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Viscosity Effects of the Precursor Solution and Surface Structure of Gadolinium Oxide (Gd_2O_3) and Gadolinium Oxide Europium Doped ($Gd_2O_3:Eu^{3+}$) Sol-Gel Films

Quianna S. Johnson[1], Matthew Edwards[1*], Josh Herring[2], Michael Curley[1]

[1]Department of Physics, Chemistry and Mathematics, Alabama A & M University, Normal, AL, USA
[2]Department of Food and Animal Sciences, Alabama A & M University, Normal, AL, USA
Email: [*]matthew.edwards@aamu.edu

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Abstract

The sol-gel method is a novel technique for the preparation of thin films. In this research, gadolinium oxide (Gd_2O_3) and gadolinium oxide europium doped ($Gd_2O_3:Eu^{3+}$) films prepared via the sol-gel and dip coating methods were investigated. In addition to the elaboration on the sol-gel preparation routes and additional observations of the films' surface morphology as characterized by scanning electron microscope (SEM), we determined via viscosity measurements that the sols were stable for 398 days. FTIR analysis of the Gd_2O_3 and $Gd_2O_3:Eu^{3+}$ dip coated films was made to monitor the decomposition and oxidation reactions that occurred during processing as well as process stability.

Keywords

Gadolinium Oxide Thin Film, Sol-Gel, Dip Coating, Viscosity, SEM, FTIR

1. Introduction

Gadolinium oxide films have received increasing attention due to their novel electronic and optoelectronic properties. It has been determined that these films possess high refractive index, large band gap, high resistivity and relative permittivity, and an innate ability to be readily doped with rare earth ions [1]-[7]. In this work undoped gadolinium oxide and europium doped gadolinium oxide films were prepared via a sol-gel route based on

[*]Corresponding author.

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a gadolinium pentantdionate precursor solutions that were used for the formation of the oxide layers. The formation of the Gd_2O_3 grains was investigated as a function of the annealing time studying the evolution of the chemical composition and the morphology of the samples during the heat treatment for sintering at 500˚C. Gd_2O_3 grain-size increased with time and the temperature of the annealing process ranging from 5 nm up to 150 nm when the temperature increased from 650˚C to 1000˚C [3] [8]. As it relates to this study, samples were annealed for 3 hours. The temperature and sintering treatment greatly influence the porosity, grain sizes and crystalline phase of the obtained films. It is these features of the sol-gel process that are crucial in controlling the film structure and makes possible the tailoring of its functional properties [9]. This study was a continuation of our preliminary work which determined that: 1) methanol was a suitable solvent medium for the synthesis of doped and undoped Gd_2O_3 planar waveguides; 2) there was a direct relationship between the number of layers and annealing on the refractive index and thickness of the film; 3) film prepared in ethanol and methanol solvent mediums were physically capable of propagating laser light down the length of the film; and 4) the measured variations of the refractive index of the films could possibly be due to birefringence, high porosity, and interference from the boundaries between the film, substrate and formed crystallites [10]. In the present study, FTIR was employed on Gd_2O_3 and Gd_2O_3:Eu^{3+} samples grown on borosilicate glass (BSG) to ascertain the chemical composition of the coatings as a function of sintering time whereas the sol-gel film formation process involved hydrolysis, decomposition and oxidation processes. The transitions of the films from amorphous to crystalline were further investigated by scanning electron microscopy (SEM).

2. Experimental and Methods

2.1. Sol-Gel Processing of Gd_2O_3 and Gd_2O_3:Eu^{+3}

In essence, the sol-gel process usually consists of four steps. In the first step, the desired colloidal particles are dispersed in a liquid, from which the sol will be formed. The next step involves the deposition of the sol solution that produces the coatings on the substrates by spraying, dipping or spinning. Next, the particles in the sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network. The fourth and final step consists of a final heat treatment that pyrolyzes the remaining organic or inorganic components with the gel thereby forming an amorphous or crystalline coating [11]. The undoped Gd_2O_3 and Gd_2O_3:Eu^{+3} films were prepared by the sol-gel and dip coating methods.

The undoped sol was prepared by making a 3.2 mmol solution of gadolinium pentantdionate hydrate (99.9%, Sigma Aldrich) in 95 mL of methanol (99.9%, Sigma Aldrich) at 40˚C and stirred vigorously for 1 hr. Finally, 1.5 mL of 2,4-pentanedione (99%, Alfa Aesar) was added to the solution and was stirred overnight. No additional water was added to the sol. The sol was filtered through a 0.22 µm filter prior to being used.

The Gd_2O_3:Eu^{+3} sol was prepared by making a 3.2 mmol solution of gadolinium pentantdionate hydrate (99.9%, Sigma Aldrich) in 95 mL of methanol (99.9%, Sigma Aldrich) at 40˚C and stirred vigorously for 1 hr. Separately, a 1.2 mmol solution of europium (III) nitrate (99.9%, Sigma Aldrich) in 90 mL of methanol was prepared. To the prepared precursor solution, 1 mL of europium (III) nitrate was added, and the solution was stirred vigorously for 1 hr. Finally, 1.5 mL of 2,4-pentanedione (99%, Alfa Aesar) was added to the solution and was stirred overnight. No additional water was added to the sol. The sol was filtered through a 0.22 µm filter prior to being used.

2.2. Film Deposition

The thin films were obtained by dipping a precleaned substrate into the filtered sols. The cleaning procedure of the borosilicate glass (BSG) used in this study consisted of a solution bath of detergent, followed by an acetone bath, and finished with a methanol bath. The BSG substrates (Corning® microscope slides) with an area of 75 × 25 mm^2 were used in this study. Before coating, the sols were filtered through a 0.22 µm filter to remove dust or contamination from the deterioration of the sols. Extreme care was taken to avoid contamination at all stages of the coating process. Deposition of the film from the solution was executed via a dip coating apparatus. The motorized, lifting sample holder shaft was used to soak the substrates into the sol and to raise them carefully with a smooth movement of 3.9 mm/min. 10 and 50 successive coatings of undoped and europium doped Gd_2O_3 sols were cast on the substrate in the laboratory and clean room environment. The solution cup and the motor were isolated from vibration in order to ensure that the liquid surface remains completely undisturbed. The coatings were performed using an HWTL-01 Desktop Dip Coater (MTI Corporation, USA) to reduce dust contamination.

The films were cast in a Class 1000 clean room to determine if there were any detectable variations in the surface morphology, physical and optical properties of the films.

2.3. Annealing Treatment

Complete conversion to oxide film requires a drying stage and a heat treatment in order to obtain a dense and a hard coating. The layers were heat-treated at 100˚C for 5 min between coatings by direct insertion into the CMF-1100 Programmable Compact Muffle Furnace (MTI Corporation, USA). The heating rate was very slow (1.5˚/min) up to the final required temperature (300˚C and 500˚C) in order to reduce strain coming from the slight mismatch between the dilatation coefficient of the layer and the substrate [10]. The temperature of the sample was kept constant for three hours at the specific annealing temperature and was allowed to cool to room temperature as the furnace cooled down.

2.4. FTIR Characterization

The FTIR spectra of the modified and unmodified Gd_2O_3 and Gd_2O_3:Eu^{3+} films deposited on BSG under atmosphere and clean room conditions were collected in transmission mode at room temperature with a spectrophotometer (Nicolet iS10FTIR) equipped with the Smart iTR accessory. Each spectrum, recorded in the frequency region of 4000 - 400 cm^{-1}, was the average of 32 scans at a resolution of 0.4 cm^{-1}.

2.5. Process Stability Analysis Based on Viscosity Measurements

In order to ascertain the stability of the sol, viscosity measurements were taken. The viscosity of the sol was measured with a HYDRAMOTION Viscolite VL7-100B-d15 rheometer DV digital programmable viscometer at room temperature (RT). The synthesized films were filtered through a 0.22 μm filter prior to each viscosity measurement being made. The films were stored over the course of 398 days at ambient conditions.

2.6. SEM Characterization

The surface morphology of the Gd_2O_3 and Gd_2O_3:Eu^{3+} films annealed for 3 hours at 300˚C and 500˚C was investigated and analyzed by SEM observations with a Jeol SEM Model JSM-6390lv with an acceleration voltage of 10 kV. The samples were directly mounted to the sample holder by placing silver paste on the outer edges of the substrate. The center of the samples was imaged and examined for their morphological features—see SEM images in section 3.3.

3. Results and Discussion

3.1. FTIR Analysis

Figure 1 shows the overlaid transmission spectra in the spectral range of 4000 - 400 cm^{-1} of the raw organic starting materials. Each spectrum was collected individually and overlaid for the purpose of emphasizing the regions of activity with respect to all raw materials and individual samples. Relative to **Figure 1**, where characteristic absorption peaks are shown, **Figures 2(a)-3(b)** show the transmission spectra with fewer such peaks indicating the formation of oxide materials in the spectral range of 4000 - 400 cm^{-1} and 1400 - 400 cm^{-1} of selected modified and unmodified Gd_2O_3 and Gd_2O_3:Eu^{3+} films deposited on BSG under atmosphere and clean room conditions and heat treated at 300˚C and 500˚C for 3 hours. The spectra of the samples show two absorptions around 1454 cm^{-1} and 820 cm^{-1} that could be respectively ascribed to stretching and bending vibrations of CO groups. The absorption bands peaked at 955 cm^{-1} and 952 cm^{-1} were ascribed to C-C and CH_3-C-CH_3 stretching vibrations. Absorptions in these regions mean that the decomposition reaction was not terminated, as reported in the literature [5]. This outcome in term suggests the possibility that the formed doped and undoped Gd_2O_3 contain traces of organic residues. The FTIR spectra of the samples also exhibit peaks located in the region 600 - 400 cm^{-1}. The peaks located near 538 cm^{-1} and 456 cm^{-1} can be assigned to the Gd-O vibrations in the cubic Gd_2O_3 phase [5]. This result suggests the formation of polycrystalline Gd_2O_3 films.

3.2. Viscosity Measurements

Figure 4 & **Figure 5** show the undoped and doped viscosity curves that were obtained from solutions that were

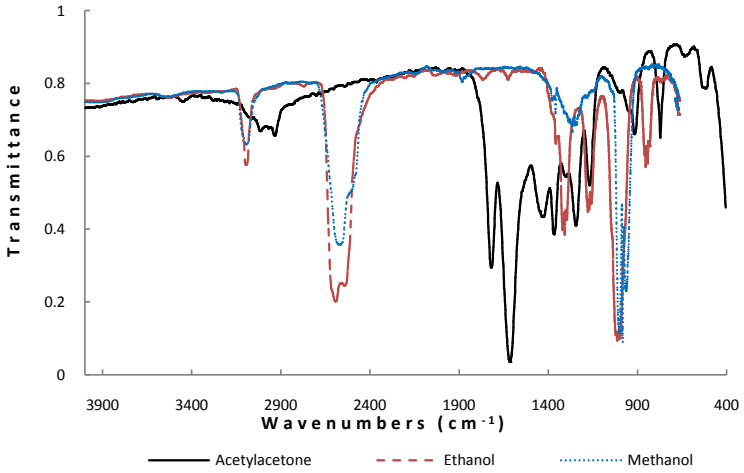
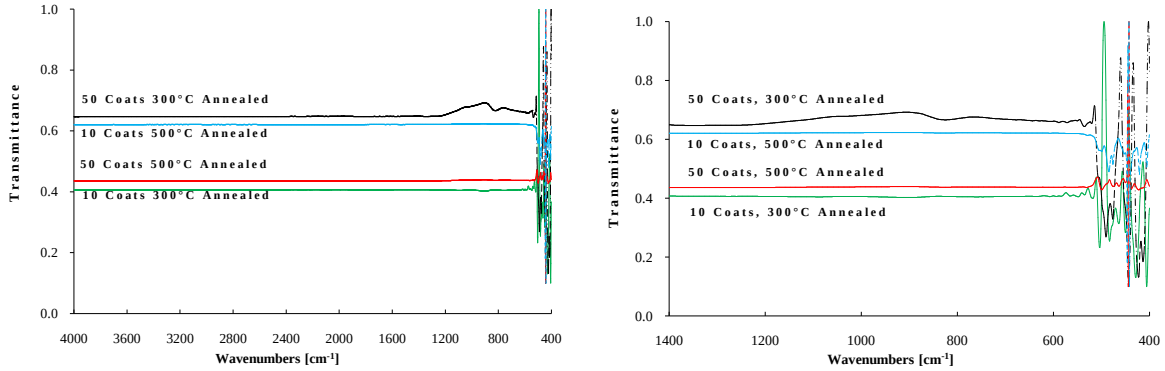
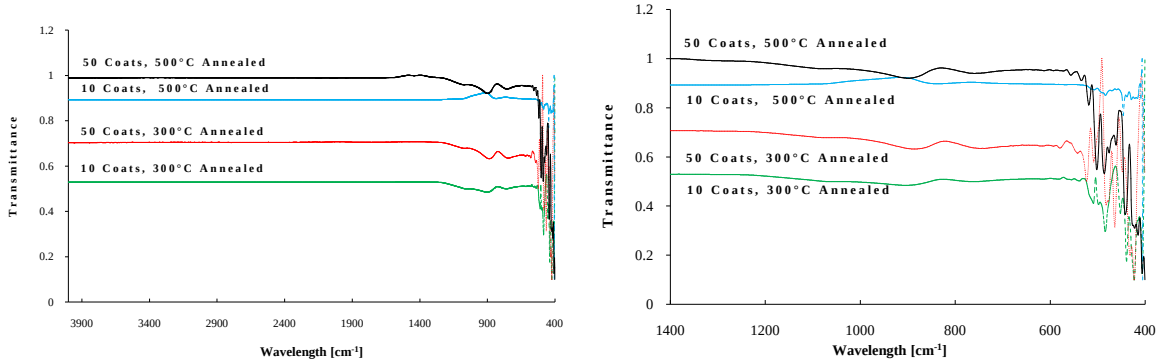


Figure 1. Transmission FTIR spectra in the spectral range 4000 - 400 cm^{-1} of the organic starting materials (acetylacetone, methanol and ethanol) as used for the preparation of doped and undoped Gd_2O_3.



(a) (b)

Figure 2. (a) Transmission FTIR spectra in the spectral range 4000 - 400 cm^{-1} of ethanol based Gd_2O_3 films as deposited on BSG substrate and annealed at 300˚C and 500˚C for 3 hours; (b) Transmission FTIR spectra in the spectral range 1400 - 400 cm^{-1} of ethanol based Gd_2O_3 films as deposited on BSG substrate and annealed at 300˚C and 500˚C for 3 hours.



(a) (b)

Figure 3. (a) Transmission FTIR spectra in the spectra range of 4000 - 400 cm^{-1} of methanol based Gd_2O_3 films as deposited on BSG substrate and heat-treated at 300˚C and 500˚C for 3 hours; (b) Transmission FTIR spectra in the spectra range of 1400 - 400 cm^{-1} of methanol based Gd_2O_3 films as deposited on BSG substrate and heat-treated at 300˚C and 500˚C for 3 hours.

prepared in methanol and ethanol solvent mediums with the reaction time varied.

As shown in **Figure 4** & **Figure 5**, the viscosity of the precursor solution continuously increases with the aging time. In **Figure 4**, the viscosity of the undoped and doped methanol based sol have similar behavior, that is, it first increases rapidly and for longer aging time exhibits little variation. With respect to **Figure 5**, the viscosity of the undoped and doped ethanol based sol also exhibits similar behavior. In this system, the viscosity first rapidly increases and, over the course of approximately 200 days, the system began to slowly increase in viscosity. The time at which the viscosity of the solution increases abruptly can be defined as the gelation time. This time is approximately 15, 26, 9 and 15 days for the undoped methanol based, doped methanol based, undoped ethanol based, and doped ethanol based solutions respectively. It should be noticed that the methanol based solutions have a viscosity of about 0.35 cP while the ethanol based solutions have a viscosity of about 0.85 cP when the gelation time is reached. The slower increase in viscosity in the later stage may be caused by absorption of water from the ambient atmosphere. This behavior may be attributed to the fact that there is relatively trace amounts of water present in the absolute ethanol.

3.3. SEM Analysis

The heating rate and solution viscosity are two critical parameters that must be taken into account in order to produce crack-free films. **Figures 6(a)-8(b)** show SEM photographs of the modified and unmodified Gd_2O_3 films that were prepared with 10 and 50 layers and annealed at 300˚C and 500˚C. The images show that crack-free

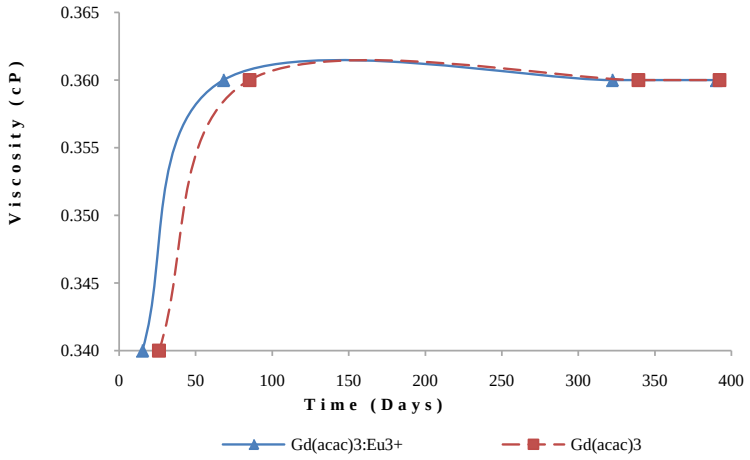


Figure 4. Variation of the viscosity measured at RT of the sol synthesized in a methanol medium.

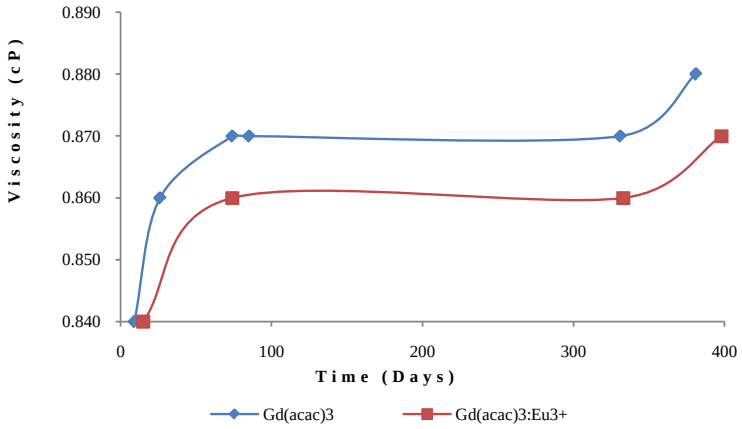
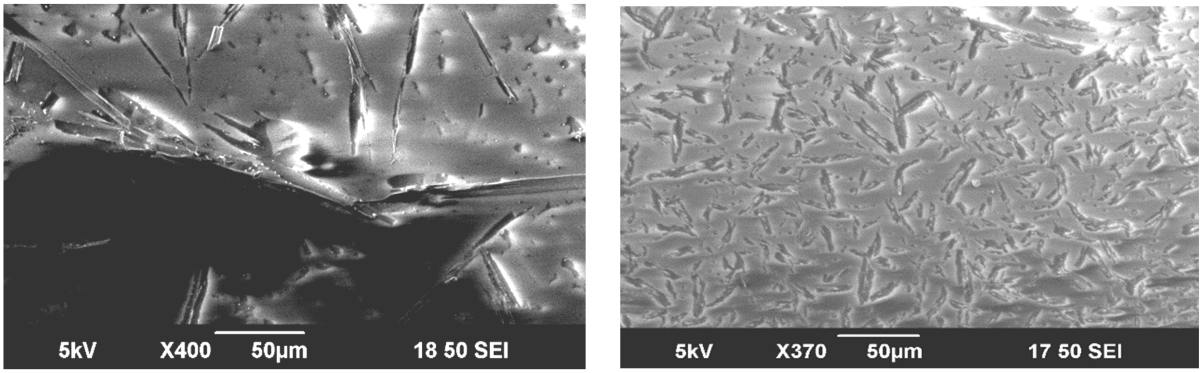
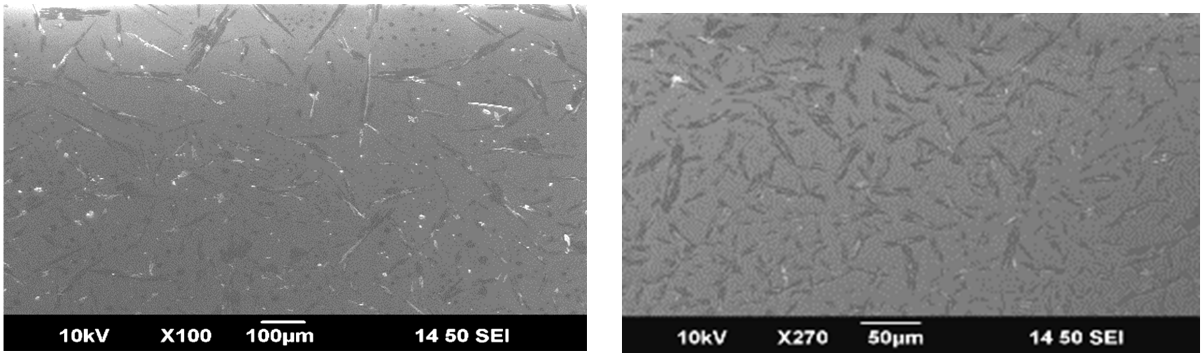


Figure 5. Variation of the viscosity measured at RT of the sol synthesized in an ethanol medium.



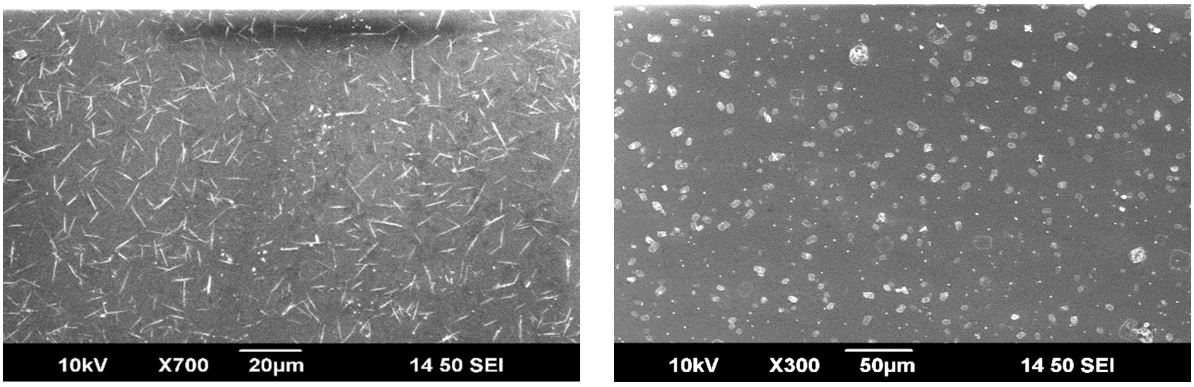
(a) (b)

Figure 6. (a) SEM of 10 layers of methanol based Gd_2O_3 films annealed at 500˚C; (b) SEM of 50 layers of methanol based Gd_2O_3 films annealed at 500˚C.



(a) (b)

Figure 7. (a) SEM of 10 layers of methanol based Gd_2O_3 films heat-treated at 300˚C; (b) SEM of 50 layers of methanol based Gd_2O_3 film annealed at 300˚C.



(a) (b)

Figure 8. (a) SEM of 10 layers of ethanol based Gd_2O_3 film annealed at 500˚C; (b) SEM of 50 layers of ethanol based Gd_2O_3 film annealed at 300˚C.

films can be obtained at low viscosity (~0.3 cP for methanol based and ~0.8 cP for ethanol based sol gels) with a heating rate of 1.5˚/min, and no crack appears even with 50 repeated coatings. Samples annealed at 300˚C exhibit crystallite growth that resembles islands and what appears to be the initial formation of crystallites that resembles fiber networks. In contrast, samples annealed at 500˚C exhibit crystallite growth that resembles fiber networks. It has been reported in the literature that these films become crystalline annealed between 500˚C-2200˚C [3]-[9]. The appearance of the crystallite structures could be attributed to the material's transition from

amorphous to crystalline.

4. Conclusion

From this work, we have used the sol-gel and dip coating methods to synthesize undoped $Gd_2O_3$and Gd_2O_3:Eu^{3+} films in methanol and ethanol solvent mediums for planar optical waveguides. We determine from this study that the annealing process and the number of layers directly influence the physical properties and surface morphology of the films. We also determine that the fabricated films possess detectable levels of organic materials, which can be minimized with increased annealing time. Viscosity measurements revealed that the ethanol and methanol based sols were stable over the course of 398 days. More investigation will be done on this material to determine the presence of potential structural defects in the material, verify the occupational sites of Eu^{3+} ions, and to ascertain the optical and physical character of the films.

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