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# Photoluminescence of the Eu-doped thin film heterojunction GaAs/SnO<sub>2</sub> and rare-earth doping distribution

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**Abstract.** Tin dioxide (SnO<sub>2</sub>) thin films doped with Eu<sup>3+</sup>, are deposited by the sol-gel-dip-coating process on top of GaAs films, which is deposited by resistive evaporation on glass substrate. This heterojunction assembly presents luminescence from the rare-earth ion, unlike the SnO<sub>2</sub> deposition directly on a glass substrate, where emissions from the Eu<sup>3+</sup> transitions are absent. The Eu<sup>3+</sup> transitions are clearly identified and are similar to the observation on SnO<sub>2</sub> pressed powder (pellets), thermally treated at much higher temperatures. However, in the form of heterojunction films, the Eu emission comes along a broad band, located at higher energy compared to Eu<sup>3+</sup> transitions, which is blue-shifted as the thermal annealing temperature increases. The size of nanocrystallites points toward quantum confinement or electron transfer between oxygen vacancies, originated from the disorder in the material, and trivalent rare-earth ions, which present acceptor-like character in this matrix. This electron transfer may relax for higher temperatures in the case of pellets, and the broad band is eliminated.

## 1.Introduction

The interest for rare-earth ions has been grown considerably in the past years, due to their optical emission lines in a large wavelength range [1], with considerable technological interest towards electroluminescent devices construction [2]. Doping semiconductors with rare-earth ions contributes to innovation in optoelectronics and, to make the emission useful for devices application, the ion must be incorporated into a matrix with adequate format, allowing the coupling to the circuit. The format of thin films is rather convenient in this direction because it is easy to link to an electronic circuit through electrical connections, such as deposited metallic contacts.

The ion Eu<sup>3+</sup> present emission lines in the red region, mainly about 595nm and 615nm, which correspond to dipole magnetic transition (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>) and electric dipole transition (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>), respectively [3]. Tin dioxide, doped with Eu, exhibits outstanding properties of cathode luminescence, thermoluminescence and photoluminescence [4]. This semiconductor oxide has a wide bandgap (3.6-4.0eV), and has been investigated showing high applicability in many areas, such as gas sensors [5] and solar cells [6]. It presents n-type conductivity due to oxygen vacancies and tin interstitial atoms [7]. Gallium arsenide (GaAs) is an important semiconductor for the microelectronic industry, due to high mobility and direct bandgap transition [8], allowing the interaction between light and electricity, being used in heterostructures [9], light emitting diodes [10], lasers [11], among other applications.

The formation of heterojunctions, using transparent oxides deposited on top of semiconductors has



unique performances concerning the emission efficiency and optical characteristics, crucial points to the operation of functional devices [12]. A heterojunction ZnS-CdS showed properties modulated by the semiconductor ZnS [13]. Investigation on the heterojunction SrTiO<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> has shown higher efficiency in the charge separation when compared to separated SrTiO<sub>3</sub> or Bi<sub>2</sub>O<sub>3</sub> [14]. ZnO films were deposited on boron-doped silicon substrate (p<sup>-</sup> e p<sup>+</sup>), showing rectifying behavior for the heterojunction ZnO/p<sup>-</sup>-Si, whereas ZnO/p<sup>+</sup>-Si has exhibited electroluminescence [15]. ZnO films has also been grown on GaAs substrate, forming a heterojunction with rectifying characteristics, with violet-blue and infrared electroluminescence [16], adequate for optical fiber communications.

The heterojunction SnO<sub>2</sub>/GaAs in the form of thin films, have been successfully obtained, giving birth to smooth interface and improved electrical properties [17,18]. In this paper, luminescence from Eu-doped SnO<sub>2</sub> films, deposited on top of GaAs as a heterojunction, is reported. The Eu<sup>3+</sup> transitions are clearly identified in the PL spectra, unlike the films of SnO<sub>2</sub>:Eu alone, annealed at similar temperatures as the heterojunction. A broad band also shows up, which is blue shifted as the thermal annealing temperature increases, being destroyed for pressed powder, annealed to higher temperature.

## 2. Experimental

GaAs thin films are deposited by the resistive evaporation technique using a tungsten boat, and controlling the electrical current through the boat, under low pressure (10<sup>-5</sup> mbar). After evaporation, films were submitted to annealing at 150°C by 30 min. The deposition of Eu<sup>3+</sup> - doped SnO<sub>2</sub> layer has been described in details elsewhere [19]. The deposition takes place in air atmosphere, and after each layer, samples are dried in air at 200°C by 10 min. This procedure was repeated 10 times. The final annealing was at varying temperature (300 to 500°C) by 1 h. The xerogel (powder) SnO<sub>2</sub>:2%Eu was obtained by evaporating the solvent, and treating at 1000°C by 1h. The remaining powder was pressed down to pellet format with 5000kgf/cm<sup>2</sup> by 3 min, and treated again at 1000°C by 20min.

X-ray diffraction data were obtained using a Rigaku diffractometer, model D/MAX 2100PC operated with a Cu K<sub>α</sub> radiation source (1.5405 Å) and a Ni filter for reducing the undesirable K<sub>β</sub> radiation. The data are collected with 0.02° of step and scanning rate of 1°/min in the 2theta mode for films (fixed incident angle of 1.5°) in the angular range of 20° ≤ 2θ ≤ 80°.

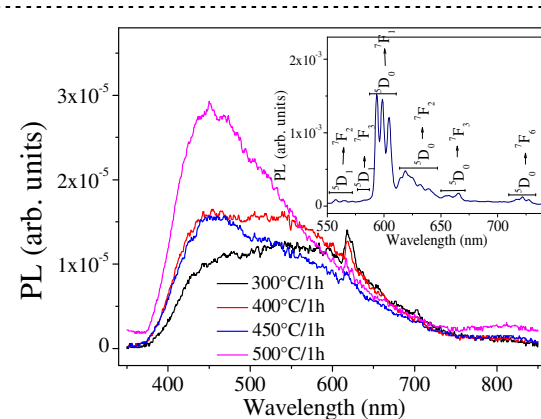
For the photoluminescence (PL) measurements, samples were excited with a modulated 350 nm line of a Kr<sup>+</sup> laser and the signal was detected by a R955 PMT from Hamamatsu and a SR530 Lock-in Amplifier from Stanford Research System. A single configuration monochromator was used for scanning the PL spectra. Morphological characterization and compositional analysis were carried out with a scanning electron microscopy (SEM) system (FEI model Quanta 200), equipped with an energy dispersive X-ray (EDX) microanalysis system (Oxford model Inca 250P20).

## 3. Results and Discussion

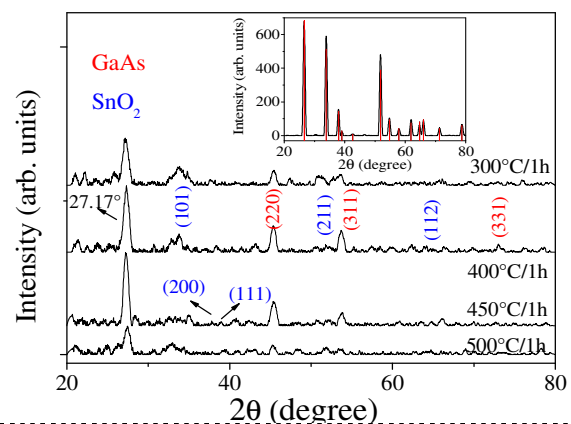
Figure 1 shows the PL of the heterojunction with distinct thermal annealing. The inset of figure 1 is the same measurement carried out for a sample of SnO<sub>2</sub>:2at%Eu, in the format of pellet (pressed powder). Three well defined peaks are identified for the heterojunction samples and are coincident with Eu<sup>3+</sup> transitions: <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> (about 596nm), <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> (about 618nm) and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>4</sub> (about 704nm). Besides, a broad band is also identified, with peak about 550 nm for the sample treated at 300°C, and blue-shifted for the samples treated at higher temperatures. The peak is about 470nm for the sample treated at 500°C. The emission spectra of SnO<sub>2</sub>:2at%Eu film, not coupled to a GaAs layer on a heterojunction, presents only the broad band, not allowing the identification of the Eu<sup>3+</sup> transitions. Concerning the transition identified for the powder SnO<sub>2</sub> samples (inset of figure 1), they are easily identified and take place on a wider range. No broad band is obtained for the powder. Eu<sup>3+</sup> peaks are seen at 557, 565 and 572 nm corresponding to the transition <sup>5</sup>D<sub>1</sub>→<sup>7</sup>F<sub>2</sub>, 583 nm corresponding to <sup>5</sup>D<sub>1</sub>→<sup>7</sup>F<sub>3</sub>, 593, 598 and 604 nm (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>), 614, 618 and 625 nm (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>), 633, 638 e 657 nm (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>3</sub>), and 716, 721 and 727nm (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>6</sub>). Peaks related to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition are the most intense, unlike the PL for the heterojunction films shown in fig. 1, where the transition <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> turned

out as the most intense. It is also different from excitation with the fourth harmonic of a Nd:YAG laser (266 nm) for the same level of doping concentration, where the transition  $^5D_0 \rightarrow ^7F_2$  is the most intense [19]. The dipole magnetic transition  $^5D_0 \rightarrow ^7F_1$  is related to  $\text{Eu}^{3+}$  ion substitutional to  $\text{Sn}^{4+}$  in the  $\text{SnO}_2$  matrix sites whereas radiation from the electric dipole transition  $^5D_0 \rightarrow ^7F_2$  is mainly due to ions located at particles surface. Then, it is expected that the former transition be more evident for the films where the crystallites are smaller compared to the pellets and then, the depletion layer regions are wider.

For the heterojunction films, the Eu emission comes along a broad band which is blue-shifted as the thermal annealing temperature increases. It is well-known that increasing the annealing temperature, the crystallite size must increase. Although quantum confinement seems to be an explanation, this evidence is in opposition to what would be expected, since the dependence on the crystallite size is similar to quantum dots. Then, for a particle localized in a nanocrystallite, as the size decreases, the emission spectra should shift to high energies [20,21], in opposition to what was observed here. Another possible contribution for the detected broad band is related to electron transfer between oxygen vacancies and acceptor  $\text{Eu}^{3+}$  ions. These phenomena relax for annealing at higher temperatures and longer times, in the case of pellets, and eliminate the broad band from the PL spectra. Reported results for Sb-doped  $\text{SnO}_2$  samples ascribe the main origin of the UV-violet luminescence band to the electron transition between the donor level and the acceptor level formed by Sb ions [22]. Considering that it is much more common to a trivalent rare-earth ion, such as  $\text{Eu}^{3+}$ , to form an acceptor level in  $\text{SnO}_2$ , than a Sb ion, whose predominant state is pentavalent [23], it is expected that the broad band seen in Fig. 1 has contribution related to the electron transition between the donor level, formed by oxygen vacancies, and the acceptor level formed by  $\text{Eu}^{3+}$  ions. It also leads to high charge compensation as determined by electrical characterization measurements [24].



**Figure 1.** PL of the heterojunction with distinct thermal annealing. Inset: PL of sample  $\text{SnO}_2:2\text{at}\%\text{Eu}$ , in the format of pressed powder (pellet)

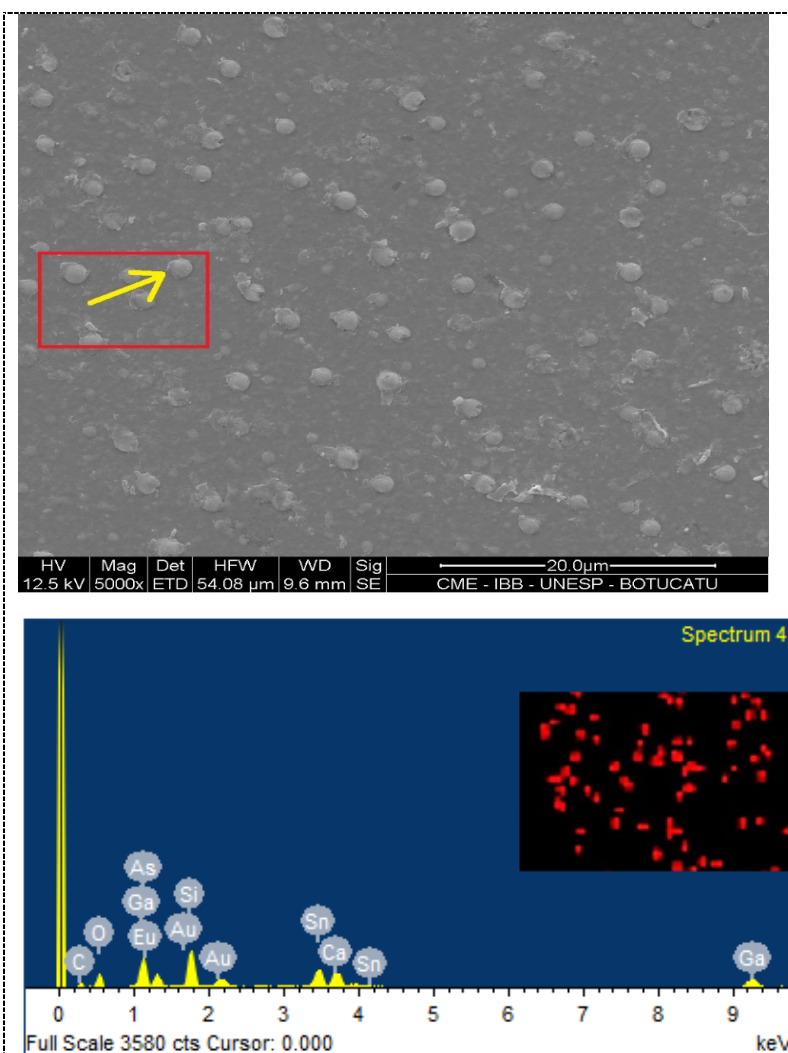


**Figure 2.** X-ray diffractogram of heterojunctions. Annealing temperatures are indicated and main directions are labeled. Inset: diffractogram of the  $\text{SnO}_2:2\%\text{Eu}$  powder. Red vertical lines are from the reference JCPDS- 41-1445 for tin dioxide..

Figure 2 shows X-ray diffratograms for these samples, which exhibit the noisy and diffuse profile typical of materials composed of nanocrystalline building blocks. The labeled peaks correspond to the planes of rutile structure of tin dioxide (JCPDS- 41-1445) and planes of GaAs (JCPDS-80-0016). Characteristic peaks of  $\text{SnO}_2$  are seen at  $33.7^\circ$  and  $51.5^\circ$  corresponding to (101) and (211) crystallographic planes, and characteristic peaks of GaAs at  $45.4^\circ$  and  $53.7^\circ$ , related to (220) and (311) planes. At  $27.17^\circ$  there is a probable overlapping of two peaks: one related to plane (100) of  $\text{SnO}_2$ , and another peak corresponding to plane (111) of GaAs. Concerning the diffractogram of the powder sample, it exhibits many peaks related to the rutile  $\text{SnO}_2$ , as can be seen in the inset of fig. 2, by the very good match with the red lines of the JCPDS- 41-1445 reference. Crystallite size evaluated

according to the Scherer equation in the (101)  $\text{SnO}_2$  direction grows from 11.3nm for heterojunction sample annealed at 300°C to 15.6nm for annealing at 500°C, and 22.1 for the powder. It confirms the expectation of crystallize growing with increasing annealing temperature.

Figure 3 (a) is a SEM image of a heterojunction  $\text{GaAs}/\text{SnO}_2:2\text{at}\%\text{Eu}$ , annealed at 400°C by 20min. Figure 3(b) is the EDX spectra for the same sample, in the region indicated by the yellow arrow in the figure 3(a). The SEM image shows some prominences, which means most external particles. The EDX analysis carried out the sample surface identified variation of up to 700% in the relative Eu/Sn composition, for these prominent rounded regions. Although it is not possible to ensure that electrons interacted only with the elements within the demarked area under this magnification and so high voltage, these regions seem to be very important in this variation. The EDX spectra shown in figure 3(b) clearly confirm the Eu peaks. The inset of figure 3(b) shows an EDX general field of the marked region (squared) of the figure 3(a), showing an illustration of the Eu distribution on the sample surface. Although the Eu ions are spread over the whole surface, there are clearly regions where they are more concentrated. These prominent regions were not identified for samples where the  $\text{SnO}_2$  layer is deposited directly on the substrate, nor on heterostructures surface where the top layer is GaAs [17]. Then, we believe that these regions play a fundamental rule in order to concentrate the  $\text{Eu}^{3+}$  ions and provide luminescence from them.



**Figure 3. (top)** MEV of the heterojunction  $\text{GaAs}/\text{SnO}_2$  where the top layer is annealed at 400°C by 20min, magnitude 5000x: **(bottom)** EDX spectra for the same material in the region indicated by the red arrow in the top figure. **Inset**: EDX general field of the heterojunction  $\text{GaAs}/\text{SnO}_2:2\%\text{Eu}$  treated at 400°C/20min, showing the Eu distribution.

#### 4. Conclusion

Main transitions from  $\text{Eu}^{3+}$  were identified in the matrix  $\text{SnO}_2$  in a heterojunction with GaAs, unlike films of sole  $\text{SnO}_2$  with the same doping. It comes along a broad band, blue shifted for larger crystallites

The luminescence from Eu in thin films is a rather convenient way, providing accessibility to construction and operation of luminescent and electroluminescent devices. The combination with GaAs in the form of heterojunction films provides the red emission, not seen from Eu-doped films deposited in an isolated way, when thermally annealed at same temperature range.

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