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Tuning Eu^{3+} emission in europium sesquioxide films by changing the crystalline phase

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ABSTRACT

We report the growth of europium sesquioxide (Eu_2O_3) thin films by pulsed laser deposition (PLD) in vacuum at room temperature from a pure Eu_2O_3 ceramic bulk target. The films were deposited in different configurations formed by adding capping and/or buffer layers of amorphous aluminum oxide (a-Al_2O_3). The optical properties, refractive index and extinction coefficient of the as deposited Eu_2O_3 layers were obtained. X-ray photoelectron spectroscopy (XPS) measurements were done to assess its chemical composition. Post-deposition annealing was performed at 500 °C and 850 °C in air in order to achieve the formation of crystalline films and to accomplish photoluminescence emission. According to the analysis of X-ray diffraction (XRD) spectra, cubic and monoclinic phases were formed. It is found that the relative amount of the phases is related to the different film configurations, showing that the control over the crystallization phase can be realized by adequately designing the structures. All the films showed photoluminescence emission peaks (under excitation at 355 nm) that are attributed to the intra 4f-transitions of Eu^{3+} ions. The emission spectral shape depends on the crystalline phase of the Eu_2O_3 layer. Specifically, changes in the hypersensitive $^5D_0 \rightarrow {}^7F_2$ emission confirm the strong influence of the crystal field effect on the Eu^{3+} energy levels.

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1. Introduction

Europium oxide films have received large attention for their use in the fields of microelectronics, spintronics, lighting, magnetism and photonics, among others. However, applications remain a challenge due to the difficulties for the fabrication of high quality crystalline pure europium oxide thin films. Europium oxide (EuO_x) films growth on Si substrates has been usually obtained by two methods. In the first one, deposition is performed starting from a pure metallic europium target and the formation of the oxide is achieved by adding an oxygen gas partial pressure during deposition in order to obtain different stoichiometries [1]. In the second method, the authors start from a europium oxide target and use post-deposition annealing treatments in reduction atmospheres at high temperatures (1000 °C). However, in the second case, as a result of the high temperature post-annealing treatments and due to the direct deposition of the Eu oxide on the Si substrates, formation of Eu-silicate phases has been reported, which precludes obtaining pure europium oxide films [2–4].

The aim of this work is to report a simplified two step growth process, which yields stoichiometric, good quality, crystalline and optically active europium sesquioxide (Eu_2O_3) thin films with intense Eu^{3+} red light emission. We have prepared the thin films using pulsed laser deposition (PLD), which has proven to be excellent for the preparation of complex oxides, and production of high-density films with good adhesion [5]. To obtain good quality crystalline films, we used relatively low temperature annealing treatments in air. In fact, it will be shown that good crystallinity of both the cubic and monoclinic phases can be accomplished for temperatures as low as 500 °C.

2. Experimental

The PLD system consists of a UV laser ArF excimer (λ = 193 nm, 20 ns pulse duration) and a vacuum chamber equipped with a multi-target system that can accommodate up to four targets. In order to ablate the materials the laser beam was focused at an incidence angle of 45° onto the targets. During the process of ablation,

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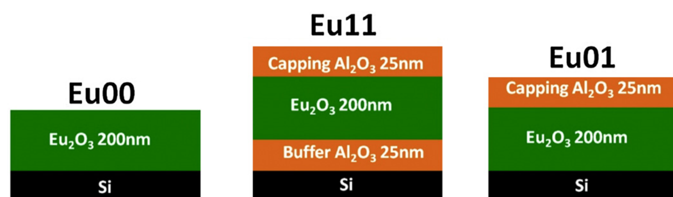

Fig. 1. Schematic representation of the films configuration Eu00, Eu11 and Eu01.

the targets were rotated to prevent crater formation. The films were deposited on Silicon (1 0 0) wafers placed at 43 mm from the target surface at room temperature. The ablation was performed in the so-called off-axis configuration, i.e. the center of the substrate did not coincide exactly with the plasma expansion axis. The substrate was also rotated during deposition with the purpose to obtain a large area of homogeneous film thickness. All the experiments were performed at vacuum 1.3×10^{-6} mbar. The energy density value used to ablate the targets was chosen to be 3.5 J/cm^2. To calibrate film deposition rates, reference films of both materials, Eu_2O_3 and Al_2O_3 were grown separately. To monitor the growth progress, in situ reflectivity measurements during growth of these reference films were performed with a chopped diode laser (647 nm), having an incidence angle of about 45° respect to the normal of the substrate surface.

For sample preparation two targets were used: a non-commercial Eu_2O_3 monoclinic phase target (fabricated by Ceramics of Smart Systems Group – CSIC), sintered at 1400 °C for 2 h [6] and a commercial α-Al_2O_3 (99.9%) target. Films were prepared under three configurations by ablating alternatively the two targets: (a) Eu00: only the Eu_2O_3 optically active film was deposited in direct contact to the substrate (no capping nor buffer layers); (b) Eu11: the Eu_2O_3 film with buffer and capping layers, i.e., it was sandwiched between an a-Al_2O_3 buffer layer deposited on top of the substrate before the Eu_2O_3 film deposit, and a Al_2O_3 capping layer deposited on top of the film; finally (c) Eu01: only capping layer deposited on top of the Eu_2O_3 film. A scheme of the different thin film configurations is shown in Fig. 1. In all films, the europium oxide layer (Eu_2O_3) and each of the a-Al_2O_3 buffer and capping layers, were set to have a thickness of 200 ± 10 nm and 25 ± 5 nm respectively. The role of the amorphous aluminum oxide (a-Al_2O_3) layers is twofold. First, they prevent the europium oxide layer from chemical reactions, either from the external environment (capping layer on top of the active film) or with the Si substrate (buffer layer on top of the Si substrate deposited) before the Eu_2O_3 film. Second, as it will be shown, the deposition of these layers influences the Eu_2O_3 crystallization. The a-Al_2O_3 is also a dense oxide that shows no crystalline structure up to 900 °C, is chemically stable at low temperatures and optically transparent, being suitable for luminescence applications [7,8].

After the films deposition, spectroscopic ellipsometry (SE) measurements were performed in the 300–1500 nm wavelength range at incidence angles of 60°, 65° and 70° using a VASE ellipsometer (J.A. Woollam Co., Inc.). The combined analyses of the optical in situ and ex situ measurements were used firstly, to obtain the film thickness of the reference films and secondly, to determine the deposition rates and optical linear properties for the as-grown films.

Post-deposition annealing treatments were performed in a furnace in air. The temperature was increased at rate of 10 °C/min and the final temperature was maintained during 1 h. The films were annealed at 300 °C to activate emission, and then at 500 °C, 700 °C and 850 °C. The photoluminescence was measured after each annealing treatment. The formation of the crystalline phases was assessed by using X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) with Cu Kα radiation.

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and the oxidation state of the samples. XPS spectra were acquired in an ultrahigh vacuum (UHV) chamber with a base pressure of 10^{-9} mbar equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150 spectrometer) and a delay-line detector in the nine-segment mode, using a non-monochromatic Al Kα (1486.61 eV) X-ray source. XPS spectra were recorded at normal emission take-off angle, using an energy step of 0.1 eV and a pass-energy of 20 eV [9,10]. A small amount of contaminants, carbon and hydroxyl (OH) species was detected in the sample surface because the samples were exposed to air after growth and prior to XPS measurements. The signal from adventitious carbon at 284.6 eV was used for energy calibration. This surface contamination was removed by Ar ion bombardment. The overall surface composition of as-grown samples was determined from survey spectra with regions of interest (Eu3d, O1s and C1s). The integral peak areas after background subtraction and normalization using sensitivity factors provided by electron energy analyzer manufacturer were used to calculate the atomic concentration of each element. Data processing was performed using CasaXPS software (Casa Software Ltd., Cheshire, UK).

Photoluminescence (PL) measurements were done under excitation at λ = 355 nm at a nominal power of 160 mW from a solid state Genesis CX 355-200 Optically Pumped Semiconductor Laser (Coherent). The light emitted by the sample was collected by a microscope objective (10× Mitutoyo Plan Apo NIR Infinity-Corrected Objective), focalized over a Czerny-Turner type Monochromator (Acton Spectra Pro 300i, with a diffraction grating of 1200 g/mm) and detected through a photomultiplier EMI 9659QB. The signal was amplified with the standard lock-in technique and collected by a CPU.

3. Results and discussion

3.1. Linear optical properties

The complex refractive index ($\mathbf{n} = n + ik$) of the active Eu_2O_3 films was determined from the spectroscopic ellipsometry (SE) measurements for the films in the different configurations. For the as-grown films, Fig. 2 shows the corresponding refractive index (n) and extinction coefficient (k) values as a function of wavelength. The SE parameters of the Eu_2O_3 layers were fitted using a Cauchy dispersion law for the refractive index, $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$, with A, B, and C being free parameters. For the k value, the Urbach dispersion was used:

$$k(\lambda) = A_k \exp B_k \left(\frac{hc}{\lambda} - E_u \right) \quad (1)$$

where E_u is the Urbach energy [eV], and A_k and B_k are free parameters. For the refractive index of the Al_2O_3 layers (buffer and capping) data from [11] were used. The fit process was performed in three steps: (1) Eu00 was used to obtain the thickness and optical constants for the Eu_2O_3. (2) With these data fixed, the thickness for Al_2O_3 layer in Eu01 was fitted. (3) All the films were refitted with data feedback. The results yielded a thickness value for the Eu_2O_3 layer of 200 ± 10 nm for all the studied configurations and of 25 ± 5 nm for the a-Al_2O_3 layers.

It can be observed that the Eu_2O_3 films show very good transparency in the full spectral range; the absorption coefficient is always well below 0.05 for wavelengths larger than 400 nm. The differences in absorption coefficient between films cannot be considered significant since they are close to our fitting error. The refractive index of the Eu_2O_3 at 620 nm is 2.02 ± 0.02 for Eu00 configuration, very similar to [12], and 2.06 ± 0.02 for Eu11 and Eu01 configurations. This refractive index is much higher than that of Al_2O_3 films, which is 1.76 at 620 nm. This index contrast enables

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