Optical properties of differing nanolayered structures of divalent europium doped barium fluoride thin films synthesized by pulsed laser deposition

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Abstract:

Optically-active thin films are employed in a variety of applications, such as LEDs and photovoltaics, due to their ability to act as up- or down-photon energy converters. Their performance depends critically on their composition and structure; thus, the use of novel synthesis techniques that allow for their control at the nanoscale level can result in improved efficiency and practicality. Layered thin films consisting of Eu²⁺-doped BaF₂ nanocrystalline layers separated by amorphous Al₂O₃ were synthesized via sequential pulsed laser deposition using three separate targets for the different components; this synthesis technique provides precise control of layer thickness at the nanoscale along with dopant distribution within the film. Cross-sectional transmission electron microscopy analysis verified the desired nano-layering. Post-deposition heat treatments in a nitrogen atmosphere resulted in samples exhibiting steady and emission with a broad peak ranging from 400-600 nm and a shoulder at 410 nm. The CIE 1931 chromaticity coordinates are $x = 0.26-0.29$ and $y = 0.32-0.35$ as a function of the sample configuration. Because the chromaticity coordinates are close to those of a pure white light ($x = 0.33, y = 0.33$), these films demonstrate advantageous properties for applications with UV-pumped white light LEDs.

Introduction

Light-emitting diode (LED) solid-state lighting boasts many advantageous characteristics including low energy consumption, high brightness, and a long lifetime [1-3]. Currently, the most common commercially-available white-LEDs use an InGaN chip, which produces blue light, combined with the phosphor YAG:Ce³⁺, which downshifts a portion of the blue emission to create broadband emission [4-6]. A white light LED producing broadband visible emission and incorporating a single-phase host material would result in a simpler manufacturing process. Different materials are being investigated to improve commercially-available white-LEDs [7]. A possible concept that is in its infancy of development is an ultraviolet (UV)-pumped white-LED, in which UV photons are downshifted to provide broadband visible emission [8].

Divalent europium can present broadband emission that is highly susceptible to crystal field splitting [9]. The broad tunable emission has made Eu²⁺ a popular doping candidate for single-phase host materials with white-LED applications [10]. The Eu²⁺ emission is associated with the 4f⁶5d¹ to 4f⁷ electron transition which occurs in the outer orbitals [11]. The location of this transition allows coordinate surroundings of the host to influence the energy of the emitted photon [7]. Changes in the nephelauxetic effect of different host lattices along with crystal field splitting allow Eu²⁺ emission to emit over the range of ultraviolet to red light [12]. The effects of crystal field splitting on Eu²⁺ emission is illustrated in Figure 1.

Figure 1. Partial energy level diagram of Eu^{2+} demonstrating how broadband emission is an outcome of crystal field splitting. Adapted from [13].

The europium-doped nanocrystal luminescence depends upon many factors. Pure, single crystal, europium-doped barium fluoride typically reveals only Eu^{3+} luminescent centers due a narrow band gap, which differs from europium-doped calcium fluoride containing Eu^{2+} [14, 15]. $\text{BaF}_2:\text{Eu}$ nanocrystals within a glass host reveal emissions of either singly Eu^{2+} or both Eu^{2+} and Eu^{3+} depending on the ambient conditions [16, 17]. Previous work has revealed that factors such as dopant concentration, nanocrystalline size, and synthesis temperatures play a crucial role in the ability to synthesize divalent europium doped BaF_2 nanocrystalline complexes [18, 19].

Glass-ceramics containing rare-earth doped fluoride crystalline material have been developed for potential applications such as wavelength shifters for solar cells and LEDs [20, 21]. The low phonon energy fluoride nanocrystalline matrix provides a favorable host for rare-earth dopants [22, 23]. Likewise, an oxyfluoride amorphous material provides a low phonon energy environment advantageous for optically-active dopants [24]. It has been shown that when europium is added to aluminum oxide, the Al^{3+} cation facilitates the reduction of Eu^{3+} to Eu^{2+} to develop materials capable of broadband emission ideal for white light LED applications [25, 26]. Their performance depends

critically on their composition and structure; thus, the use of novel synthesis techniques that allow for control at the nanoscale level can result in improved efficiency and practicality.

In this study, optical behavior of thin films with layers of nanocrystalline BaF₂, amorphous Al₂O₃, and a europium dopant, were synthesized by using sequential pulsed laser deposition. This synthesis technique provides precise control of layer thickness at the nanoscale level along with dopant distribution within the film. The amorphous Al₂O₃ layers contribute to encapsulating the fluoride host to prevent oxidation, which can limit optical performance. Different nanolayered structures were synthesized and photoluminescent (PL) emission measurements were obtained using a 355 nm excitation laser to determine the ability of the material to act as a UV-pumped LED. The objective of this study is to demonstrate the ability to manipulate nanolayer structure to affect optical properties. While all three produced sample structures show promising optical characteristics for UV-pumped white-LED applications, the differences in the nanolayered structures give a better understanding as to how the emission is affected by the Eu²⁺ coordinate environment. Cross-section transmission electron microscopy (TEM) analysis was conducted to verify the nanolayered structure of the samples.

Materials and Methods

Commercially available targets of Al₂O₃, BaF₂, and Eu₂O₃ were ablated to produce layered thin films via pulsed laser deposition (PLD). The pressure in the system was maintained below 3.0×10^{-6} Torr during deposition. An ArF excimer laser with a 193 nm wavelength beam with a rated pulse length of 20 ns was used. Films were deposited on single side polished, 475-575 μ m thick, test grade silicon wafers in the <100> crystalline orientation. The substrates were cleaned with an acetone rinse, ultrasonically in ethanol for 5 minutes, then dried with compressed nitrogen prior to their placement in the

deposition chamber. Al_2O_3 , BaF_2 , and Eu_2O_3 deposition parameters are detailed in Table 1. The different substrates positions are illustrated in Figure 2.

Table 1. PLD parameters of all of the materials that were ablated.

Material	Laser Fluence	Laser Frequency	Substrate Position ^a	Target-substrate Distance
Al_2O_3	$4.7 \text{ J}\cdot\text{cm}^{-2}$	20 Hz	20°	37.8 mm
BaF_2	$4.7 \text{ J}\cdot\text{cm}^{-2}$	20 Hz	180°	86.0 mm
Eu_2O_3	$1.3 \text{ J}\cdot\text{cm}^{-2}$	10 Hz	20°	37.8 mm

^a Substrate position is angle off-axis relative to the shared axis position.

Figure 2. Illustration displaying different substrate positions used to deposit Al_2O_3 and Eu_2O_3 , rotated 20° from the conventional shared axis position (substrate position 1), and BaF_2 , rotated 180° from the shared axis position (substrate position 2).

Three different layer configurations were designed in order to explore the Eu doping of BaF_2 (Structures 1 and 3) and the potential of having the Eu doping at the $\text{BaF}_2/\text{Al}_2\text{O}_3$ interface (Structure 2). Schemes of the different samples structure are shown in Figure 3.

Figure 3. Illustration of different thin film layer configurations synthesized to investigate dopant incorporation. (a) Sample Structure 1, (b) Sample Structure 2, and (c) Sample Structure 3.

Sample Structure 1 (Figure 3a) was synthesized by sandwiching an Eu_2O_3 layer between two BaF_2 layers and the Al_2O_3 matrix layers. An initial 2000 laser pulses were used on the Al_2O_3 target, followed by 2140 laser pulses on BaF_2 , 430 laser pulses on Eu_2O_3 , and 2140 laser pulses on BaF_2 . This sequence ($\text{Al}_2\text{O}_3/\text{BaF}_2/\text{Eu}_2\text{O}_3/\text{BaF}_2$) was initially repeated 5 times and a final 2000 pulse Al_2O_3 layer was grown as a protective cap. At this point in the process, a sample was removed from the deposition chamber, and an additional 5 layers with a final cap was grown on top of a sample that remained in the chamber.

Sample Structure 2 (Figure 3b) was synthesized by depositing an Eu_2O_3 layer on top of BaF_2 layers with Al_2O_3 base layers. An initial 2000 laser pulses were used on the Al_2O_3 target, followed by 4280 laser pulses on BaF_2 and 430 laser pulses on Eu_2O_3 . This sequence ($\text{Al}_2\text{O}_3/\text{BaF}_2/\text{Eu}_2\text{O}_3$) was initially repeated 5 times and a final 2000 pulse Al_2O_3 layer was grown as a protective cap. Identical to the previous structure, a sample with 5 layers and another sample with 10 layers was grown.

Sample Structure 3 (Figure 3c) was synthesized by alternating BaF_2 and Eu_2O_3 between Al_2O_3 layers. After an initial 2000 laser pulses on the Al_2O_3 target, 1710 laser pulses were used on the BaF_2 target, followed by 100 laser pulses on the Eu_2O_3 target. The $\text{BaF}_2/\text{Eu}_2\text{O}_3$ sequence was repeated 10 times and a final 2000 pulse Al_2O_3 layer was grown as

a protective cap. A sample was kept with 1 ($\text{Al}_2\text{O}_3/(\text{BaF}_2/\text{Eu}_2\text{O}_3) \times 10$) sequence and 2 additional sequences were grown on a separate sample, resulting in a total of 3 repeating sequences.

Cross-sectional TEM samples were prepared from Sample Structure 1 films by focused ion beam (FIB) milling. To protect the films from FIB damage, the samples were coated with a layer of Au using electron-beam evaporation before milling. TEM was carried out using a JEM-2100F instrument with 200 kV incident electron energy, in order to investigate the structure of the cross-section samples.

Heat treatments were performed in both ambient atmosphere and using nitrogen purge gas to determine the effects of the different heat treatment conditions. Samples heat treated in an ambient atmosphere will be referred to as (amb) and samples heat treated in a nitrogen atmosphere will be referred to as (N_2). The ambient atmosphere heat treatments were performed in a MESTRA HP-25 muffle furnace. The heat treatments in a nitrogen atmosphere were performed in a Thermconcept 50/250/12 tube furnace using a lab-grade N_2 purge gas. In both atmospheres, the samples were heat treated at a heating ramp of 10 K/min to 300 °C, and held at that temperature for 1 hour, then allowed to cool to ambient temperature over time.

After the emission from the different sample structures were compared, the best sample configuration for UV-pumped white light LEDs was determined. Using this configuration, the emissions of a sample with 5 repeating sequences and 10 repeating sequences were compared to determine the effect of layer numbers on emission intensity. Both samples were heat treated to 300 °C in a nitrogen atmosphere for 1 hour. Following the post-deposition heat treatments, emission data were collected, and emission intensities were compared.

Photoluminescence studies were conducted by using a 355 nm Genesis CX 355-200 Optically Pumped Semiconductor Laser (Coherent) with a power of approximately 8 mW as the excitation source. A monochromator (ActonSpectraPro300i, diffraction grating=1200 g/mm (Vis)) filtered the light emitted by the samples, which was detected through a photomultiplier tube (EMI9659QB-S20). In addition, the signal was amplified with a standard lock-in technique. CIE 1931 chromatic coordinates were obtained by processing the emission data in Origin 2021 version 9.8 (OriginLab) and utilizing the Chromaticity Diagram v1.1 application.

Results and Discussions

Microscopy

Cross-section TEM analysis verified that the films were grown with the intended layered nanostructures. Figure 4 shows a TEM cross-section of Structure 1 as-made with 5 and 10 layers. Both samples show clear layering with the layers being uniform throughout the film. The darker contrast layers correspond to the Eu_2O_3 deposits, the lighter contrast layers are attributed to Al_2O_3 , and the BaF_2 show an intermediate contrast. The 5 layer film has a total thickness of 50 nm and the 10 layer sample has a total thickness of 99 nm. The 10 layer film (Figure 4b) presents an anomaly in the multilayer periodicity, two layers down from the gold protective cap, where the layer does not show the dark contrast associated with Eu_2O_3 . This anomaly is likely due to a malfunction of the stepper motor that controlled the target position, resulting in Eu_2O_3 not being ablated for that layer; such malfunctions have occurred with this particular deposition system in the past and are the subject of ongoing troubleshooting. The wide light layer in the middle of the sample seen in Figure 4b is because of the double thickness of Al_2O_3 deposited between the first and second 5 layer sequences (see Figure 3a). Electron diffract patterns reveal that BaF_2 is deposited as amorphous when the layer thickness is less than 3 nm, and begin to exhibit

a $\langle 111 \rangle$ FCC crystal structure as layer thickness is increased. The structural evolution is detailed in the aforementioned complimentary article.

Figure 4. TEM cross-section images of as-made Sample Structure 1 Al₂O₃/ BaF₂/ Eu₂O₃ thin films synthesized with (a) 5 layers and (b) 10 layers.

Optical characterization

The emission spectra of the three as-deposited sample structures are shown in Figure 5. The three sample structures resulted in distinctly different PL emission. These differences demonstrate the consequence of their structural configuration on the emission of these materials. Structures 1 and 2 were synthesized with the same amount of Al₂O₃, BaF₂, and Eu₂O₃, with the only difference coming from the fact that in Structure 1, the Eu₂O₃ is sandwiched between two BaF₂ layers in each repeat, yet a difference in emission is seen. The layer sequence determines the local coordination environment of the luminescent center (Eu), which can be manipulated depending on the desired emission.

Figure 5. Emission spectra from a 355 nm excitation source for as-made (a) Structure 1 with 5 layers, (b) Structure 2 with 5 layers, and (c) Structure 3 with 1 layer .

The emission spectra for Sample Structure 1 with 5 layers as-made and heat treated are shown in Figure 6. The as-made sample did not exhibit any measurable emission expected from crystalline BaF₂, thus indicating that all of the layers in the sample were amorphous. A peak at 410 nm and a broad emission from 450 – 600 nm is seen in Structure 1 (amb). The 410 nm peak can be attributed to the 4f⁶5d¹ to 4f⁷ transition of Eu²⁺ incorporated in BaF₂ nanocrystals. The authors hypothesize that the broad emission from 400 – 600 nm can be attributed to Eu²⁺ in different environments such as the BaF₂ nanocrystalline matrix, the BaF₂/ Al₂O₃ interface, and the Al₂O₃ layers as shown in Figure 7. In Structure 1 (N₂), the intensity of the broad emission increases and the 410 nm emission is expressed as a shoulder indicating the movement of the Eu dopant into different environments. The emission spectra of all sample structures display a small peak at 700 nm, which can be attributed to the presence of Eu³⁺ exhibiting photoluminescence associated with the ⁵D₀ to ⁷F₄ electron transition [27].

Figure 6. Emission spectra of Sample Structure 1 with 5 layers from a 355 nm excitation source after (a) 1-hour heat treatment at 300 °C in ambient atmosphere, (b) 1-hour heat treatment at 300 °C in a nitrogen atmosphere, and (c) as-made sample.

Figure 7. Illustration showing atomic layers of a barium fluoride/aluminum oxide thin film and three different possible locations of a europium dopant.

The emission spectra for Sample Structure 2 with 5 layers as-made and heat treated are shown in Figure 8. The as-made film exhibited a broad emission centered at 540 nm. The spectrum of Structure 2 (amb) shows a 410 nm peak along with a broad emission that is comparable to Structure 1 (amb). Structure 2 (N₂) exhibits a broad emission from 400 – 600 nm and a shoulder at 410 nm are shown, but of lesser intensity when compared Structure 2 (amb). Both the emission spectra of Structure 2 (N₂), and Structure 2 as-made,

exhibit a slight peak at 610 nm that can be attributed to a 5D_0 to 7F_2 electron transition of Eu^{3+} [28]. This sample structure had the largest amount of $\text{Eu}_2\text{O}_3/\text{Al}_2\text{O}_3$ adjacent layers, which could prevent Eu from migrating into a reducing atmosphere due to the smaller percentage of adjacent $\text{BaF}_2/\text{Eu}_2\text{O}_3$ layers or the amount of oxygen present in the Al_2O_3 layers.

Figure 8. Emission spectra from a 355 nm excitation source for Sample Structure 2 with 5 layers after (a) 1-hour heat treatment at 300 °C in ambient atmosphere, (b) 1-hour heat treatment at 300 °C in a nitrogen atmosphere, and (c) as-made.

The emission spectra for Sample Structure 3 with 5 layers as-made and heat treated are shown in Figure 9. Unlike the previous two sample structures, the as-made Structure 3 exhibited the most intense emission when compared to the emissions after heat treatment. A sharp peak at 410 nm with a broader peak at 430 nm was found. Growing thicker layers of BaF_2 resulted in the layers being nanocrystalline as deposited, which then were able to luminesce prior to any post- synthesis heat treatment. With the Structure 3 (amb) emission, the 410 nm peak intensity decreased resulting in a broader, less intense, peak with a range from 400 - 500 nm. A broad emission with consistent intensity between 400 - 650 nm was measured in Structure 3 (N_2).

Figure 9. Emission spectra of Sample Structure 3 with 5 layers from a 355 nm excitation source after (a) 1-hour heat treatment at 300 °C in ambient atmosphere, (b) 1-hour heat treatment at 300 °C in a nitrogen atmosphere, and (c) as-made sample.

The 410 nm peak, attributed to $\text{BaF}_2:\text{Eu}^{2+}$, is seen in all three structures following heat treatment in an ambient atmosphere. This peak shows that heat treatments facilitated Eu diffusion into the BaF_2 matrix and could have resulted in oxygen-aided emission quenching in the Al_2O_3 layers. Structure 3 exhibits the most intense $\text{BaF}_2:\text{Eu}^{2+}$ emission due to an increased percentage of adjacent $\text{Eu}_2\text{O}_3/\text{BaF}_2$ layers when compared to Structure 1 and 2. The authors hypothesize that broadening of the emission peaks following heat treatments in an inert atmosphere could be caused by the Eu dopant diffusing into Al_2O_3 layers, but without the emission quenching that was found with ambient atmosphere heat treatments. The dramatic changes in the emission of Structure 3, a structure with a relatively small amount of $\text{Eu}/\text{Al}_2\text{O}_3$ adjacent layers, found after different heat treatment conditions, support this hypothesis.

When repeated emission measurements were conducted at the same sample location on films that had been heat treated in an ambient atmosphere, the emission intensity decreased as demonstrated by Structure 1 in Figure 10. The longer the excitation laser was focused on the same location, the more the emission intensity decreased. A decrease

in emission intensity due to UV laser degradation was found for all sample structures following post synthesis heat treatments in an ambient environment and is repeatable for different sample locations. The main proposed mechanism in the literature for the degradation is photogeneration of defects [29, 30]. When Structure 1 was heat treated in nitrogen, no emission degradation occurred after exposure to the UV excitation laser, as shown in Figure 11. This could be related to the passivation of the Eu with nitrogen bonds, which leads to samples with a very robust response. These results agree with the work conducted by Amidani et al. [31], who stated that oxidation of Eu^{2+} to Eu^{3+} is the main mechanism that results in emission quenching. Further studies need to be conducted to determine if the degradation of these samples is reversible through heat treating or laser stimulation.

Figure 10. Emission spectra of Sample Structure 1 with 5 layers from a 355 nm excitation source after a 1-hour, 300 °C post- synthesis heat treatment in an ambient atmosphere. The spectra were obtained from consecutive measurements at the same sample location. Spectrum (a) is the first measurement, (b) is the second measurement, and (c) is the third measurement.

Figure 11. Emission spectra of Sample Structure 1 with 5 layers from a 355 nm excitation source after a 1-hour, 300 °C post- synthesis heat treatment in a nitrogen atmosphere. The spectra were obtained from consecutive measurements at the same sample location. Spectrum (a) is the first measurement and (b) is the second measurement.

Since emission intensity that does not significantly diminish over time is necessary for the proposed LED application, and we have seen that the emission stability against UV laser degradation of the samples heat treated in nitrogen was superior to that of samples subject to an ambient atmosphere, we have only analyzed the chromatic coordinates of the nitrogen heat- treated samples. The chromatic coordinates of all three sample structures following a 1-hour, 300 °C post-synthesis heat treatment in nitrogen, using CIE 1931, are shown in Figure 12. The coordinates were ($x = 0.26$, $y = 0.33$) for Structure 1, ($x = 0.26$, $y = 0.32$) for Structure 2, and ($x = 0.29$, $y = 0.35$) for Structure 3. Pure white CIE 1931 chromatic coordinates are considered to be ($x = 0.33$, $y = 0.33$). The chromatic coordinates show that all three sample structures emit white light that could be used for UV-pumped white-LED applications. Structure 1 (N2) exhibits a white light emission that was more intense and had the best emission stability against UV laser degradation when compared to that of Structures 2 and 3; therefore, Structure 1 is the best layer configuration for the intended application.

Figure 12. Color points in the CIE 1931 chromaticity diagram of (1) Sample Structure 1, (2) Sample Structure 2, and (3) Sample Structure 3 after a 1-hour heat treatment at 300 °C in a nitrogen atmosphere.

The emission spectra of Structure 1 (N₂) consisting of 5 layers and 10 layers are shown in Figure 13. The emission exhibited a 39% increase in intensity at 472 nm when the number of layers doubled from 5 to 10. This demonstrates an increase of light output from the films when more material is deposited. The increase in emission due to increase in the number of layers is expected to reach an asymptote due to self-absorption. Although the emission intensity was increased, the emission spectrum became less favorable for white light applications. The spectrum exhibited a broad emission throughout the entire measured range, showing a broad apex peak from 440 – 460 nm, a shoulder at 410 nm, and a broad shoulder near 500 nm. This emission demonstrates chromaticity coordinates of ($x = 0.25$, $y = 0.32$).

Figure 13. Emission spectra of Sample Structure 1 after a 1-hour heat treatment at 300 °C in a nitrogen atmosphere from a 355 nm excitation source with a sample containing (a) 10 layers and (b) 5 layers.

Conclusion

Nanolayered barium fluoride/europium oxide/aluminum oxide films were synthesized via sequential pulsed laser deposition using three different layer configurations. Cross-section TEM analysis of the samples showed that the layers are uniform throughout the film. The different sample structures were subjected to post-synthesis heat treatments in ambient and nitrogen atmospheres to precipitate optically-active nanocrystals. Photoluminescent emission was measured from the samples, both as-made and following heat treatments. The different emission spectra for each of the 3 sample structures confirm the ability to affect optical properties by manipulating sample structure. All sample structures subject to ambient atmosphere heat treatments exhibited emission degradation when subject to the excitation laser. However, it is found that with heat treatments in a nitrogen atmosphere this degradation can be suppressed. Sample Structure 1, consisting of europium sandwiched between barium fluoride layers, was determined to be the best performing structural configuration based on its emission intensity and stability against UV laser degradation; after a heat treatment in nitrogen, the film exhibited a broad emission from 400 - 600 nm with a shoulder at 410 nm. Chromaticity coordinates plotted

from the acquired emission spectra ranged from $x = 0.26-0.29$ and $y = 0.32-0.35$, which demonstrates a potential application in UV-pumped white light LEDs. Emission intensity was compared to film thickness to show a 39% increase in light output when the number of sample layers were doubled from 5 to 10. A complementary article focusing on BaF_2 structural evolution and film growth of BaF_2 films deposited by controlled PLD conditions and analyzed by TEM and electron diffraction has been submitted for review.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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