Laser Ablation Deposition of Ga_2S_3-La_2S_3 Glass Films

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ABSTRACT

Gallium - lanthanum sulphide glasses (GLS) show wide range transparency and low non radiative relaxation rates for dopant ions such as Ho^{3+}, Er^{3+} etc. They also show permanent photomodification of the refractive index under visible illumination. We report laser ablation deposition of these glasses and preliminary results on film stoichiometry and deposition rate as a function of excimer laser fluence. The sulphur to metal and Ga/La ratios are found to have marked fluence dependencies. The films show considerably more Urbach tail absorption than bulk material. A novel method has been developed for mapping the permanent photomodified index.

INTRODUCTION

Gallium-lanthanum sulphide (Ga_2S_3-La_2S_3) ('GLS') glasses [1] have a range of novel optoelectronic applications. The material is transparent from ~0.65μm to ~10μm, covering the important near infrared telecommunications and mid infrared 'fingerprint' spectral regions. The lanthanum content ensures very high solubility for other rare earth dopant ions such as Er^{3+},Ho^{3+},Pr^{3+},Nd^{3+} [2] etc which can be used as active laser or optical amplifier species. The low phonon energy of GLS glass gives rise to low non radiative relaxation rates, which opens the possibility of operating lasers in this host material in the mid infrared. Laser action to wavelengths approaching 5μm may be feasible in high quality films. An unusual property of the material is that the refractive index can be substantially and permanently modified by exposure to illumination above the band gap, typically at 0.5145μm wavelength or shorter [3,4].

FILM DEPOSITION

Target fabrication

The use of these large targets ensures consistency of target material over mAblation targets are manufactured as gallium lanthanum sulphide glass disks of typically 40mm diameter by 10mm thick. any ablation experiments and freedom from target thermal damage and cracking. Gallium sulphide (70% molar) and lanthanum sulphide (30% molar) are weighed out under dry nitrogen into a vitreous carbon crucible pre placed in a silica ampoule. Particular care is taken with the source of the sulphide (Merck) to minimise contamination with oxysulphides. The silica ampoule is evacuated and heated to 1200C for two hours and then water quenched. The glass disc is clear orange/yellow, with some superficial bubbles where gas adhered to the crucible/glass interface.

The discs release easily from the crucible and there is no evidence of attack. The targets are visually homogeneous and show visible and IR spectra typical of GLS glass. Energy dispersive X ray analysis shows the targets to be homogeneous and stoichiometric to within experimental error. The disc is ground down to a flat surface, cleaned, and mounted in a cup designed to provide a surface to radiate the absorbed power load and minimise conduction to the in-vacuum stepper motor drive.

Ablation

The ablation chamber is dedicated to GLS deposition to minimise cross contamination. The vacuum system is oil free with 400ls^{-1} pumping speed at the chamber, and sustains pressures of a few times 10^{-7} mB during deposition. The substrate is introduced via a load lock, and oscillated vertically through typically +/- 1cm to improve film uniformity in one plane. The substrate mount permits the target to substrate distance and angle of incidence on the substrate to be adjusted while the mount is in the load lock.The target is rotated on a high vacuum compatible stepper motor at ten revolutions per minute. Target to substrate distance is typically 8cm. A KrF laser (247nm) is used operated at 5Hz with energies up to 850mJ, focused with a 45cm focal length silica lens. Fluences were varied by changing the laser energy. Ablation times range up to 20 minutes depending on the required thickness, target fluence, and substrate-target distance.

The substrate holder is equipped for heating and cooling to -100C. Results in this paper are for nominally room temperature deposition.

RESULTS AND DISCUSSION

Film composition

Figure 1 shows the ablation threshold to be approximately 2.8J/cm^2. At a laser repetition rate of 5Hz, rates are in the range 10-25nm per minute for practical incident energy densities. For device applications the required thickness is in the 0.5 to 1μm region, leading to deposition times of typically 10-40 minutes.

Under SEM examination, the films are entirely featureless showing a smooth surface with occaisional particles as is usual in laser ablation deposition.

Figure 2 shows the sulphur to total metal ratio (atomic) for the films as measured by energy dispersive SEM. For the starting compounds this ratio is 1.5; bulk glass targets typically are very close to stoichiometric. Films ablated at just above the threshold show ratios very slightly above 1.5, but are probably stoichiometric to within experimental error. At higher fluences the ratio falls abruptly to below one, indicating a substantial loss of sulphur. This can quite readily be understood in general terms in the context of the high volatility of elemental sulphur and the existence of other gallium and lanthanum sulphides with lower sulphur to metal ratios such as LaS, La_3S_4, Ga_2S, GaS and Ga_4S_5. Only one compound, LaS_2 exists with a sulphur to metal ratio greater than 1.5.

More surprising is the apparently rapidly changing Ga:La ratio, Figure 3. The bulk glass value is 2.33. However, the SEM energy dispersive measurement leads to difficulties in precise lanthanum concentration determination owing to poor count statistics and count to background ratios, so that detailed interpretation must await more precise analytical measurements.

For GLS glass, the often quoted advantage of laser ablation deposition, namely 'replication' of the target composition in the film deposited on the substrate, does not always appear to apply. The great majority of laser ablation work to date has been on oxide based materials, and it is unclear if the problems experienced with GLS are fundamentally related to its chalcogenide nature or to the widely differing properties of the two sulphides.

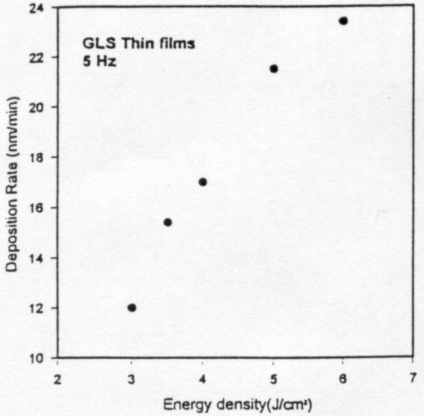

Figure 1. Deposition rate versus fluence.

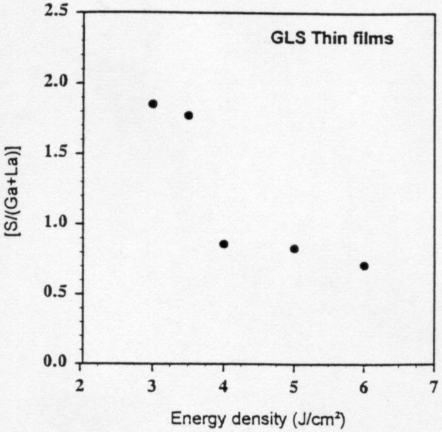

Figure 2. Sulphur stoichiometry versus fluence.

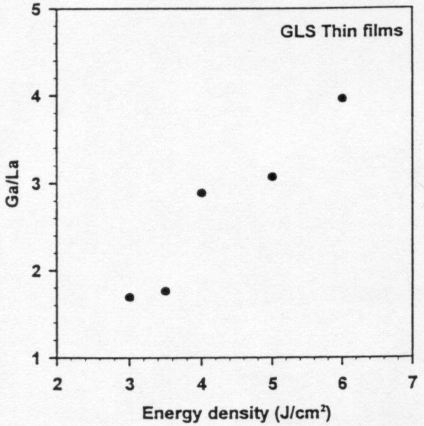

Figure 3. Gallium to lanthanum ratio versus fluence.

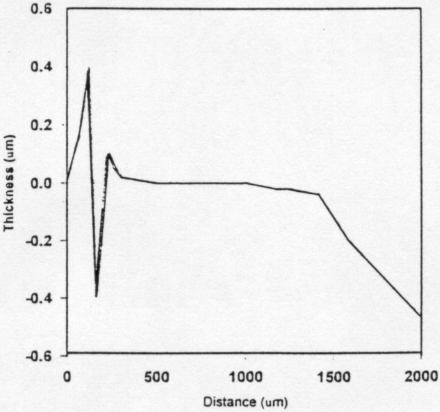

Figure 4. 'Talysurf' measurements of photomodified region.

Optical Properties

Figure 5 shows a typical spectrum for a layer of physical thickness 0.45μm deposited on a calcium fluoride substrate. In the mid infrared the transmission at the fringe peak (optical thickness an integral number of half waves) is very close to that of the uncoated substrate transmission, indicating a low loss film. However, in the near infrared, substantial loss is evident, whereas bulk glass samples remain essentially loss free down to below 0.8μm. The film is clearly showing substantial 'tail' or Urbach edge absorption, which will need to be greatly reduced for device applications. The tail absorption is probably linked to the S/(Ga+La) non stoichiometry.

The films show strong permanent photorefractive effects. Previous publications [5] have utilised the writing of grating structures into the film to derive the induced index change. This technique suffers from difficulties owing to widely varying diffraction angles when it is desired to measure the index change over a wide wavelength region. It is also intrinsically unable to measure the sign of the index change, only the magnitude. We have developed a novel method of measuring the index change by mapping the reflectivity difference between two closely adjacent spots, as shown in figure 6. The photorefractive structure is written as a narrow parallel sided strip by illumination with a low power, 100mW, argon laser beam at 0.5145μm through a 1.25mm slit. During the measurements a low power probe laser at any desired wavelength, 0.67μm in our initial experiments, is deflected by an oscillating galvanometer mirror through a small angle, typically two milliradians. The beam is then focused on the sample resulting in the beam oscillating between two closely spaced points, in our case 250μm apart. Beams from both points are reflected onto a common large area silicon photodiode. The diode signal is processed with a phase sensitive detector (lock in amplifier) using the galvanometer drive signal as reference. For a uniform film no signal results; the magnitude and sign of the signal as the sample with the photorefractive changes written in it traverses the oscillating spot pattern measures the differential reflectivity from which the magnitude and sign of the index change is easily derived. Figure 7 shows an initial recording made using this technique. A strong positive signal occurs as the spots straddle the first edge of the modified strip; the signal falls to zero as both spots lie in the strip, and reverses sign as the spots exit the photomodified region. In this case the index change is negative. The apparent noise is in fact fully reproducible and represents small scale length fluctuations in the film properties. Reflectivity variations below 10^{-5} are readily measured. Small differences in galvanometer mirror reflectivity with angle, lens transmission and detector sensitivity with position can easily be 'nulled' by an angled glass plate into the oscillating beam and adjusting the angle of incidence to obtain a null result from a sample known to be uniform.

Superficially similar photorefractive effects are well know in other chalcogenide glasses such as those based on arsenic and germanium sulphides [5,6]. In such glasses the photo induced index changes are often accompanied by changes in density, usually photodensification. In device applications substantial photodensification would be inconvenient, leading to loss of planarity. 'Talysurf' stylus measurements taken on photomodified samples (figure 4) show that thickness changes are below 20nm in an ~700nm thick film; the sharp structure to the left in figure 4 is a scratch to identify the region, the photomodified area being within the plateau region. Based on previous results [4] the index change in this region was probably ~1%, so photodensification cannot yet be excluded but it would not be serious for device use. A further difference as compared to the non GLS chalcogenide films is that a photobleaching effect is apparent to the eye in GLS whereas arsenic films photodarken. The mechanisms involved in photomodification of GLS and 'traditional' chalcogenide glasses therefore appear quite different.

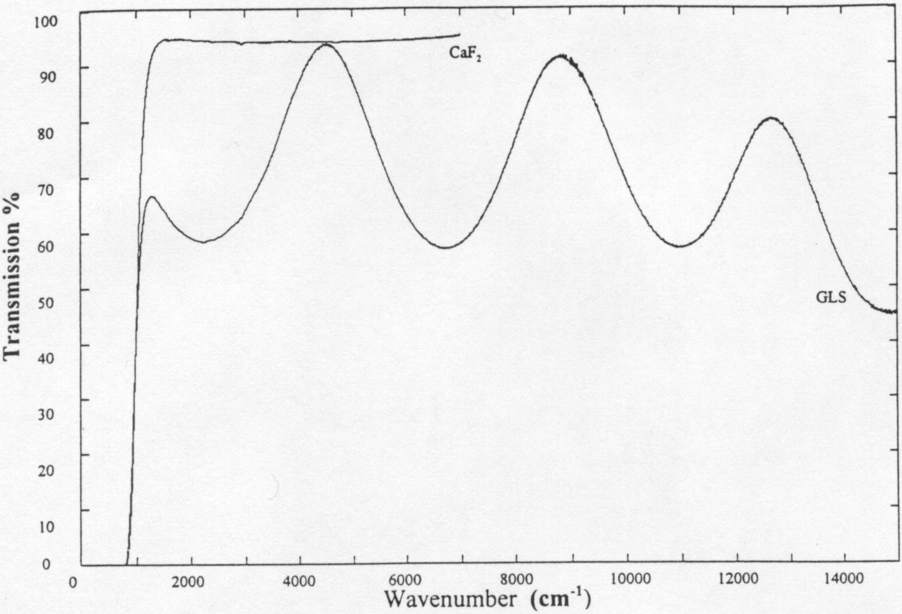

Figure 5. Transmission of GLS film deposited on a CaF$_2$ substrate.

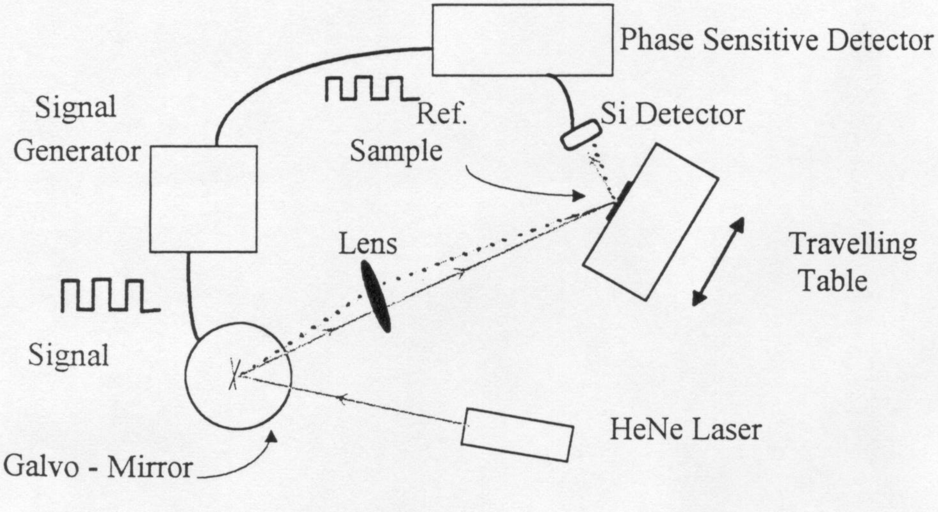

Figure 6. Differential Reflectance technique.

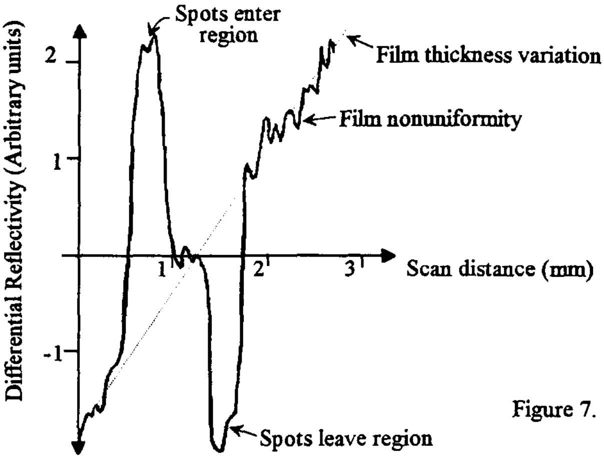

Figure 7. Preliminary Differential Reflectance Results.

CONCLUSIONS

Laser ablation of gallium lanthanum sulphide glass readily forms films which are featureless under SEM examination and show low scatter. Strong permanent photorefractive effects are readily observed. The resulting refractive index change is negative, and any thickness change below 3% for an ~1% index change. The films show low mid infrared absorption, but in the near infrared there is a strong tail absorption which does not occur in the bulk glass. The tail absorption may be related to stoichiometry variations in the film, which are strongly fluence dependant, an unusual situation for ablative deposition. As yet no clear correlation exists between tail absorption and stoichiometry. Practical exploitation of the highly desirable properties of GLS thin films will require a substantial reduction in this tail absorption. Numerous parameters are available to optimise this property, including film post processing such as annealing, and studies of these are in progress. A new, simple and sensitive technique to map the permanent photorefractive effect has been demonstrated.

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