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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 (ά), 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 byproducts which are lost from the film. The metal remains on the

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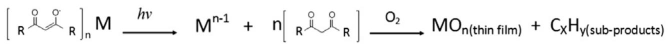
surface and either gives rise to the formation of a metal film, or as in the case of concern to us here, reacts with oxygen in the air to produce an amorphous metal oxide film (Eq. (1)) [7,8].



(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 ($\lambda = 254$ 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 photodeposited 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].