Photoluminescence and Stoichiometry Correlation in Nanocrystalline EuO \(_x\) Thin Films: Tunable Color Emission

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**ABSTRACT:** The development of broadband and ultracompact optoelectronic devices relies on the possibility of fabricating bright and tunable emitters at the nanoscale. Here, we show emission from EuO \(_x\) (1 ≤ \(x\) ≤ 1.4) thin films on silicon formed by nanocrystals with average sizes in the range of 5 nm. The photoluminescence emission of the nano-EuO films is tunable as a function of the oxygen concentration changing from a green broadband Eu\(^{2+}\)-related emission to a narrow red Eu\(^{3+}\)-related emission. To reach these results has been instrumental through the use of a new methodology specially designed to achieve high-quality europium oxide films whose compositional properties are controlled by the growth base pressure and preserved thanks to a chemically stable and transparent cover layer of Al\(_2\)O\(_3\). Our findings confirm the outstanding potential of nanostructured EuO films as "one-compound" optical elements with tunable emission properties for their implementation in integrated silicon-based devices.

**INTRODUCTION**

Luminescence from rare earth Eu (europium) ions holds great promises for applications compatible with silicon technologies, such as optical recording and encryption,\(^1\) white cathodoluminescence emission,\(^2\) and phosphors with excellent stability and color performance.\(^3\) To answer this interest, Eu-doping in Si-based materials has been a very active field of research that has included studies not only of the photoinduced luminescence\(^4\) but also of the electrical excitation of oxides suitable for Si integration doped with trivalent Eu (Eu\(^{3+}\))\(^5\) and more recently, the cathodoluminescence of oxides and oxynitrides doped with divalent Eu (Eu\(^{2+}\)) has been reported.\(^6\)

In this context, the photoluminescence of europium oxides has been less investigated, although they hold a great potential for different optoelectronic applications. While the europium trioxide (EuO\(_3\)) is a wide band gap oxide relevant mainly for lighting applications, such as sensitization in lanthanide-doped inorganic nanocrystals,\(^7\) additive-free red-emitting transparent ceramics,\(^8\) high quantum efficiency phosphors,\(^9\) dense translucent ceramics,\(^10\) and much more, the europium monoxide (EuO) is a ferromagnetic semiconductor,\(^11\) showing interesting magnetic properties, becoming ferromagnetic below a Curie temperature at 69 K.\(^12\) Recently, for example, inducing magnetism by proximity in two-dimensional materials such as graphene has been reported.\(^13\) Moreover, europium monoxide belongs to a compact group of magnetic semiconductors (europium chalcogenides) with unique electronic, magnetic, optical, and magneto-optical (MO) properties.\(^14\) For applications in optoelectronics, it is particularly significant that the band gap of EuO at room temperature is 1.12 eV, which is comparable to that of silicon, which would allow spin-polarized electronic injection.\(^15\) These special features have opened prospects for the fabrication of optoelectronic and spintronic devices based on EuO, which would be compatible with the current CMOS semiconductor technology.\(^16\) However, most of these attractive properties have been studied in high-quality monocrystalline EuO thin films,\(^17\) which is difficult and costly to prepare.\(^18\) In this context, there has been insufficient research related to the study of the magnetic and optical properties of nanocrystalline and nanodimensional EuO and might have new and unexpected properties. Additionally, the preparation of nanocrystalline EuO films following a relatively simple procedure would be highly desirable. Note that, by preparing light emitting pure Eu-based films, the effective number of emitting ions per unit volume can be effectively increased compared to that in Eu-doped materials. In this regard, we have recently shown the successful preparation of
transparent nanocrystalline EuO thin films in the near infrared, which expands the potential for optical applications of this material. However, the potential of light emission of nano-EuO films has not been yet addressed, although ions are generally used as dopant for phosphors in lighting application because of their extraordinary emission properties. In previous works, the tuning of the luminescence europium-doped oxides, for example, silicon oxides and CaYAlO$_4$, has been investigated as a function of the annealing conditions. In particular, the emission of Eu$^{3+}$ ions consists of narrow emission peaks with long lifetimes originated from the intra-4f electronic transitions. By contrast, the emission of the Eu$^{2+}$ ions shows a broad band with short lifetimes influenced by a strong dependence of the host matrix because the 5d orbitals of Eu ions are very sensitive to the changes of the surroundings due to them being in the outer electronic shell compared with the inner 4f orbitals. For the specific case of the crystalline EuO (an ionic crystal with a rock-salt structure with Eu cations octahedrally coordinated by oxygen anions), Eu cations exhibit a 2+ oxidation state. The ligand crystal field splits the empty 5d shells into a lower $t_{2g}$ triplet and an upper $e_g$ forming the conduction band of EuO. In this work, we perform a comprehensive study of the photoluminescence light emission of EuO thin films formed by nanocrystals and prepared at room temperature with no post-annealing treatment. These nano-EuO thin films are fabricated following a flexible and straightforward deposition procedure that allows a fine-tuning of their oxygen content by adjusting the background pressure in the vacuum chamber during pulsed laser deposition. In addition, we encapsulate the films with a protective layer of Al$_2$O$_3$ to prevent the EuO thin film transformation once they are in contact with the ambient background pressure in the vacuum chamber during pulsed laser deposition. To avoid electron beam-induced damage or modifications of the EuO film crystal structure, the electron beam is kept at low electron density and short exposition times. The crystal structure and phase identification have been obtained from fast Fourier transform (FFTs) analysis of high-resolution TEM images. The photoluminescence (PL) measurements have been carried out under excitation at $\lambda = 355$ nm at a nominal power of 100 mW (spot of 1 mm) from a solid-state Genesis CX 355-200 optically pumped semiconductor laser (Coherent). The light emitted by the EuO nanocrystals has been collected by a microscope objective (10X 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 is amplified with the conventional lock-in technique and collected by a LabVIEW program. In addition, the chromatic coordinates of the emission have been analyzed. For this purpose, the three-color matching functions established by the Commission Internationale de l’Eclairage (CIE) in 1931, i.e., CIE 1931 $x$-$y$ color matching functions, have been used. The chromatic coordinates are calculated by means of a MATLAB script.

**RESULTS AND DISCUSSION**

Figure 1a shows the XPS spectra corresponding to the Eu 3d nuclear level for a set of films prepared under the base pressure of 13.8×10$^{-7}$ mbar. Structural analysis of the EuO has been also performed by means of high-resolution transmission electron microscopy (HRTEM) techniques, including Z-contrast scanning TEM (STEM) mode using a high-angle annular detector (HAADF) and high-resolution energy dispersive X-ray spectroscopy (EDS). The following procedure has been applied for the preparation of the TEM specimens: (i) deposition of a (15–20) nm of EuO$_2$ on a microscopy grid—the Si (100) grid is hexagonal 200 μm thick and has a 50 nm-thick amorphous SiN membrane at its center; (ii) deposition of a 15 nm-thick Al$_2$O$_3$ protective layer on the EuO film. In this way, the EuO film is protected by the SiN membrane at the bottom and by the Al$_2$O$_3$ layer on the top. The TEM images and chemical distributions have been obtained with Philips X’Pert MPD equipment in the θ–2θ configuration (1.5406 Å, Cu Kα). Structural analysis of the EuO has been also performed by means of high-resolution transmission electron microscopy (HRTEM) techniques, including Z-contrast scanning TEM (STEM) mode using a high-angle annular detector (HAADF) and high-resolution energy dispersive X-ray spectroscopy (EDS). The following procedure has been applied for the preparation of the TEM specimens: (i) deposition of a (15–20) nm of EuO$_2$ on a microscopy grid—the Si (100) grid is hexagonal 200 μm thick and has a 50 nm-thick amorphous SiN membrane at its center; (ii) deposition of a 15 nm-thick Al$_2$O$_3$ protective layer on the EuO film. In this way, the EuO film is protected by the SiN membrane at the bottom and by the Al$_2$O$_3$ layer on the top. To avoid electron beam-induced damage or modifications of the EuO film crystal structure, the electron beam is kept at low electron density and short exposition times. The crystal structure and phase identification have been obtained from fast Fourier transform (FFTs) analysis of high-resolution TEM images. The photoluminescence (PL) measurements have been carried out under excitation at $\lambda = 355$ nm at a nominal power of 100 mW (spot of 1 mm) from a solid-state Genesis CX 355-200 optically pumped semiconductor laser (Coherent). The light emitted by the EuO nanocrystals has been collected by a microscope objective (10X 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 is amplified with the conventional lock-in technique and collected by a LabVIEW program. In addition, the chromatic coordinates of the emission have been analyzed. For this purpose, the three-color matching functions established by the Commission Internationale de l’Eclairage (CIE) in 1931, i.e., CIE 1931 $x$-$y$ color matching functions, have been used. The chromatic coordinates are calculated by means of a MATLAB script.

**METHODS**

EuO$_2$ films with a nominal thickness of 100 nm have been prepared by pulsed laser deposition (PLD) using an ultraviolet Argon-Fluor excimer laser ($\lambda = 193$ nm; 20 ns pulse duration) focused on a Eu$_2$O$_3$ target with an energy density of 1.4 ± 0.2 J/cm$^2$ at a repetition rate of 10 Hz on Si (100) substrates held at room temperature. The base pressure in the vacuum chamber has been changed in the $10^{-7}$ to $10^{-8}$ mbar range. To isolate the EuO$_2$ nanocrystals from ambient conditions and hinder their oxidation upon exposure to air, the EuO$_2$ deposits have been capped with a 15 nm-thick amorphous Al$_2$O$_3$ protecting film. We have found that this encapsulation procedure is crucial to preserve the stoichiometry of the EuO$_2$ films, as detailed below. The stoichiometry of the EuO$_2$ nanocrystals has been assessed by X-ray photoemission spectroscopy (XPS) measurements using a Theta Probe XPS system from Thermo Fisher Scientific with monochromatic 1486.6 eV Al-Kα X-rays operated at 15 kV and an emission current of 6.7 mA. For the measurements, we have used a maximum spot size of the X-ray beam of 400 μm in diameter and a constant energy mode with a constant pass energy of 50 eV (1.00 eV full width at a half-maximum on Ag 3d$_{5/2}$). The X-ray diffraction study of the EuO$_2$ nanocrystals has been performed with Philips X’Pert MPD equipment in the θ–2θ configuration (1.5406 Å, Cu Kα). Structural analysis of the EuO$_2$ has been also performed by means of high-resolution transmission electron microscopy (HRTEM) techniques, including Z-contrast scanning TEM (STEM) mode using a high-angle annular detector (HAADF) and high-resolution energy dispersive X-ray spectroscopy (EDS). The following procedure has been applied for the preparation of the TEM specimens: (i) deposition of a (15–20) nm of EuO$_2$ on a microscopy grid—the Si (100) grid is hexagonal 200 μm thick and has a 50 nm-thick amorphous SiN membrane at its center; (ii) deposition of a 15 nm-thick Al$_2$O$_3$ protective layer on the EuO film. In this way, the EuO film is protected by the SiN membrane at the bottom and by the Al$_2$O$_3$ layer on the top. To avoid electron beam-induced damage or modifications of the EuO film crystal structure, the electron beam is kept at low electron density and short exposition times. The crystal structure and phase identification have been obtained from fast Fourier transform (FFTs) analysis of high-resolution TEM images. The photoluminescence (PL) measurements have been carried out under excitation at $\lambda = 355$ nm at a nominal power of 100 mW (spot of 1 mm) from a solid-state Genesis CX 355-200 optically pumped semiconductor laser (Coherent). The light emitted by the EuO$_2$ nanocrystals has been collected by a microscope objective (10X 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 is amplified with the conventional lock-in technique and collected by a LabVIEW program. In addition, the chromatic coordinates of the emission have been analyzed. For this purpose, the three-color matching functions established by the Commission Internationale de l’Eclairage (CIE) in 1931, i.e., CIE 1931 $x$-$y$ color matching functions, have been used. The chromatic coordinates are calculated by means of a MATLAB script.
pressures of $1.3 \times 10^{-7}$, $3.3 \times 10^{-7}$, and $53 \times 10^{-7}$ mbar. Four peaks are observed in the spectra, Eu$^{3+}$ 3d$_{5/2}$ and 3d$_{3/2}$ and Eu$^{3+}$ 3d$_{5/2}$ and 3d$_{3/2}$. The emissions centered around 1125 and 1155 eV are assigned to the components due to the spin–orbit coupling of EuO$_{2}$ in the 2$^{+}$ state, i.e., Eu$^{3+}$ 3d$_{5/2}$ and 3d$_{3/2}$, with a spin–orbit splitting of $(30 \pm 1)$ eV. The asymmetry of the peaks is attributed to (i) the presence of the divalent multiplet of the 3d$^{9}$ 4f$^{7}$ Eu$^{2+}$ 3d$^{5/2}$ and 3d$^{3/2}$. The emissions centered around 1134 and 1163 eV correspond to the trivalent doublet, Eu$^{3+}$ 3d$_{5/2}$ and 3d$_{3/2}$, i.e., to the components due to the spin–orbit coupling of EuO$_{3}$ in the 3$^{+}$ state.

In the analysis of the XPS data in Figure 1, we assume a similar contribution of the cross section for the 3d core level of Eu$^{3+}$ and Eu$^{2+}$ peaks (Caspers et al.$^{27}$ Zavala-Sanchez et al.$^{28}$ and Kumar et al.$^{29}$). Hence, the fraction of Eu in the 3$^{+}$ state has been determined considering the integrated spectral intensities (areas under the curve) of the peaks, yielding

$$f_{\text{Eu}^{3+}} = \frac{\sum A_{\text{Eu}^{3+}}}{\sum A_{\text{Eu}^{3+}} + \sum A_{\text{Eu}^{2+}}} \times 100$$

(1)

where $\sum A_{\text{Eu}^{3+}}$ is the sum of the areas under the Eu$^{3+}$ curves peaked at 1134 and 1163 eV and $\sum A_{\text{Eu}^{2+}}$ is the sum of the areas under the Eu$^{2+}$ curves peaked at 1125 and 1155 eV. In Figure 1b, the values calculated using eq 1 with an uncertainty of $\pm 5\%$ are represented as a function of the background pressure during growth. With increasing the background pressure in the chamber, the oxygen content in the films also rises, as confirmed by the enhancement of intensity of the peaks corresponding to the Eu$^{3+}$ oxidation state, with respect to those related to the 2$^{+}$ oxidation state. The 1.3 EuO$_{2}$ film (grown at a pressure of $1.3 \times 10^{-7}$ mbar presents a Eu$^{3+}$ relative percentage fraction of 2.7%, i.e., it consists of 97.3% EuO and 2.7% Eu$^{3+}$, and therefore, we can conclude that it is essentially stoichiometric EuO$_{2}$. The relatively low amount of Eu$^{3+}$ in the film is even lower than the 4% recently reported for nominally stoichiometric EuO.$^{27}$ In contrast, when analyzing the film deposited at the highest pressure (53-$10^{-7}$ mbar), it is found that the contribution from Eu$^{3+}$ is considerably reduced in comparison to 1.3 film and the spectrum is dominated by the emissions from EuO.$^{31}$ Here, the Eu$^{3+}$ relative percentage fraction is 75.3%, giving 24.7% of EuO in the film. The 3.3 film (grown at $3.3 \times 10^{-7}$ mbar) contains an Eu$^{3+}$ relative percentage fraction of 37.5%. These results confirm that the stoichiometry of the films can be suitably controlled by adjusting the base pressure in the growth chamber, showing consistent results with our previous work.$^{30}$ Therefore, according to the XPS data, the stoichiometry of the films is EuO for the 1.3 film, EuO$_{1.2}$ for the 3.3 film, and EuO$_{1.4}$ (close to Eu$_{1.3}$O$_{3.7}$) for the 53 film. The process that enables the preparation of EuO$_{3}$ with a different oxygen content by controlling the base pressure during deposition is linked to the special characteristics of the plasma created by the laser ablation. The basic concept is that, starting from a target with a Eu$_{3}$O$_{5}$ stoichiometry and performing the deposition in vacuum, there is an oxygen loss process when the laser plasma is formed, and as a consequence, reduced EuO films can be produced if the base vacuum is low enough. By increasing the base pressure, it is possible to obtain films of fully oxidized Eu$_{3}$O$_{5}$. However, it is also necessary to understand the underlying physics that leads to the formation of the EuO$_{3}$ thin films at room temperature. The Gibbs free energy (GfE) of formation in standard material states is given by the equations

$$\Delta G_f = \Delta H_f - T \Delta S_f$$

(2)

$$\Delta H_f = \sum_{i} a_i \Delta H_f^{products} - \sum_{f} b_f \Delta H_f^{reagents}$$

(3)

$$\Delta S_f = \sum_{i} a_i \Delta S_f^{products} - \sum_{f} b_f \Delta S_f^{reagents}$$

(4)

where $\Delta G_f$ represents the GfE of formation, $\Delta H_f$ and $\Delta S_f$ are the enthalpy and entropy variations, respectively, and $T$ is the temperature. In this work, we are changing the base pressure, and therefore, we can determine the change in the Gibbs free energy due to a change in pressures at constant temperature through

$$\Delta G_f = G(p_f) - G(p_i) = \int_{p_i}^{p_f} V dP$$

(5)

where $p_f$ and $p_i$ are the final and initial pressures, respectively, and $V$ is the material volume. For our case, we can use the GfE of formation in standard states (298 K and 1 atm) to discuss the results because the sensitivity of GfE to changes in pressure is negligible (this means that $V$ may be treated as a constant and taken outside the integral in eq 5). The GfE of formation in standard states of Eu$_{2}$O$_{3}$ and EuO are $\approx 1565$ and $\approx 557$ kJ mol$^{-1}$, respectively.$^{31}$ The negative values are in agreement with the observed spontaneous formation of our compounds. From these values, it follows that the Eu$_{2}$O$_{3}$ is the most stable phase, and therefore, it should be the dominant phase in the films. However, under a base pressure of $1.3 \times 10^{-7}$ mbar, the lowest used in this work, the films have EuO composition. Therefore, in the plasma generated by the laser ablation upon vaporization of the Eu$_{2}$O$_{3}$ target, the oxygen are more easily defected that the europium species in the plasma collisions and fail to reach the substrate.$^{32}$ In these conditions, EuO films are formed. When the base pressure is increased, the plasma generated by the laser is more confined due to the residual vapor pressure in the chamber, and less oxygen is deviated in the collision processes and more oxygen species reach the substrate. In these conditions, rich EuO$_{3}$ films ($1 < x < 3/2$) are formed. As long as the films remain in the vacuum chamber, the formed films are stable; however, because GfE (Eu$_{2}$O$_{3}$) < GfE (EuO) in ambient conditions, i.e., oxygen-rich atmosphere, the oxidation of the EuO is dramatically enhanced. Ideally, to keep the desired stoichiometry unaltered in the as-grown film when exposed to air, a protective encapsulating coating would be highly desirable. In our films, this is provided by a Al$_{2}$O$_{3}$ nanometer-thick layer owing to its higher value of GfE ($\approx 1582$ kJ mol$^{-1}$) in comparison with that of EuO, which makes unlikely its reaction with the underlying EuO$_{3}$ thin films.

To gain a deeper insight into the structure of the films, XRD measurements have been performed on the EuO$_{3}$ films, confirming the presence EuO nanocrystals with average sizes of $\approx 5$–7 (± 1) nm, obtained by means of the Scherrer equation, independently of the background pressure used during deposition. Details on the XRD measurements are
provided in the Supporting Information. In particular, the XRD spectra show broad peaks corresponding to EuO nanocrystals with crystalline planes (111) and (220) for the EuO and EuO$_{1.4}$ thin films and only EuO nanocrystals with the crystalline plane (111) for the EuO$_{1.4}$ thin film. In the following, we will refer to the films by their composition. In Figure 2a, a representative image of the HRTEM measurements is reported. The detailed HRTEM analysis has been performed on the EuO$_{1.2}$ because it is the most interesting film and, according to the XPS and XRD analyses, contains Eu both in the 2+ and 3+ oxidation states. The FFT of this figure is given in Figure 2b where the reflections corresponding to nanocrystals with a NaCl structure are resolved, oriented along the [011] zone axis for the (220) crystalline plane and [001] for the (200) crystalline plane, and a lattice parameter of $a_0 = 5.14 \pm 0.02 \text{ Å}$, comparable to the one of bulk EuO. The intermediate areas are represented in a blue color, and the brighter FFT spots correspond to the (222) planes in Eu$_2$O$_3$ with a lattice spacing of $(3.15 \pm 0.02) \text{ Å}$ and a lattice parameter $a_0 = (10.86 \pm 0.02) \text{ Å}$. As evidenced in Figure 2b, the Eu$_2$O$_3$ regions, together with the noncrystallized zones (dark zones), are situated in the free volume between the EuO nanocrystals. The Al$_2$O$_3$ protecting layer (not shown) is found in the dark zones, are situated in the free volume between the EuO nanocrystals. The (200) protecting layer (not shown) is found in the dark zones, are situated in the free volume between the EuO nanocrystals. The Al$_2$O$_3$ protecting layer (not shown) is found in the dark zones.

In Figure 2c, it is shown through a high-resolution detail of the EuO nanocrystal where the interatomic planes are resolved with an interplanar distance of $2.58 \text{ Å}$ (theoretical value of $2.57 \text{ Å}$). These results indicate the formation of EuO nanocrystals surrounded by Eu$_2$O$_3$ nanocrystalline and amorphous regions. The HRTEM observations are in excellent agreement with the XRD analysis that showed the formation of nanocrystals with average sizes in the 5−7 (±1) nm range. The TEM analysis is in good agreement with the XPS results that show the coexistence of Eu$^{2+}$ and Eu$^{3+}$ oxidation states.

Photoluminescence (PL) measurements have been performed under an ultraviolet laser ($\lambda = 355 \text{ nm}$) to obtain the optical emission of the EuO$_{x}$ thin films. It is known that the luminescent properties of the europium ions depend on their valence state. In particular, the emission of Eu$^{3+}$ ions shows a series of narrow emission peaks with long lifetimes, i.e., electronic transitions $D_0 \rightarrow F_j$ ($j = 0, 1, 2, 3, 4, 5, 6$) of the 4f orbitals. However, the emission of the Eu$^{2+}$ ions is characterized by a broad emission band with short lifetimes due to the transitions of the electrons from the 5d to the 4f orbitals. Figure 3a shows the visible (VIS) photoluminescence of the EuO$_{x}$ thin films displaying a different behavior depending on the oxidation state for EuO, EuO$_{1.2}$, and EuO$_{1.4}$ thin films. In particular, EuO shows a broadband emission centered in $\approx 525 \text{ nm}$ associated to the 5d $\rightarrow$ 4f electronic transitions. The EuO$_{1.2}$ thin film in which both 2+ and 3+ oxidation states are found is relevant according to the XPS and HRTEM analysis presents a mixture behavior. First, there are two bands centered at $\approx 460$ and $560 \text{ nm}$, which are associated to emissions of the 5d $\rightarrow$ 4f electronic transitions of the Eu$^{3+}$ ions. Second, there is a small and narrow emission line at $615 \text{ nm}$, attributed to the emission of intra-4f transitions of the Eu$^{3+}$ ions. At this point, it is important to note that the 5d orbitals of Eu$^{2+}$ ions are very sensitive to the changes of the crystal field because they are in the outer electronic shell compared with the inner 4f orbitals. It is reported also that the incorporation of oxygen on the nanocrystals surface has strong consequences as it modifies the concentration of charge carriers, thus affecting the electronic, magnetic, and optical properties. Therefore, the emission spectra strongly depend on the nature of the Eu$^{2+}$ surroundings. Indeed, by means of HRTEM, we found EuO nanocrystals surrounded by both amorphous and crystalline areas, which affects differently to the configuration of the 5d orbitals, which would explain the two emission bands found in the EuO$_{1.2}$ PL spectrum. Finally, the spectrum of the EuO$_{1.4}$ thin film presents narrow emissions corresponding to Eu in the 3+ oxidation state associated to $D_0 \rightarrow F_2$ intra-4f electronic transitions, which is also in agreement with the XPS results. The emission trend of the films as a function of

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) HRTEM image of the film (EuO$_{1.2}$). (b) FFT-filtered TEM image. In green color: EuO nanocrystals with the (220) and (200) crystalline orientations. In blue color: nanocrystalline Eu$_2$O$_3$ areas. (c) Detail of a EuO nanocrystal (green zone in panel b) with the (200) crystalline orientation.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a) Photoluminescence spectra and (b) interpolated PL intensity map of the EuO$_x$ films obtained under UV (355 nm) laser excitation. (c) The filled color of each graph represents the color emission established by the Commission Internationale de l’Eclairage (CIE) in 1931, known as the CIE 1931. (b) CIE 1931 x-y color matching functions for the corresponding EuO$_x$ thin films.
their oxygen content is more clearly seen in Figure 3b where an interpolated intensity map of the emission is represented. The main PL contribution for the EuO film (centered in ≈525 nm) is shifted to the red to ≈550 nm for the EuO1.4 thin film, i.e., as the oxidation state in the surroundings of the EuO nanocrystals increases. This is further verified by the emission of the Eu ions in the 3+ oxidation state, as observed in the PL spectrum by the narrow emission in 615 nm. Finally, for the most oxidized sample, the EuO1.4 thin film, we only find emission of Eu ions in the 3+ oxidation state. Hence, these results are in perfect agreement with XPS, XRD, and HRTEM analysis where we can control the oxidation state by setting the base pressure, eventually leading to a tuning of the optical emission.

To determine the visible “color” emission of the EuO thin films, we have calculated the chromatic coordinates of the photoluminescence using a MATLAB script. For this purpose, we have chosen the three-color matching functions established by the Commission Internationale de l’Eclairage (CIE) in 1931, i.e., the CIE 1931 x-y color matching functions. The resulting chromaticity plot is represented in Figure 3c and shows the eye perception of color emission for each thin film. It is remarkable for the broad emission spectrum obtained for the films EuO (green) and EuO1.2 (yellow), which is intrinsically related to the surroundings of the Eu3+ ions present in the Eu3+ nanostructured EuO1.4 thin film presents a narrow and pure red emission attributed to the intra-4f transitions of the Eu3+ ions. The results confirm the possibility of shifting the color emission from green to red by controlling the Eu oxidation state, opening a way to the fine-tuning of the visible emission for the development of optically active nanometer-sized emitters integrated on silicon, which are very promising for one-compound nanostructured displays.

# CONCLUSIONS

In this work, we have prepared EuO thin films that show tunable photoluminescence by varying their stoichiometry in a wide range (1 ≤ x < 1.4). The compositional and structural analysis show that they are formed by EuO nanocrystals. The different nominal stoichiometries have been successfully achieved by simply controlling the background pressures of the vacuum chamber from 1.3·10⁻⁷ mbar (EuO) to pressures above 53·10⁻⁷ mbar (EuO1.4). The photoluminescence light emission of the EuO films evolves from a broadband band centered in the green attributed to 5d → 4f transitions of Eu²⁺ ions to a narrow red emission attributed to the intra-4f transitions of the Eu³⁺ ions. The experimental findings reported in this work open wide perspectives of nanodimensional EuO films for “one-component” tunable optoelectronic applications for their incorporation in integrated silicon-based devices.

# ASSOCIATED CONTENT

4 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c03052.

Information about the analysis and discussion of the XRD data (PDF)

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