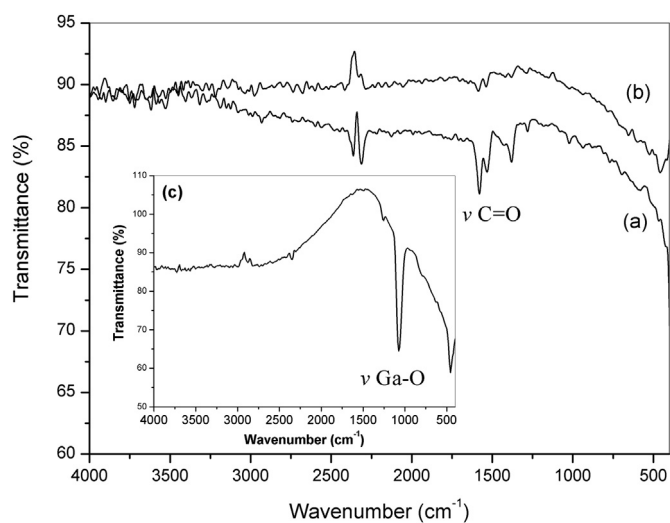

Fig. 2. FT-IR spectra of (a) a film of Ga(tmhd)$_3$ precursor complex on Si(100) wafer (b) a film of gallium oxide as-deposited upon 24 h irradiation with 254 nm light (c) a film of gallium oxide annealed in air at 900 °C for 2 h.
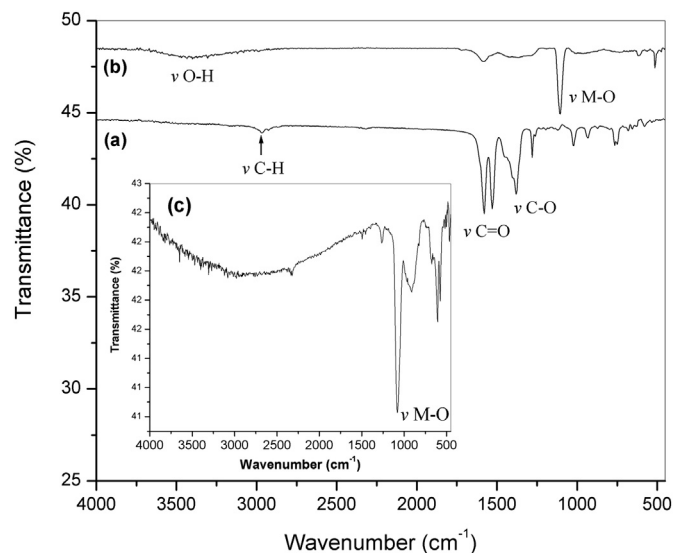

Fig. 3. FT-IR spectra of (a) a film of Ga(tmhd)$_3$ with 10 mol % proportions of Tb(tmhd)$_3$ and Eu(tmhd)$_3$ complexes on Si(100) wafer (b) a film of gallium oxide co-doped as-deposited upon 24 h irradiation with 254 nm light (c) a film of gallium oxide co-doped with Tb and Eu annealed in air at 900 °C for 2 h.

For the photo-deposition of thin films gallium oxide co-doped with terbium and europium, solutions of Ga(tmhd)$_3$ with 10 mol % proportions of Tb(tmhd)$_3$ and with different proportions of the Eu(tmhd)$_3$ complexes (10, 5 and 1 mol %) were spin-coated on Si(100) or quartz substrates and the thin films irradiated for 24 h. The irradiation of these films co-doped, led to a decrease of the absorptions associated with the ligands at 2968 cm^{-1} assigned to vibration modes C—H, at 1576 and 1525 cm^{-1} corresponding to C═O groups and at 1365 cm^{-1} associated to C—O bonding, as show by FT-IR monitoring of the reaction (Fig. 3a). At the end of the photolysis, after a 24 h irradiation period, minimum absorptions observed in the infrared spectrum, except by one at 3408 cm^{-1} attributed to O—H stretching vibration which is due to the presence of adsorbed moisture and the appearance of new band located at 1105 cm^{-1} probably to the vibration modes metal—oxygen (Fig 3b). The FT-IR spectra of gallium oxide co-doped films with Tb and Eu calcined at 900 °C for 2 h is presented in the inset of Fig. 3 reveals some signals at 1080 and 914 cm^{-1} assigned to vibrations metal—oxygen and other signals located at 609 and 577 cm^{-1} corresponding to vibrations M—O—M. The number and intensity of these bands revealed the formation of oxides of the lanthanide elements (Tb or Eu) because these elements are prone to oxidation under these conditions.

3.2. Characterization of the thin films

The elemental composition of the as-deposited Gallium oxide co-doped thin films was analyzed by XPS, in order to study the chemical nature of the deposited surface. Fig. 4 shows the wide scan XPS spectrum, in the binding energy (BE) range 0—1300 eV. The surface analysis revealed the presence of Ga, O, Tb, Eu and C. The carbon amount was drastically reduced after mild Ar$^+$ erosion, thus indicating that the carbon is mainly due to atmospheric exposure and to the organic residue from precursor complexes.

In Fig. 5 shows high resolution spectra of Ga 2p$_{3/2}$ located at 1117.6 eV corresponding to Ga—O bonding and that is consistent with other values (1117.0—1117.9 eV) reported in the Ga$_2$O$_3$ formation [11—14]. The O 1s spectra (inset Fig. 5) shows a broad peak has been fitted to two overlapped peaks with binding energy at
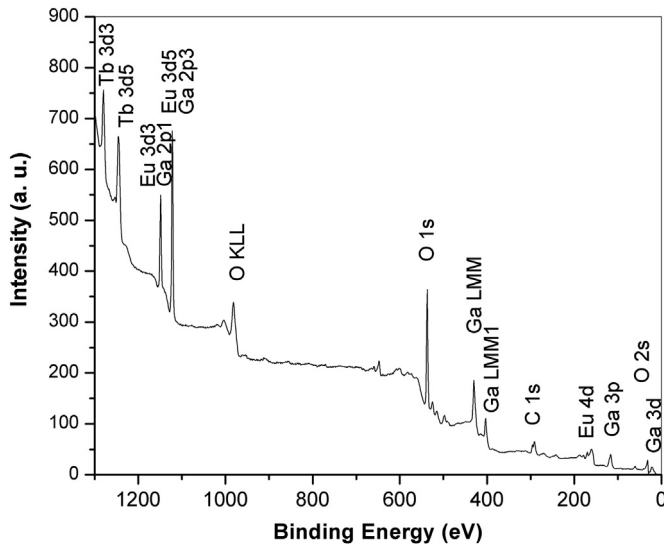
Fig. 4. XPS survey spectrum of an as-deposited Ga_2O_{3-X}–Tb–Eu thin films prepared by UV irradiation at 254 nm.

529.4 and 531.6, implying the existence of O in two kinds of chemical states. The binding energy at 529.4 (designated as O_L) is attributed to the contribution of the lattice oxygen. The binding energy at 531.6 eV (designated as O_H) arises from the chemisorbed oxygen species or corresponds to oxygen in water molecules bound in the film structure or adsorbed on the sample surface [15]. The relative contribution of these components to the spectrum, as determined by fitting, is 94% (O_H) and 6.0% (O_L), respectively. Other studies [16] have attributed the O 1s peak between 530.7 and 531.6 eV to oxygen in non-stoichiometric oxides in the surface region. However, some of these deficiencies of oxygen are compensated in the sub-surface of various metal oxides by the ionization of oxygen species described as O^- and that have a higher covalence of the metal–oxygen bonds [15].

For terbium, the most intense core level is Tb 3d at high binding energy between 1230 and 1290 eV (see Fig. 4). It has been reported [17] that usually the $3d_{5/2}$ and $3d_{3/2}$ binding energy of Tb^{3+} ions appears at 1241 and 1275 eV, respectively, while the binding energy peaks for the Tb^{4+} appears at 1244 and 1278, respectively. However the Tb 3d core level analysis is very difficult to distinguish
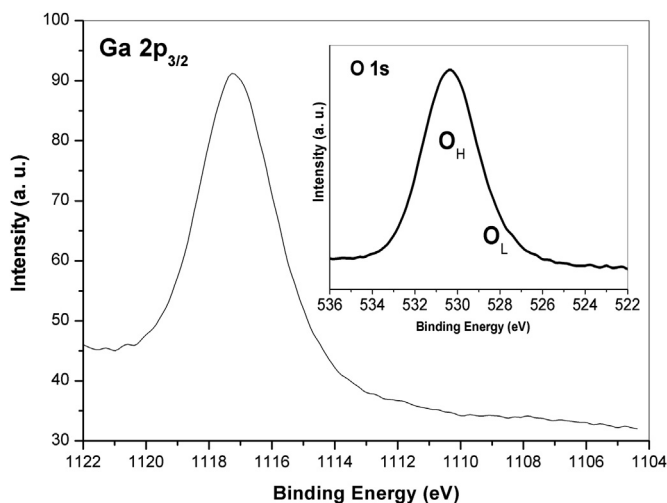

Fig. 5. XPS photoelectron peaks of Ga $2p_{3/2}$ for representative as-deposited Ga_2O_{3-X}/Tb/Eu thin films. In figure inset XPS spectra of O 1s peak in the 536–522 eV region.

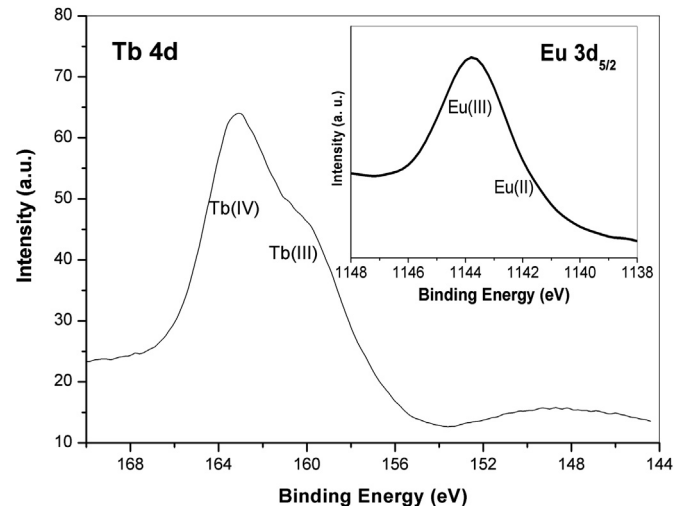**Fig. 6.** X-ray photoelectron spectrum of Tb 4d level for representative as-deposited Ga_2O_{3-X}/Tb/Eu thin films. In figure inset XPS spectra of Eu $3d_{5/2}$ peak in the same sample. In both spectra are shown the coexistence of two oxidation sates.

accurately the chemical states of terbium with the commercial X-ray Al K_α source (1486.6 eV) due to the very low kinetic energies of the photoemitted electrons [18–20]. Therefore, next most intense core level (Tb 4d) is used for present analysis. Fig. 6 shows the Tb 4d core level XPS spectra of the as-deposited films reveals a broad peak can be fitted in two main sub-peaks at 163.8 and 160.8 eV associated with the presence of at least two oxidation states Tb^{4+} (42%) and Tb^{3+} (58%) respectively. These values are higher than those reported in other studies in which Tb 4d XPS pattern, Tb^{3+} gives a signal below 150 eV whereas Tb^{4+} shows features above 150 eV ($\sim$155 eV) [18–21].

The Eu 3d region (Fig. 4) showed two peaks in the 1110–1170 eV range. These two peaks are due to multiple splitting of the spin-orbit $J = 5/2$ and 3/2 components at energy levels of 1136–1134 and 1167–1164 eV respectively, which are assigned to the Eu(III) species. On the other hand, If these two components appears at 1126–1125 and 1157–1155 eV respectively, are attributed to a Eu(II) configuration [22–25]. With respect to the Eu $3d_{5/2}$ peak position shows two well resolved peaks centered at 1144.6 and 1142.3 eV binding energy (inset Fig 6). The higher binding energy peak is related to the (3+) oxidation state and the lower binding energy peak corresponds to a (2+) oxidation state [26], the contribution of these two components is 84% (Eu^{3+}) and 16% (Eu^{2+}), respectively.

The phase composition of the as-deposited films and the effect of the thermal treatment on the film crystallinity, was examined by XRD technique. The XRD pattern of a Ga_2O_3–Tb–Eu film as-deposited and annealed at 900 °C for 2 h is shown in Fig. 7.

The peaks related to Ga_2O_{3-X} co-doped for both films cannot be observed, except for the reflection from Si (100) substrate located at $2\theta = 33.2°$. However, for the calcined sample shows a peak at $2\theta = 15.9°$ index as (100) plane consistent with the presence of β-Ga_2O_3 (JCPDS No 11-370) [27]. Thus, our calcined samples may consist in a mixture of amorphous phase and other small fraction of a crystalline phase. Our studies [9,28] have revealed that the use of β-diketonate complexes as precursors in this methodology often result in amorphous deposits.

3.3. Optical properties of the films

Fig. 8 shows the optical transmission spectra of the doped Ga_2O_{3-X}/Tb and co-doped Ga_2O_{3-X}/Tb/Eu films photo-deposited. The samples thickness is about 300–400 nm. As shown in Fig. 8,

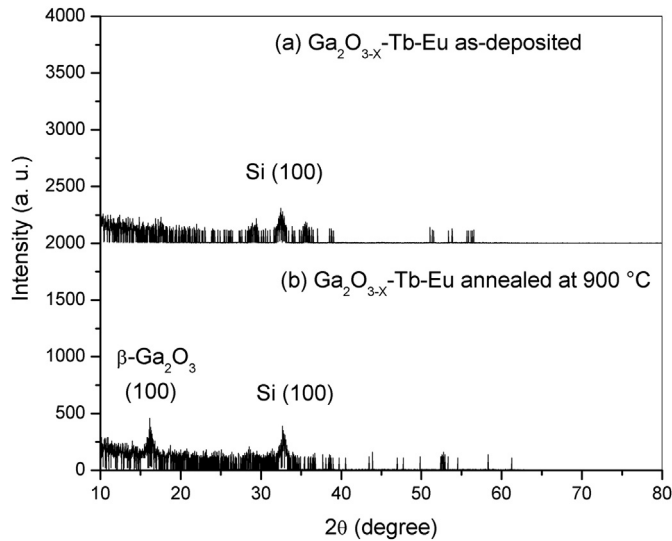**Fig. 7.** XRD pattern of a photodeposited Ga_2O_{3-X}–Tb–Eu film: (a) as-deposited and (b) annealed in air at 900 °C for 2 h.

the transmittance spectra of the doped films have a high transmittance exceeding 85% from the 260 nm. The transmittance of the co-doped films slightly decrease, this indicates that the co-dopant is activated, increasing the number of defects on the surface of film.

The optical band gaps of all films are estimated by extrapolating the linear portion of the square of absorption coefficient against photon energy using the Eq. (2) where B is a constant.

$$(\alpha h\nu)^2 = B(h\nu - E_g) \qquad (2)$$

The inset of Fig. 8 shows the plots of $(\alpha h\nu)^2$ versus photon energy of the samples. The optical band gap of the Ga_2O_{3-X} doped and co-doped films varies between 5.6 and 5.4 eV, respectively. These decrease of band gap after co-doping is probably caused by an impurity energy level of Eu in the Ga_2O_{3-X}/Tb films.

3.4. Luminescence properties of the samples

Fig. 9(a) shows the emission spectra of gallium oxide doped and co-doped thin films under excitation at 254 nm. The emission
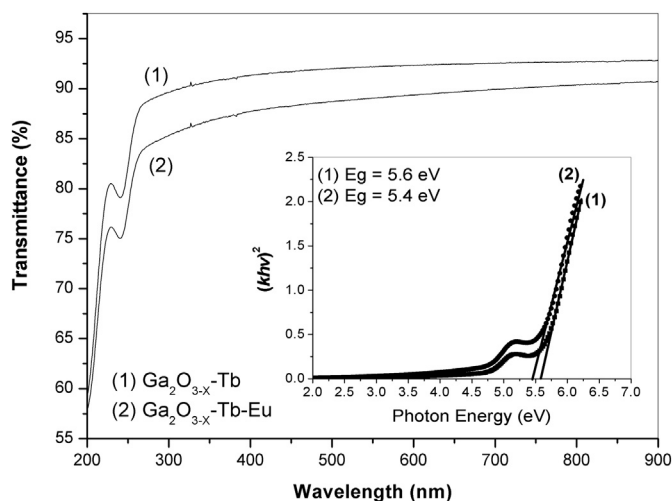

Fig. 8. Transmittance spectra of photo-deposited thin films of: (1) Ga_2O_{3-X}/Tb and (2) Ga_2O_{3-X}/Tb/Eu. Inset: square of absorption coefficient as a function of photon energy.
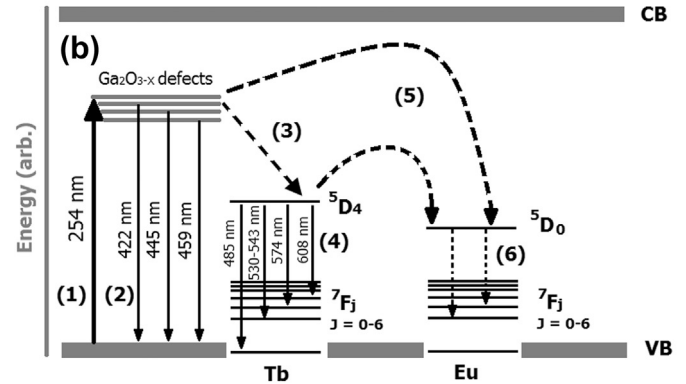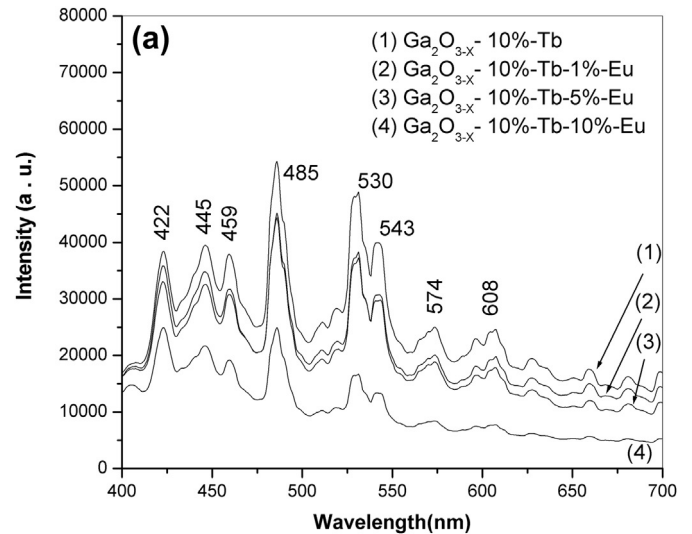

Fig. 9. (a) The photo-luminescence spectrum of the doped and co-doped samples and (b) schematic illustration of possible mechanism of energy transfer from Ga_2O_{3-X} host to lanthanide elements dopants.

spectrum of the Ga_2O_{3-X}/Tb films exhibits a set of characteristics optical transitions $^5D_4 \rightarrow {}^7F_J$ of Tb^{3+} ion, which are situated at about 485, 530, 543, 574 and 608 nm, due to $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions [29]. Broad overlapping lines are observed instead of narrow lines due to the stark splitting. This shape of the spectra is characteristic for amorphous materials and glasses. The bands at 442, 445 and 459 nm is due to host material. These signals are attributed due to oxygen vacancies that induce the donor levels and the recombination of an electron on a donor with a hole on an acceptor formed by a gallium vacancy or a gallium–oxygen vacancy pair [30]. On the other hand, for the co-doped films (Ga_2O_{3-X}/Tb/Eu) it is possible to observe the same spectral pattern of the signals but their intensities decreased significantly. An interesting phenomenon coexists in which with an increase in concentration of europium, the intensities of terbium decrease. There are no signals that can be assigned to europium ion. Therefore, we propose an energy transfer process from terbium to europium, as we have reported in other studies using other activators [9,28]. Fig. 9(b) illustrates a possible mechanism for the energy transfer from defects centers of gallium oxide host to lanthanide elements which consist in an (1) absorption of light (254 nm) and excitation from valence band to defects centers of gallium oxide located near the conduction band, induced by oxygen vacancies; (2) some portion of this energy is translated into a radiative energy process of the material host; (3) the other portion is translated into a non-radiative energy transfer process from defects centers to $^5D_4$ excited state of Tb ion;

(4) followed by a radiative energy process from the excited state $^5D_4$ to the ground levels of $^7F_J (J = 6, 5, 4, 3)$ of Tb ion; and (5) energy transfer process takes place from $^5D_4$ state of Tb to the acceptor energy states of Eu ion or from defects levels of gallium oxide host to some acceptor level of Eu ion (in this case there is shown only the $^5D_0$ level) (6) which decay non-radiatively from $^5D_0$ to various lower levels of $^7F_J (J = 0–6)$ of Eu ion. As a result the co-doping of Eu(III) leads to the increase of the energy transfer process and the non-radiative transitions leading to the decrease in emission intensity of the films.

However, a study of decay times or decay processes of photoluminescence is necessary to confirm the proposed energy transfer mechanism. One purpose of this preliminary study was to determine the influence of europium spectral in the $Ga_2O_{3-X}/$Tb thin films, as reported in other articles, co-emissions of both activators [31,32]. The different luminescence properties of metal oxides depend on the crystalline structure adopts the material finally, and the different bond lengths between the activators and the oxygen in the matrix. The charge transfer process depend on the bonds lengths between activators and host material and on the coordination environment around of the activators. With increasing bond length, the bands shifts to lower energies and the luminescence intensity decreases. Thus, controlling the crystalline structure of the material in the deposition process can accurately determine their luminescent properties; hence, it is possible to obtain co-emissions of both lanthanide elements. However, given the amorphous nature of our thin films, the controls of these properties are difficult to achieve and the emission intensities decrease in the presence of both activators. Our studies indicate that the presence of a second activator leads to an increase of surface defects that will be involved and the non-radiative relaxation rate will increase. Moreover, the decrease observed in emission intensity with the increase of co-dopant concentration is probably due to a concentration-quenching effect.

4. Conclusions

Ga_2O_{3-X} thin films co-doped with terbium and europium were prepared by photochemical metal–organic deposition. X-ray photoelectron spectroscopy (XPS) results showed that the resulting films are non-stoichiometric and the structural characterization of the samples using XRD revealed the amorphous structure of the films. These characteristics of the films strongly determine the non-crystalline nature and their photoluminescent properties. The Ga_2O_{3-X} doped with Tb films showed emissions attributed to $^5D_4 \rightarrow {}^7F_J (J = 6, 5, 4, 3)$ transitions of Tb ion. For the co-doped films (Ga_2O_{3-X}/Tb/Eu) it was not possible to observe co-emissions of both activators, only a decrease of the emission intensities of Tb ion. These results suggest a possible energy transfer from terbium to europium that produces the non-radiative energy transfer process. A clear understanding of the structure of the systems is crucial for the development of future optical materials.

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