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Europium luminescence from amorphous yttrium alumina films on fused silica substrates

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Abstract. In this work, we investigate photoluminescence of sol-gel derived films corresponding to yttrium alumina garnet $\text{Y}_3\text{Al}_5\text{O}_{12}$ doped with trivalent europium. The films with three concentrations of europium 0,02; 0,025; 0,03 M with the thickness 210-220 nm were deposited on fused silica substrates by the corresponding sols' spinning followed by drying and high temperature annealing at 1000 °C for 30 min. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis as well as ellipsometry, photoluminescence (PL) and photoluminescence excitation spectroscopy (PLE). All of the fabricated samples were amorphous and revealed room-temperature luminescence bands within the range of 550 – 750 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j=0,\dots,4$) transitions of trivalent europium ions with the most intensive bands at 610 – 630 nm and 680 – 710 nm. The intensity of europium luminescence increases with europium concentration. The photoluminescence excitation spectra measured at the emission wavelength 710 nm exhibit strong bands at 220 nm, which could be associated with absorption of exciting light within $\text{Eu}_3^{+} - \text{O}_2^{-}$ bands. Practical application of the obtained films transforming ultraviolet irradiation into visible is discussed.

1. Introduction

Materials that are transparent in the visible and near infrared range when doped with light emitting impurities receive interest as light convertors of UV irradiation into visible, which increases the efficiency of silicon solar cells [1]. Particularly, trivalent europium ions are characterized by strong visible luminescence [2]. Luminescence properties of Eu-doped materials (particularly of the PL and PLE spectra) depend on host material, synthesis conditions and annealing temperature, as well as europium concentration. For most of the host materials, the band at 610 nm is the most intensive as compared to the band at 710 nm. However, for silicon-based photodetectors, conversion of UV irradiation into emission at about 710 nm is of great importance, considering their spectral sensitivity. Recently, strong Eu PL with efficient 710 nm emission was observed from aluminates codoped with Eu and Bi [3]. Eu-doped film structures, which exhibited strong visible PL, were created using magnetron sputtering, laser ablation, molecular beam epitaxy, deposition from the salt solutions and other techniques. The properties of sol-gel derived films depend on the type of substrate. In this work



we characterized Eu-doped amorphous yttrium alumina films with europium concentrations of 0,02, 0,025, and 0,03 M deposited on fused silica substrates.

2. Experiment

The components of the sol preparation were ethanol (C_2H_5OH), citric acid ($C_6H_8O_7$), aluminium nitrate nonahydrate $Al(NO_3)_3 \cdot 9H_2O$, 98.5% (Riedel-de Haen), pentahydrate nitrate, europium ($Eu(NO_3)_3 \cdot 5H_2O$, 99.9%, Aldrich) and yttrium nitrate pentahydrate ($Y(NO_3)_3 \cdot 6H_2O$, 99.999%, Aldrich). Preparation of sols with different europium concentrations was carried out by changing the mixing ratio of europium and yttrium, which ensured the concentration of Eu^{3+} in three sols 0.02; 0.025 and 0.03 M. Sols were deposited on a quartz substrate by spinning at a rate of 2700 rpm for 30 seconds. After drying at 200 °C of the first layer, the second layer was deposited and dried at the same conditions. Finally, the samples were subjected to heat treatment at 1000 °C for 30 min.

The photoluminescence (PL) and PLE spectra were studied using the spectrofluorometer CM2203, which allows measurements of luminescence and excitation spectra in the range of 210-800 nm. A high pressure xenon arc lamp with 150 Watts was used as an excitation source. In the channels of excitation and registration of luminescence, double monochromators with dispersion summation were installed. To reduce the penetration of ambient light so as to reduce the influence of scattered light, the studied samples were mounted in a special holder of the detection channel at an angle of 30° between the normal to the sample plane and exciting beam.

X-ray diffraction analysis was performed on the diffractometer D8 Advance, Bruker AXS (Germany), using $CuK \alpha$ -radiation. Morphological analysis of the films was investigated using a HITACHI S-4800 scanning electron microscope equipped with an X-ray microanalyzer for EDX-analyses. The refractive index and the film thickness were measured by laser ellipsometry 3M LEF-1 with a wavelength of 6328 Å.

3. Results and discussion

The EDX analyses performed for the sample with concentration 0,025 M confirms that the yttrium alumina composite contains the elements in the ratio $(Y+Eu)/Al=3:5$ with the accuracy of experimental error. The EDX analyses performed for the sample with concentration 0,025 M confirms within range of the accuracy of the experiment of that the yttrium alumina composite contains the elements in the ratio $(Y+Eu)/Al=3:5$. The XRD spectra revealed that the films doped with three Eu concentrations are amorphous (Figure 1). According to SEM-data, the typical thickness of the films is about 210 nm and vague images of grains are slightly resolved. (Figure 1 in the inset). For the film of 216 nm thickness, the refractive index was found to be 1.81, according to ellipsometry analysis.

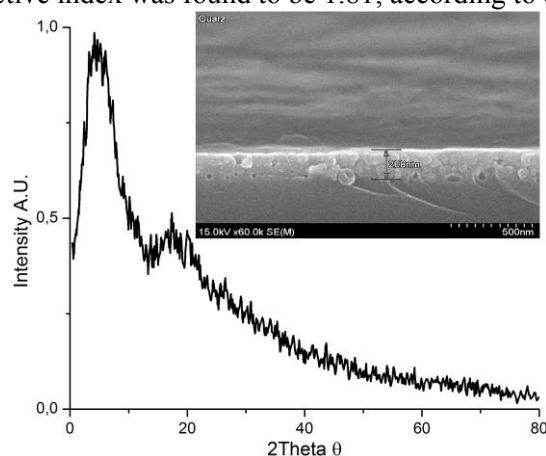


Figure 1. XRD spectra of Eu-doped yttrium alumina film on fused silica substrate after annealing at 1000 °C for 30 min for Eu concentrations 0,03 M. XRD spectra for 0,02 and 0,025 M is basically the same. SEM-image of the film with Eu concentration 0,02 M is given in the inset.

Figure 2 gives the PL spectra of these films with three Eu concentrations recorded for the excitation wavelength 260 nm. For all of the fabricated films, the PL spectra reveal the bands corresponding to optical transitions between the terms of trivalent europium ions: $^5D_0 \rightarrow ^7F_1$ (585 - 600) nm; $^5D_0 \rightarrow ^7F_2$ (610 - 630) nm; $D_0 \rightarrow ^7F_3$ (640 - 660) nm; $^5D_0 \rightarrow ^7F_4$ (680 - 710) nm [4,5]. The PL intensity of all of the observed bands increases with Eu concentration. For the sample with the highest Eu concentration, additional weak band 570 - 585 nm is observed corresponding to $^5D_0 \rightarrow ^5F_0$ transition.

PLE spectra of Eu-doped films with three concentrations 0,02; 0,025 and 0,03 M were investigated for the most intensive 710 nm $^5D_0 \rightarrow ^7F_4$ band. The observed bands in PLE spectra correspond to trivalent Eu transitions between the terms: $^7F_0 \rightarrow ^5H_6$ (318 nm); $^7F_0 \rightarrow ^5D_4$ (365 nm); $^7F_0 \rightarrow ^5G_2$ (380 nm); $^7F_0 \rightarrow ^5L_6$ (393 nm); $^7F_0 \rightarrow ^5D_3$ (413 nm)[6]. The intensive wide band 214 - 280 nm is associated with the absorption of charge transfer band $\text{Eu}^{3+} - \text{O}^{2-}$ [7,8].

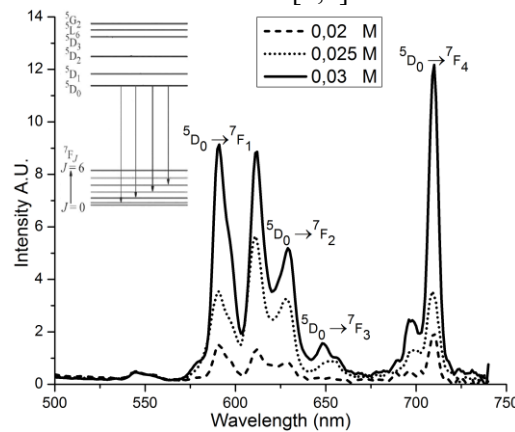


Figure 2. PL spectra of Eu-doped yttrium alumina films obtained for 3 concentrations of europium after annealing at 1000 °C for 30 min: (Eu^{3+}) 0.02, 0.025, 0.03 M. Excitation wavelength $\lambda_{\text{ex}} = 260$ nm.

Transmission spectra of yttrium alumina composites with Eu concentration 0.03 M are presented in Figure 4. The absorption bands in the range 200—394 nm correspond to the bands in PLE spectra.

Eu-doped films could find application as transparent convertors of UV-irradiation into visible [9], raising the efficiency of silicon solar cells and converting UV irradiation into visible due to reducing electron thermalization and degradation of the solar cell. Eu-doped amorphous films also receive interest in the investigation of spontaneous emission properties when embedded in microcavities [10], photonic crystals [11], lighting sources [12] and other matrices with anisotropy of photonic density of states [13, 14].

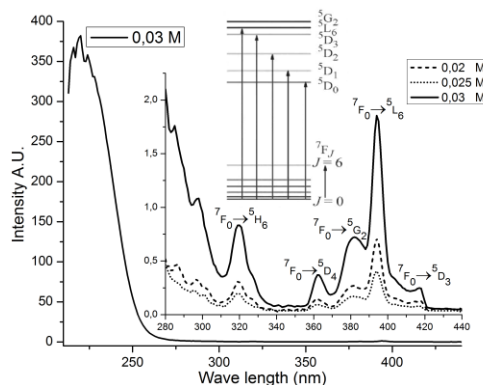


Figure 3. PLE spectra of Eu-doped yttrium alumina films. PLE spectrum in the range 214-440 nm of Eu-doped film with concentration 0.03 M for the emission wavelength 710 nm. The inset depicts PLE spectra in the range 280 – 440 nm for the samples with three europium concentrations: 0.02, 0.025 and 0.03 M.

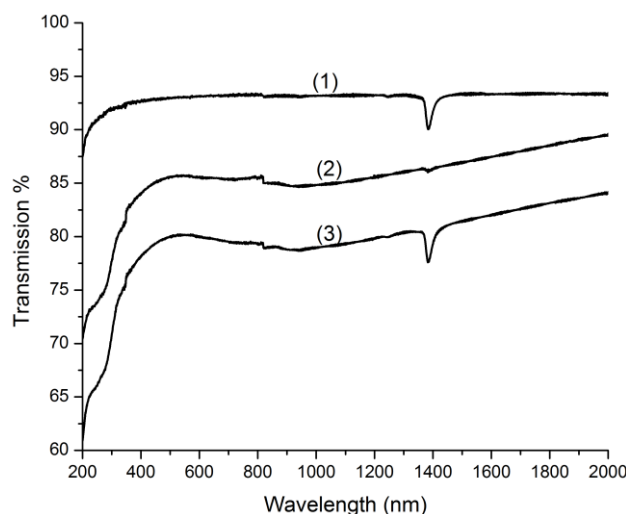


Figure 4. Transmission spectra: (1) – uncoated fused silica substrate; (2) - fused silica substrate with yttrium alumina film with Eu concentration 0.03 M in reference channel, (3) fused silica substrate with yttrium alumina film with Eu concentration 0.03 M without fused silica substrate in the reference channel.

4. Conclusion

The method of sol-gel synthesis of Eu-doped yttrium alumina films has been described in this article. The films, comprising two layers deposited by spinning on fused silica substrate, are about 210 nm thick and are amorphous after conventional furnace annealing at 1000 °C. The films reveal visible Eu-related PL with the bands $^5D_0 \rightarrow ^7F_1$ (588 nm), $^5D_0 \rightarrow ^7F_2$ (608 and 629 nm), $^5D_0 \rightarrow ^7F_3$ (654 nm), $^5D_0 \rightarrow ^7F_4$ (710 nm) excited with UV irradiation in the range of 200-394 nm. The PL intensity increases for the chosen concentrations of Eu – 0,02; 0,025 and 0,03 M. The described method allows the strong conversion of UV irradiation into visible with the most intensive 710 nm PL band. The obtained film has an amorphous structure after a heat treatment at 1000 °C.

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