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Transparent and low surface roughness HfO_2: Tb^{3+}, Eu^{3+} luminescent thin films deposited by USP technique

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Abstract

In this work, the optical and morphological properties of HfO_2: Tb^{3+}, Eu^{3+} thin films deposited by the Ultrasonic Spray Pyrolysis technique from metal-organic precursors are reported. The films showed optical average transmittance values in the visible region greater than 90%, with surface roughness lower than 3.9 nm. The films deposited at 500 °C showed the lowest average roughness with a value of 0.9 nm, and the smallest thickness was 35 nm for sample deposited at 500 °C during 45 s. XRD measurements indicate a hafnium oxide monoclinic phase for films deposited at substrate temperatures higher than 500 °C. All films deposited showed the luminescent emissions (PL and CL) characteristic of Tb^{3+} and Eu^{3+} ions. A luminescence concentration quenching was observed for both Tb^{3+} and Eu^{3+} ions. The HfO_2: Tb^{3+} (5 at%) and HfO_2: Eu^{3+} (10 at%) films deposited at 500 °C, showed the highest PL and CL emission intensity. Quantum Efficiency measurements (up to about 35%) were measured for these films which have a refractive index between 1.97 and 2.04 and band gap of 5.4 eV. The chemical composition of the films as measured by XPS is also reported. In addition, decay time measurements were performed on some HfO_2: Tb^{3+}, Eu^{3+} samples.

Keywords: Thin films; Transparency; Low roughness; Luminescence; Spray pyrolysis

1. Introduction

The increasing use of electronic devices with displays, demand the research of luminescent materials that can be used as raw materials for the manufacture of luminescent devices with some advantage such as higher brightness and small size. A luminescent material for such applications should have high transmittance in the visible region, wide bandgap (>3 eV) to avoid re-absorption of the visible radiation emitted, low roughness (to avoid dielectric breakdown), high chemical and thermal stability, low thickness and high luminescent emission [1]. There are several flat panels of technological importance, including the plasma display panels (PDPs), field emission displays (FED) and the thin film electroluminescence displays (ELD) [2–4]. In recent years there has been a lot of interest in the progress of film-type phosphors for flat panel displays such as MISIM (Metal–Insulator–Semiconductor–Insulator–Metal) electroluminescent structures. The typical values of the refractive index for the luminescent materials used in an electroluminescent device are approximately among 1.5 and 2.5. Phosphors such as ZnS: Mn which is very efficient with a bandgap of 3.7 eV has been used for this type of devices. Also, phosphors with bandgaps higher than 5 eV have been used with good results as Y_2O_3:Eu^{3+} [5] and Y_2O_2S: Tb^{3+} [6]. In some cases, it is necessary to incorporate electron

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donor films to improve their efficiency, such as in the case of Y_2O_3:Eu^{3+} used together with a ZnS film [7]. Film-type luminescent materials have some advantages such as high image resolution, thermal stability, long-term stability and better adhesion to the substrate compared to powder-type phosphors [1].

Metallic oxides are very versatile materials that play an important role in the phosphors technology. Among them, the hafnium oxide (HfO_2) is a material that has been widely used in optical applications, when synthesized as thin film has a relatively high refractive index (~2.1) and a wide band gap (~5.7 eV) [8] which makes it transparent over a wide spectral range from ultraviolet to the mid-infrared [9–11]. Recently, this oxide has been used as host lattice for rare earth and transition element ions to produce phosphors. HfO_2 films activated with some trivalent rare earth ions possess remarkable luminescence characteristics [12–15]. Several techniques have been used to deposit HfO_2 thin films, including Metal-Organic Chemical Vapor Deposition (MOCVD), High Pressure Reactive Sputtering (HPRS), Atomic Layer Deposition (ALD), Assisted Ion Beam Deposition, Sputtering and Sol–Gel [16–21]. The Ultrasonic Spray Pyrolysis technique (USP) has proved to be a simple, efficient and inexpensive method that does not require vacuum systems and allows deposition of homogeneous and transparent films with low roughness and small thickness when metal-organic reagents are used as precursors. In addition, this technique is simple for the making of large area film phosphors [21]. Hafnium oxide films deposited by USP using hafnium chlorides as precursors have been studied as host material for rare-earth activators, such as Eu [12], Tb [13] and Ce [22]. The films deposited from these precursors are thick, rough and opaque; consequently they are inadequate for the applications above mentioned (flat panel displays). On the other hand, the deposition of hafnium oxide films by USP, using metal-organic precursors, results in films with excellent flatness, transparency and density characteristics. In general, rough films, induce localized dielectric breakdown because they often create weak spots in multilayered devices (MISIM for example), especially when the layers are very thin. Also, film transparency is important because a reduction of absorption and scattering of the emitted light by the luminescent material produces an improvement of the external efficiency of the luminescent devices [23].

In this contribution, the morphological and optical qualities of Tb^{3+} and Eu^{3+}-doped hafnium oxide thin films, deposited by USP process using acetylacetonates as precursors and synthesized at temperatures up to 550 °C, are reported. Specially, the dependence of the PL and the CL emission intensities from these – transparent and low roughness – thin films as a function of doping concentration (Tb and Eu) and deposition temperature is reported.

2. Experimental details

The un-doped and Tb^{3+}, Eu^{3+}-doped HfO_2 thin films were deposited by USP technique, Fig. 1 shows a schematic drawing of the deposition system used for this research, which

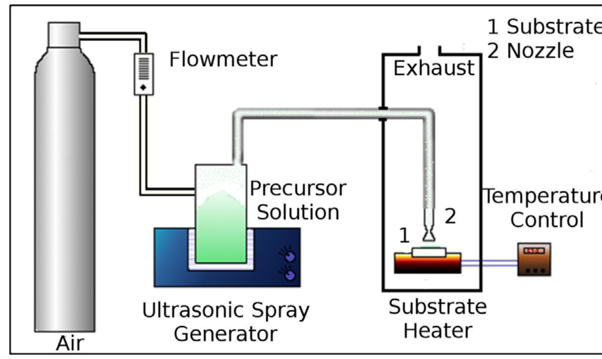

Fig. 1. Schematic diagram of the ultrasonic spray pyrolysis system for deposition of the HfO_2:Tb, Eu, thin films.

is capable to deposit films on substrate up to 20 × 20 cm. This system consists of an ultrasonic spray generator to produce the aerosol from the proper solution that is transported by a carrier gas onto the substrate placed on a tin bath whose temperature is electronically controlled. It should be mentioned that the ultrasonic spray pyrolysis technique has been reported to be used for film deposition on large areas [21]. The films, in this case, were deposited on glass, quartz and silicon single crystal (100) substrates of approximately 2 by 2 cm, these substrates were washed according to the protocol reported by Acosta [24]. The starting reagents were Hf acetylacetonate (Hf acac) dissolved in dimethylformamide (DMF) at a molar concentration of 0.035 M and Tb and Eu acetylacetonates at molar concentrations of 0, 2.5, 5.0, 7.5 and 10 at% (at%) with respect to hafnium content. The films were deposited at substrate temperatures (T_s) of 400, 450, 500 and 550 °C, with a carrier gas flow of 10 l/min (filtered air). The deposition times were 45, 90, 180 and 300 s (s). No further thermal treatments were given to the as deposited samples because there was a concern to keep the energy budget employed in the processing of these materials as low as possible. The crystalline structure of the deposited films was measured by X-Ray Diffraction (XRD) using a Bruker D8-Advance diffractometer with a Cu k_α radiation (1.5406 Å). The chemical elements present in the HfO_2: Tb^{3+}, Eu^{3+} thin films were determined by X-ray photoelectron spectroscopy (XPS). In order to corroborate the presence and incorporation of Tb^{3+} and Eu^{3+} in the films X-ray photoelectron spectra were collected using aK-Alpha spectrometer from Thermo Scientific with monochromatic AlKa (1486 eV) radiation with an energy resolution of 0.5 eV. Survey and high resolution spectra were collected at 160 and 60 eV pass energy analyzer respectively, using an X-ray spot size of 400 μm^2. The surface of the samples was ion beam etching (IBE) cleaned with Ar at ion acceleration potential of 500 eV for 15 s in order to remove the major part of adsorbed species onto the surface prior to XPS analysis. The recorded spectra were fitted through a Gaussian–Lorentzian combination based on an Offset Shirley background type. The surface morphology and roughness of the films was analyzed through Auto Probe CP Atomic Force Microscope (AFM) from Park Scientific Instruments in a contact mode (these measurements were carried out in samples deposited on silicon