

Sputtered films of Er³⁺ doped gallium lanthanum sulfide glass

J. A. Frantz^a, J. S. Sanghera^b, L. B. Shaw^b, G. Villalobos^b, I. D. Aggarwal^b, and D. W. Hewak^c

^aSFA, Inc., 2200 Defense Hwy., Suite 405, Crofton, MD 21114, USA

^bNaval Research Laboratory, Code 5606, 4555 Overlook Ave. SW, Washington, DC 20375, USA

^cOptoelectronics Research Centre, University of Southampton, Southampton, S017 1BJ, United Kingdom

Abstract

Thin films of Er³⁺-doped gallium lanthanum sulfide (GLS) glass were prepared by RF magnetron sputtering onto fused silica and BK7 glass substrates. The films were characterized by use of SEM imaging, X-ray diffractometry, and energy dispersive spectroscopy. They are shown to be glassy, uniform in composition, and to exhibit an RMS surface roughness of <8 Å. The fluorescence lifetimes of the ⁴I_{11/2}→⁴I_{13/2} and ⁴I_{13/2}→⁴I_{15/2} transitions of Er³⁺ were measured at each processing stage.

Keywords: Glasses; Optical materials and properties; Deposition; Thin films

Introduction

Rare-earth (RE) doped chalcogenide glasses show promise for use in lasers and optical amplifiers operating in the mid-IR. Their low phonon energy results in low-loss transmission in the mid-IR and also permits transitions that are unusable in silica glasses due to multiphonon quenching [1].

Gallium lanthanum sulfide (GLS) glass in particular possesses several qualities that make it well-suited for these applications [2-6]. It has a wide IR transmission window, with

transmission of 50% or higher through a 1 mm thickness over a wavelength range of 0.5 to 10 μm [3]. Its high glass transition temperature, $T_g=580^\circ\text{C}$, makes GLS appropriate for use in high-temperature applications. Additionally, high RE dopant concentrations without clustering are possible owing to the fact that the RE ions substitute for the lanthanum ion in the glass matrix [4]. The potential of GLS as a laser material been demonstrated in Nd^{3+} -doped bulk glass lasers [5] and Nd^{3+} -doped fiber lasers [6]. The spectral properties of Er^{3+} -doped GLS have been well-characterized in Ref. [7]. The $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ and $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transitions results in fluorescence at wavelengths of 2.7 μm and 1.54 μm respectively.

The development of new processing technologies for GLS could potentially result in the implementation of compact integrated-optic (IO) lasers and optical amplifiers. IO devices are desirable because the glass can be doped at higher concentrations than in fiber lasers resulting in a reduction in length. In addition, IO devices could be combined with other optical components on the same chip.

Several methods of fabricating IO waveguides in GLS have been explored previously. GLS is photosensitive, exhibiting a permanent change in refractive index when exposed to light. This photosensitivity has been exploited by directly writing waveguides into the glass with above-bandgap radiation. Attenuation as low as 0.2 dB/cm has been reported for a single-mode waveguide fabricated with this technique [8]. Optically-written channel waveguide lasers in Nd^{3+} -doped glass have also been demonstrated [9].

One technique that has recently been developed to deposit a thin film of GLS is high velocity spinning [3, 10]. In this method an inverted GLS substrate is dipped in molten GLS of a slightly different composition, withdrawn, and spun at a high speed until the film cools. The authors were able to spin an overcladding layer on top of the core and produced films with losses of <0.2 dB/cm. One potential drawback of this method is incompatibility with pre-existing structures on the substrate; it is likely that any pre-existing features would either melt or cause thickness non-uniformities in the spun film.

Vacuum deposition of a thin film of GLS offers several potential advantages. The use of a thin film reduces the volume of the costly component materials that is required. The thickness of a deposited film can be precisely controlled by adjusting the deposition time. Furthermore, thin films can be deposited on a variety of substrates including those with pre-existing optical and electronic components permitting the fabrication of more complex devices.

Pulsed laser deposition (PLD) is one type of vacuum deposition process that has been applied previously to deposit thin films of GLS [11]. GLS was ablated from a bulk sample with a KrF excimer laser, and the substrate was placed in the ablated plume. Although a thin film was fabricated, the authors were only able to deposit glass over an area of <1 cm², and the film had relatively high losses of 6 dB/cm. Furthermore, PLD is known to have several disadvantages that are not conducive to fabricating films of sufficient quality for optical waveguides. These include an angular distribution in film

thickness and composition and a rough surface morphology caused by the deposition of particulates.

Sputtering, on the other hand, is a well known vacuum deposition process that has been widely used for the fabrication of high-quality films [12]. Advantages of sputtering include good thickness and compositional uniformity, the capacity to coat large (and even non-planar) surfaces, the capability of depositing multicomponent materials with a film composition similar to that of the target, and its existing widespread commercial use.

In this Letter, we report the deposition of thin films of GLS glass by RF magnetron sputtering. Films ranging in thickness from 0.15 to 3.8 μm were fabricated. They are glassy, uniform in composition, and exhibit an RMS surface roughness of $<8 \text{ \AA}$. We report our experimental procedures for sputter deposition and discuss the characterization of these films.

Experiment

A bulk glass ingot (ChG Southampton Ltd.) with a molar composition of $70\text{Ga}_2\text{S}_3:23\text{La}_2\text{S}_3:6\text{La}_2\text{O}_3:1\text{Er}_2\text{S}_3$, was ground into a powder. A sputter target was formed by hot pressing this powder into a 3 in. diameter disk. Films were prepared by RF magnetron sputtering in a sputter-up geometry onto 2 in. diameter fused silica and BK7 substrates. This process was carried out in an Ar atmosphere with a base pressure of 5 mT and a flow rate of 20 sccm. An energy density of approximately 1 W/cm^2 was used. Before the GLS was deposited, a $\sim 60 \text{ \AA}$ layer of Cr was deposited via sputtering to act as

an adhesion layer. The substrate temperature was maintained at 100° C. The resulting deposition rate for GLS was 11 Å/min.

In order to measure fluorescence lifetimes, samples were pumped with a 980 nm laser diode modulated with a 5 Hz square wave. The 2.7 μm light was collected with a liquid nitrogen cooled InSb photodiode, and the 1.54 μm light was collected with an InGaAs photodiode. Filters were used to isolate the desired emission wavelength.

Bulk samples were pumped by illuminating them in free space. In order to measure fluorescence in a sputtered film, the sample was pumped in a slab waveguide configuration. Two parallel cleaves were made in the sample, light was coupled into one edge of the film with a silica fiber, and light at the output edge was collected with a lens and focused onto a detector.

Results and Discussion

GLS films ranging in thickness from 0.15 to 3.8 μm were sputtered onto both silica and BK7 glass substrates. The films are visibly transparent, and the surface appears to be smooth when viewed under an SEM. An SEM image of a cross section of a film on a BK7 substrate is shown in Fig. 1. The thickness of the sample shown, measured with a stylus profilometer, is 1.6 μm. The refractive index, n , was measured with an ellipsometer and found to be 2.5 at a wavelength of 0.633 μm, in good agreement with Gill *et al.*'s measurement of $n=2.45$ for bulk GLS [11].

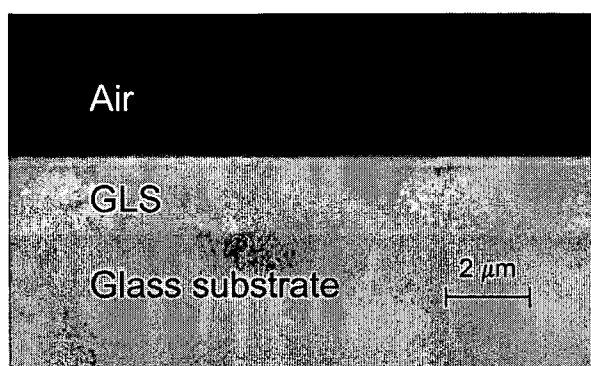


Fig. 1. SEM image of the cleaved edge of a sputtered GLS thin film.

RMS surface roughness, measured with a stylus profilometer, was found to be $<8 \text{ \AA}$. The films exhibit a slight wedge, with a thickness that varies linearly by approximately 10% over the central 4 cm of the sample. The sample was horizontally offset from the target during sputtering, and the thickest part of the wedge was the closest to the target during deposition. The thickness variation could be reduced by moving the sample further from the target during deposition but would result in a reduction in deposition rate.

XRD analysis was performed at each processing stage in order to determine the crystallinity of the sample. A piece of a bulk GLS ingot and a piece of a hot pressed target were ground into powder form before they were measured. The sputtered film was measured in its as-deposited condition while still on a silica substrate. XRD patterns are shown for each sample in Fig. 2. No peaks are present for the glass ingot or for the sputtered film. For the hot pressed target, however, a series of peaks is present indicating that the target is crystalline. The peaks are in good agreement with JCPDS file No. 27-0229 for $\text{Ga}_6\text{La}_{3.33}\text{S}_{14}$. It was confirmed that the film was thick enough for valid XRD results by heating it to its peak crystallization temperature for one hour and repeating the

measurement. In this case, peaks are clearly present in the XRD pattern (not shown in figure). These results indicates that, while the hot pressing conditions cause the GLS to crystallize, the sputtering process rearranges atomic bonds so that the sputtered film is glassy. The peak diffraction angle in the sputtered film is shifted with respect to that of the bulk glass due to the presence of the substrate in the sputtered sample.

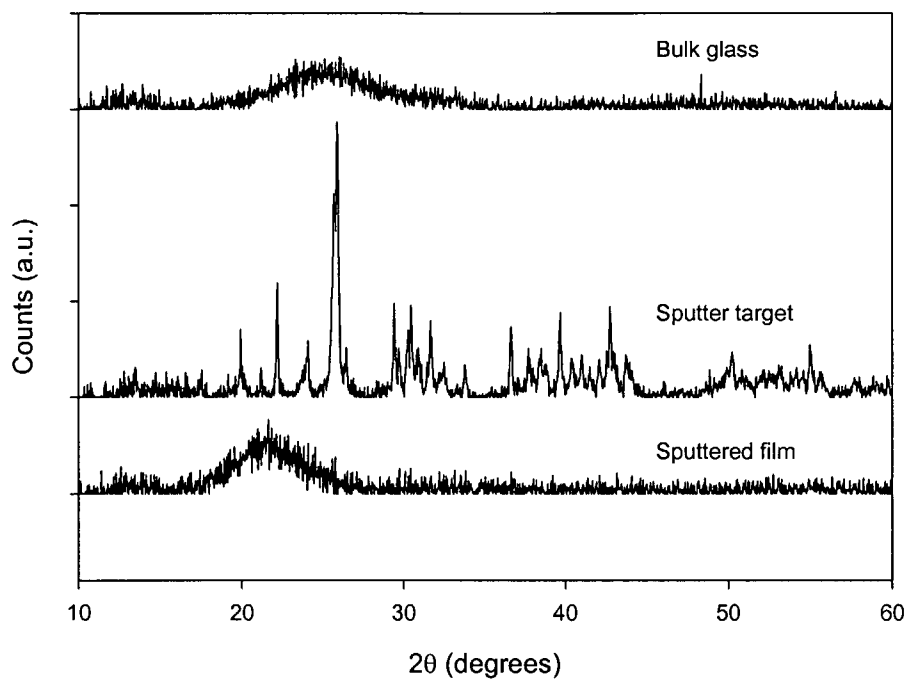


Fig. 2. XRD patterns for a bulk glass GLS, a hot pressed target, and a sputtered thin film on silica.

In order to determine whether the composition of sputtered films of GLS is uniform with respect to thickness, a new GLS sputter target was installed, and a series of films totaling 9.1 μm in cumulative thickness was fabricated. The composition at the surface of each film was measured with EDS. Oxygen is excluded from the analysis because its EDS

peaks were not measurable. A plot of the measurement results for cumulative thicknesses of 0.4, 1.6, 3.2, 6.8, and 9.1 μm is shown in Fig. 3. The composition for each component is constant after approximately 2 μm of cumulative sputtered thickness. The dotted lines in the plot indicate the mean of the last three points in each series. The S content decreases from its initial maximum of 66.4 mol% to a mean value of 59.2 mol% while the Ga content increases from its initial minimum of 23.4 mol% to a mean value of 29.7 mol%. These results indicate that, for a new sputtering target, the composition varies slightly with thickness. After a conditioning period, however, an equilibrium condition is reached, and film composition does not vary significantly.

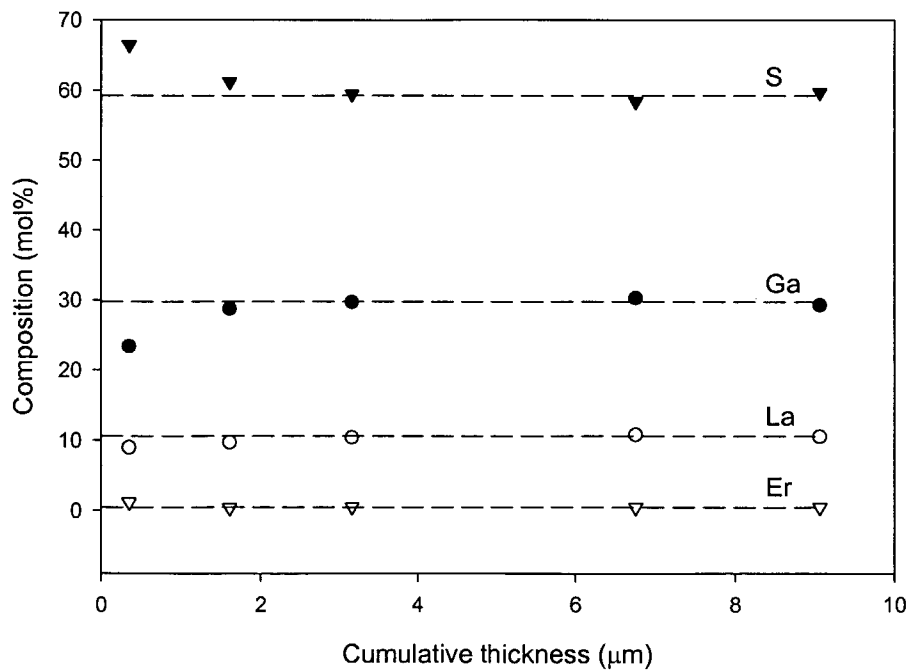


Fig. 3. EDS measurements of sputtered film composition as a function of cumulative thickness. The dotted lines indicate the mean of the last three points in each series.

The composition was also measured at multiple points across the surface of a single sample and was found to vary by less than the ± 0.5 mol% uncertainty in the measurement, indicating that the composition does not vary significantly with position.

The composition of GLS at each processing stage was also measured with EDS. The results are shown in Table 1. Oxygen is again excluded from the analysis. The composition shown for the melt stage is the nominal melt composition that was provided by the supplier. The composition shown for the sputtered film is the average of the last three points for each series in Fig. 3. The composition of the GLS is similar at each processing stage. The most prominent feature of the data is a decrease in La content from 15.3 mol% for the target to 10.6 mol% for the sputtered film. This difference – probably the result of a difference in sputter rates between the components – is not a drawback, however. The composition is still within the glass forming region for GLS, and as observed above, the film’s composition is at equilibrium and does not vary with respect to thickness.

Table 1

Atomic composition of GLS samples at each processing stage measured with EDS

Processing stage	State	Composition (mol%)			
		Ga	La	S	Er
Melt	Powder	29.0	12.0	58.5	0.5
Bulk glass	Glassy	28.5	14.8	56.3	0.5
Hot pressed target	Polycrystalline	27.0	15.3	57.1	0.6
Sputtered film	Glassy	29.7	10.6	59.2	0.5

The GLS fluoresces at a wavelength of 2.7 μm , corresponding to the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ transition and a wavelength of 1.54 μm , corresponding to the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition. The fluorescence lifetime, τ_f , of each transition was measured for a bulk glass sample, a piece of a hot pressed target, and a 3.8 μm thick sputtered film. The measured lifetimes are shown in Table 2. At a wavelength of 2.7 μm , $\tau_f = 1.3 \pm 0.1$ ms for the bulk glass and 1.2 ± 0.1 ms for the target. Fluorescence at a wavelength of 2.7 μm was not measurable for the sputtered film. At a wavelength of 1.54 μm , $\tau_f = 3.8 \pm 0.2$ ms for the bulk glass, 3.3 ± 0.2 ms for the target, and 1.1 ± 0.1 ms for the sputtered film. The decrease in fluorescence lifetimes in the hot pressed target, in comparison with the bulk glass, is slight, indicating that any clustering of the Er^{3+} ions is minor. The absence of measurable fluorescence at 2.7 μm and the decrease in lifetime at 1.54 μm for the sputtered film in comparison with previous processing stages may indicate that quenching is taking place. Refinements in processing, such as the inclusion of a rapid thermal annealing step, may alleviate this problem.

Table 2

Fluorescence lifetimes of Er^{3+} doped GLS at various processing stages

Processing stage	Fluorescence lifetime (ms)	
	$\lambda = 2.7 \mu\text{m}$	$\lambda = 1.54 \mu\text{m}$
Glass ingot	1.3 ± 0.1	3.8 ± 0.2
Hot pressed target	1.2 ± 0.1	3.3 ± 0.2
Sputtered sample	—	1.1 ± 0.1

Conclusions

Thin films of GLS with a thickness of up to 3.8 μm were deposited by sputtering onto silica and BK7 substrates. The films are glassy, showing no crystalline diffraction peaks

when measured with XRD. The RMS surface roughness of 8 Å is sufficiently small to provide low scattering losses if the sputtered films are to be used in IO devices. The GLS fluoresces at the ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} for both the bulk glass and a hot pressed sputter target. It fluoresces at the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at each processing stage, including sputtered films used as slab waveguides.

Sputtered films of Er^{3+} doped GLS show promise for active IO applications such as lasers and optical amplifiers. The material's transparency in the mid-IR, high T_g , and the potential for high RE doping concentrations make it an attractive candidate for such applications. RF magnetron sputtering has been shown to be a viable method of depositing films of this material. In future work, we plan to further characterize the optical properties of sputtered GLS films and utilize them to fabricate IO devices.

References

- [1] L.B. Shaw, B. Cole, P.A. Thielen, J.S. Sanghera, and I.D. Aggarwal, IEEE J. Quantum Electronics 48 (2001) 1127.
- [2] A. Bornstein, J. Flashaut, M. Guittard, S. Jaulmes, A.M. Loireau-Lozac'h, G. Lucazeau, and R. Reisfeld in: The rare earths in Modern Science and Technology, ed. G.J. McCarthy and J.J. Rhine (Plenum, NY, 1978) p. 599.
- [3] A.K. Mairaj, R.J. Curry, and D.W. Hewak, Electronics Lett. 40 (2004) 421.
- [4] D.W. Hewak, R.C. Moore, T. Schweizer, J. Wang, B. Samson, W.S. Brocklesby, D.N. Payne, and E.J. Tarbox, Electronics Lett. 32 (1996) 384.
- [5] T. Schweizer, D.W. Hewak, D.N. Payne, T. Jensen, and G. Huber, Electronics Lett. 32 (1996) 666.
- [6] T. Schweizer, B.N. Samson, R.C. Moore, D.W. Hewak, and D.N. Payne, Electronics Lett. 32 (1997) 414.
- [7] C.C. Ye, D.W. Hewak, M. Hempstead, B.N. Samson, and D.N. Payne, J. Non-Cryst. Solids 208 (1996) 56.

- [8] A.K. Mairaj, P. Hua, H.N. Rutt, and D.W. Hewak, *J. Lightwave Technol.* 20 (2002) 1578.
- [9] A.K. Mairaj, A.M. Chardon, D.P. Shepherd, and D.W. Hewak, *IEEE J. Selected Topics in Quant. Elect.* (2002) 1381.
- [10] A.K. Mairaj, R.J. Curry, and D.W. Hewak, *Appl. Phys. Lett.* 86 (2005) 94102.
- [11] D.S. Gill, R.W. Eason, C. Zaldo, H.N. Rutt, N.A. Vainos, *J. Non-Cryst. Solids* 191 (1995) 321.
- [12] K. Wasa, M. Kitabatake, H. Adachi, *Thin Film Technology: Sputtering of Compound Materials* (William Andrew, Norwich NY, 2004).