

Optimal composition of europium gallium oxide thin films for device applications

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Europium gallium oxide ($\text{Eu}_x\text{Ga}_{1-x}\text{O}_3$) thin films were deposited on sapphire substrates by pulsed laser deposition with varying Eu content from $x=2.4$ to 20 mol %. The optical and physical effects of high europium concentration on these thin films were studied using photoluminescence (PL) spectroscopy, x-ray diffraction (XRD), and Rutherford backscattering spectrometry. PL spectra demonstrate that emission due to the $^5\text{D}_0$ to $^7\text{F}_J$ transitions in Eu^{3+} grows linearly with Eu content up to 10 mol %. Time-resolved PL indicates decay parameters remain similar for films with up to 10 mol % Eu. At 20 mol %, however, PL intensity decreases substantially and PL decay accelerates, indicative of parasitic energy transfer processes. XRD shows films to be polycrystalline and beta-phase for low Eu compositions. Increasing Eu content beyond 5 mol % does not continue to modify the film structure and thus, changes in PL spectra and decay cannot be attributed to structural changes in the host. These data indicate the optimal doping for optoelectronic devices based on ($\text{Eu}_x\text{Ga}_{1-x}\text{O}_3$) thin films is between 5 and 10 mol %. © 2010 American Institute of Physics. [doi:10.1063/1.3319670]

I. INTRODUCTION

Beta-phase gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) has received considerable attention in recent years as a material for wide bandgap, self-assembled nanostructures,^{1,2} and as an efficient luminescent host material for a number of trivalent rare earth ions.³ In the case of europium doped gallium oxide, the radiative lifetimes can be quite long (1.4 ms),⁴ indicating it may be a viable gain medium for optically pumped lasers.

Trivalent rare earth ions are commonly used in laser gain media, cathode ray tube phosphors, fluorescent lighting, and thin film electroluminescent (TFEL) devices. Their optical properties stem from a unique electronic structure, electrons in the outer $5s$ and $5p$ orbitals substantially screen electrons in the incomplete $4f$ orbital from the local electric field of the host. This screening reduces the effect of the host on the emissive and absorptive properties of the rare earth dopant, resulting in spectrally narrow emission and absorption bands from radiative transitions within the free ion like $4f$ states.

It has been historically difficult to achieve bright red electroluminescent (EL) phosphors from traditional sulfide phosphors such as ZnS and SrS. The most efficient red EL devices were fabricated using filtered Mn:ZnS, which has a broad yellow emission band owing to the $^4\text{T}_1$ to $^6\text{A}_1$ transition in the Mn^{2+} dopant.⁵ However, filtered TFEL devices are imperfect alternatives due to reduced efficiency. More recently, bright red TFEL devices have been made from Eu:Ga₂O₃ (Refs. 6 and 3) that exploit the radiative $^5\text{D}_0$ to

$^7\text{F}_J$ transitions in Eu^{3+} . Other successful red EL phosphors include Eu:CaS (Ref. 7) but it has been reported that non-ideal device characteristics are observed for donor or acceptor type impurities and that isovalent impurities are preferred.⁸ Thus, to best exploit the unique luminescent properties of trivalent rare earth dopants, it would be preferable to implement a TFEL device using a phosphor with a group III cation. Examples of such phosphors would include III-V semiconductors such as GaN^{9,10} and sesquioxides such as Ga₂O₃ (Refs. 3 and 6) or Y₂O₃.¹¹

Rare-earth doped semiconductor materials and devices are typically fabricated with dopant concentrations on the order of a few atomic percent.^{4,12-14} Increasing dopant concentration typically results in increased optical intensity from thin films or devices but beyond a critical concentration the luminescence intensity and radiative lifetimes abruptly decrease. This observed quenching may arise from the formation of nonradiative defect states, reduced efficiency of traps at dopant sites, and the rapid nonradiative energy transfer from the rare earth ion's excited state to neighboring ions or defect states.

It is important to investigate the optimal dopant concentrations in TFEL device phosphors so that new bright, efficient devices can be realized throughout the visible spectrum, resulting in improved full-color displays. Active-matrix pixels have been demonstrated using organic light-emitting diodes (OLEDs) utilizing novel amorphous materials for the thin film transistor (TFT) backplanes.^{15,16} More recently, these amorphous TFTs were integrated with an amorphous TFEL device structure,¹⁷ resulting in a visible-transparent pixel. Integration of these backplanes with bright,

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transparent TFEL devices could be technologically important for certain applications such as heads-up displays for automotive or military applications.

In this study, the effects of high europium content on optical and structural properties of $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$ thin film samples were studied by photoluminescence (PL) and x-ray diffraction (XRD). In order to ascertain the optimal composition of such films for TFEL device applications, we quantify how the luminescence intensity and radiative lifetimes depend on structural changes in $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$ as the Eu^{3+} content x increases over the range of 2.4–20 mol %.

II. EXPERIMENTAL

A. Thin film deposition

Pulsed laser deposition (PLD) was used to deposit thin films of beta-phase $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$ onto double-side polished *c*-axis sapphire substrates. PLD was performed using a Lambda Physik Compex 201 KrF excimer laser with 250 mJ energy per 20 ns pulse at 10 Hz, incident on a 1 in. diameter target with the desired stoichiometry. The substrates are heated to 850 °C to encourage beta-phase formation. Deposition was carried out in 5 mTorr oxygen ambient while the substrate was rotated at 13 deg/s to ensure uniform film deposition. To reduce surface pitting, the PLD target was rastered along a 15° arc and rotated (12 deg/s) during ablation. The laser spot is focused to an estimated area of 0.05 cm². Deposited films were 600 to 700 nm thick.

The PLD targets contained Eu in varying amounts between $x=2.4$ to 20 mol %, as confirmed by Rutherford backscattering spectrometry (RBS). RBS spectra, not shown here, indicate that the stoichiometry of the ablated targets was successfully transferred to the films, with the films showing a moderate oxygen deficiency and very slightly more europium content than expected. Expected Eu molar percentages in the films were 2.4, 5, 10, and 20 mol %, which are in good agreement with RBS results of 2.75, 5.25, 9.5, and 21.25 mol %, respectively. These percentages were obtained by simulation of RBS spectra using RUMP software. Exact determination of the oxygen content in these thin films is complicated by the use of sapphire substrates where backscatter from Al in the substrate coincides in energy with backscatter from subsurface oxygen in the film. As such, the metal:oxygen ratio was assumed stoichiometric, providing a close fit to obtained RBS data, however, qualitative inspection of the experimental data and simulation results reveals the films were slightly oxygen deficient. The europium distribution throughout the thickness of the films was uniform, and the front and back surfaces of the films were smooth.

B. Characterization

Continuous wave PL (CWPL) spectra were captured using an Ocean Optics USB4000 fiber-coupled charge coupled device (CCD) spectrometer for a qualitative comparison of optical intensity. Films were optically pumped using a 1 mW, 280 nm LED. For time-integrated and time-resolved photoluminescence (TIPL and TRPL) spectroscopy, the samples were excited using a frequency-tripled Quantronix Titan 1 kHz pulsed Ti:sapphire amplifier (266 nm), with pulse

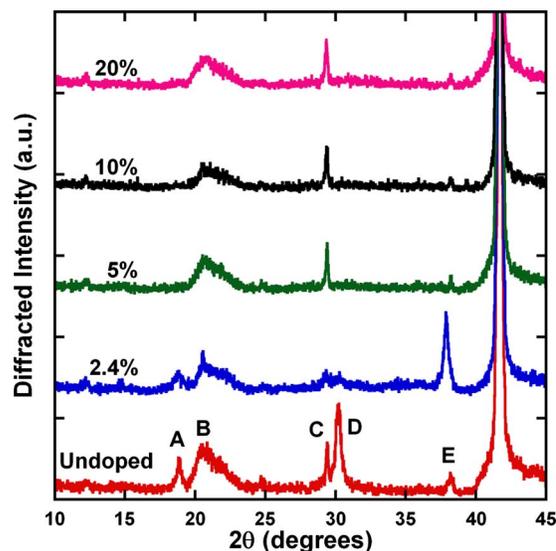


FIG. 1. (Color online) XRD spectra for undoped Ga_2O_3 and $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$ with increasing Eu molar percentage. The undoped film is polycrystalline and demonstrates characteristic monoclinic diffraction peaks. The peaks labeled A, C, D, and E have been assigned to the $(\bar{1}02)$, (004) , $(\bar{1}04)$, and $(\bar{1}13)$ planes in monoclinic Ga_2O_3 , while the B peak is an instrument artifact. The peak at 29.25° for 5 mol % is assigned to the (004) plane of monoclinic Ga_2O_3 .

widths near 100 fs. TIPL data were taken for laser intensities of $68 \pm 12 \mu\text{J}/\text{cm}^2$, while TRPL data was taken with an intensity of $\sim 100 \mu\text{J}/\text{cm}^2$. TIPL was dispersed by an Acton Research grating spectrometer with a focal length of 0.3 m and detected by a liquid nitrogen-cooled Princeton Research CCD. The spectral resolution of that instrument was 0.3 nm. For TRPL, the luminescence was dispersed by a 0.75 m Spex monochromator, coupled to a thermoelectrically cooled Hamamatsu R928 photomultiplier tube whose output was monitored by a 1 GHz oscilloscope to capture the luminescence decay with 0.5 nm and 2 μs resolution.

III. RESULTS AND DISCUSSION

XRD data was acquired using a Rigaku D/Max III diffractometer with Cu K_α radiation in the θ - 2θ configuration. XRD results indicated that all $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$ films are monoclinic and polycrystalline, as deposited. The monoclinic phase is identified by comparing measured diffraction data with known diffraction peaks listed in the International Center for Diffraction Data catalog. Films were observed to be polycrystalline as the numerous diffraction peaks correspond to multiple crystal orientations. One Ga_2O_3 film was deposited under the same conditions for comparison and produced diffraction peaks corresponding to the $(\bar{1}02)$, (004) , $(\bar{1}04)$, and $(\bar{1}13)$ planes as shown in Fig. 1 with the labels A, C, D, and E, respectively. The broad feature, labeled B, is an instrument artifact observed with all films in this study, as well as with a Si calibration standard. Also, diffraction from the (0006) plane of the sapphire substrate is observed near 42° and serves to monitor the calibration of the diffractometer between subsequent scans.

The crystalline properties of the films evolve as the europium fraction increases. With 2.4 mol % Eu the diffraction

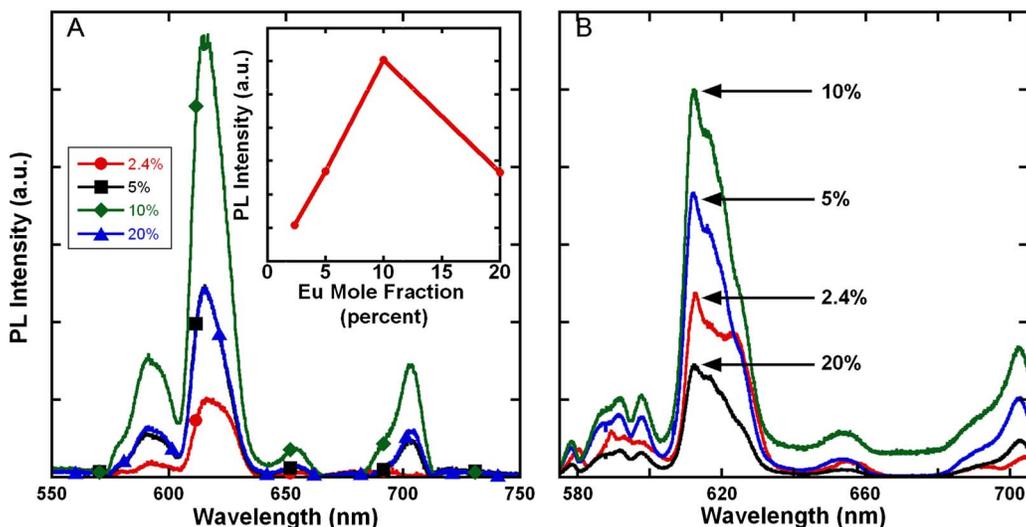


FIG. 2. (Color online) CWPL (a) and TIPL (b) spectra for $(\text{Eu,Ga}_{1-x})_2\text{O}_3$ with Eu content between 2.4 and 20 mol %. The peak intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is used to compare the relative intensity of the various films (inset).

peaks from the (004) and the $(\bar{1}04)$ planes become much weaker, while the $(\bar{1}13)$ peak is more intense and appears to have a small shift toward a larger plane spacing. This shift indicates strain in the film due to the significant difference in ionic radii between europium and gallium, an additional indicator that Eu^{3+} is substitutionally incorporated into the lattice. With further increases in europium fraction, a diffraction peak at 29.25° (two-theta) is observed and is assigned to the (004) plane in Ga_2O_3 .

CWPL and TIPL spectra in Fig. 2 demonstrate characteristic europium ion emission with the strongest peak at 611 nm caused by the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. Because the films were much thicker than the absorption depth of the excitation, variations in the intensity arise from the varying efficiency of the emission. Although the fine structure in PL spectra is unresolved at room temperature, higher europium fractions do not substantially broaden spectral features. Due to the large change in the angular orbital quantum number, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is highly sensitive to local fields and demonstrates significant Stark splitting.¹⁸ The asymmetric shape of the emission peak, with a slight shoulder at longer wavelengths, corroborates previously observed Stark splitting of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition in Ga_2O_3 .¹⁹

The intensity of the 611 nm peak was used to gauge overall emission intensity as a function of Eu fraction (inset, Fig. 2). Whereas CWPL measures emission following the establishment of a new, photoinduced equilibrium carrier distribution, TIPL measures emission as a consequence of relaxation back to equilibrium following impulsive photoexcitation. Consequently, CWPL spectra provide insight relevant to TFEL device performance, while TIPL spectra provide more insight into intrinsic properties of the emitter.²⁰ The CWPL and TIPL results agree, emission intensity grows with Eu content up to 10 mol % and then falls off as more Eu is added. This agreement between CW and pulsed excitation indicates that the increase is an intrinsic effect directly attributable to the increasing Eu fraction, minimally influenced by photoexcitation conditions and excitation-dependent carrier equilibration.

However, the CWPL and TIPL results disagree about which sample was the weakest emitter, the 2.4 mol % Eu sample for CWPL or the 20 mol % sample for TIPL. To understand the connection between emission strength and excitation conditions, the radiative decay of the samples was measured (Fig. 3). TRPL decay data were integrated from 613 to 614 nm, slightly redshift from the peak value observed by TIPL at 611 nm. TRPL spectra exhibited a biexponential decay, representing two distinguishable processes depopulating the ${}^5\text{D}_0$ state in the Eu^{3+} ions. This TRPL decay is parameterized by the repeating biexponential equation

$$I_{\text{PL}} = \sum_{n=0}^2 [A_s e^{-(t+nt_0)/\tau_s} + A_f e^{-(t+nt_0)/\tau_f}], \quad (1)$$

where the sum of the relative strengths (A_s and A_f) is normalized to unity. The repeating exponential is required when either decay constant (τ_f or τ_s) is longer than the $t_0=1$ ms pulse repetition rate of the laser. The subscripts f and s de-

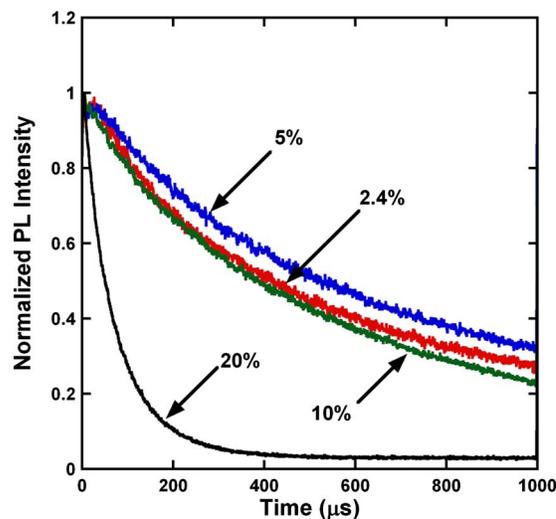


FIG. 3. (Color online) TRPL decay measured over 613–614 nm for films with varying Eu content.

TABLE I. Parameters of biexponential fit to TRPL decays shown in Fig. 3. The uncertainties in the least significant digit(s) are shown in parentheses.

Eu mole fraction x	A_f	τ_f (ms)	A_s	τ_s (ms)
0.024	0.402 (5)	0.160 (4)	0.598 (9)	0.930 (10)
0.05	0.410 (10)	0.250 (10)	0.590 (20)	1.130 (30)
0.10	0.256 (4)	0.148 (4)	0.743 (6)	0.736 (4)
0.20	0.308 (6)	0.0316 (8)	0.692 (8)	0.0885 (4)

note relatively “fast” and “slow” processes parameterized by this biexponential equation, respectively. The parameters found from this fitting procedure are summarized in Table I.

The decay constants of the 2.4 and 5 mol % samples ($\tau_f \approx 0.4$ ms, $\tau_s \approx 1$ ms) agree with previous reports of Eu-doped Ga_2O_3 thin films ($\tau_f \approx 0.2$ ms, $\tau_s \approx 1.4$ ms),⁴ indicating relaxation is still dominated by radiative decay from $^5\text{D}_0$ to the $^7\text{F}_J$ family of states. The rate constants begin speeding up for the 10 mol % sample because the increased Eu concentration introduces competing, nonradiative quenching mechanisms that sap excitation from the $^5\text{D}_0$ state,^{12,13} suggesting that the optimal Eu content is $5 \leq x \leq 10$ mol %. Both time constants accelerate sharply for the 20 mol % Eu-doped film ($\tau_s < 90$ μs), clearly indicating that the TIPL emission from the 20 mol % sample is quenched. The fact that this 20 mol % sample has a brighter CWPL spectra than the 2.4 mol % sample suggests that quenching is somewhat compensated during CW excitation by the photo-excited carrier distribution.

Although Eu ion or Eu_2O_3 clustering has been observed for large Eu concentrations in other hosts,^{21–24} formation of Eu_2O_3 phases is not believed to be responsible for the luminescence quenching observed. Characteristic Eu^{3+} luminescence from bulk monoclinic Eu_2O_3 has been reported^{25,26} with emission features that do not agree with the spectra presented in this study.

Rather, the accelerated decay parameters observed for the 20 mol % sample are attributed to the effects of rapid, nonradiative energy transfer from excited Eu^{3+} ions either to other nearby ions or directly to quenching centers. For example, as the concentration of Eu ions is increased, the average ion–ion distance decreases, subsequently increasing the likelihood of parasitic ion-ion energy transfer.^{27,28} Similar energy transfer mechanisms have been observed in $\text{Eu}:\text{GaN}$ (Ref. 13) where site-selective spectroscopy revealed that one of the sites luminesced only under CW and not pulsed excitation. The equilibrium conditions established under CWPL enabled the Eu site to be excited via a similar energy migration mechanism. However, given the experimental data presented here, it cannot be determined whether luminescence is quenched due to lossy ion–ion energy transfer or if energy is transferred to nonradiative defect centers. Both mechanisms may become dominant with increasing Eu fraction given the reduced ion–ion distance or potentially increased defect density.

IV. CONCLUSIONS

Thin films of beta-phase $(\text{Eu}_x\text{Ga}_{1-x})_2\text{O}_3$ have been deposited on sapphire by PLD with varying europium content from

$x=2.4$ to 20 mol %. RBS indicates that the stoichiometry of the prepared target is faithfully transferred to the deposited thin films. All films can be identified as having the monoclinic structure. As europium content increases above 5 mol %, the film structure remains unchanged with most crystallites having the (004) orientation. Based on CWPL and TIPL luminescence intensity and TRPL lifetimes, the optimal europium fraction lies between 5 and 10 mol %. The 2.4 and 5 mol % Eu films demonstrate similar decay characteristics to films previously reported with lower dopant concentrations. For europium fractions above 5 mol % rapid, parasitic energy transfer from excited Eu ions accelerates the observed luminescence decay.

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