PULSED-LASER DEPOSITION OF Ga-La-S CHALCOGENIDE GLASS FILMS FOR OPTICAL WAVEGUIDE APPLICATIONS

Robert W Eason, Katharine E Youden, Treena Grevatt, Harvey N Rutt,
Rajpal S Deol, George Wylangowski, Devinder S Gill.
Departments of Physics, Electronics,
and
Optoelectronics Research Centre.
Southampton University,
Southampton,
SO9 5NH, U.K.

ABSTRACT

Thin films of Ga-La-S chalcogenide glass have been ablatively deposited onto a range of substrates, including CaF_2, and microscope cover slips. The resultant films are deficient in their sulphur composition by approximately 25%, when compared to the bulk targets used, but the interesting chalcogenide photostructural effects are not compromised by this deficiency. Experiments so far have established that photorefractive effects, such as photodoping, photobleaching and grating formation, all occur readily in the thin films, and gratings have been written using laser and e-beam addressing, to create diffractive structures for optical waveguide applications.

INTRODUCTION

Chalcogenide glasses are non-oxide materials that are finding a range of applications in both visible and infrared technologies. The low characteristic vibrational frequencies of the chalcogenide bonds allow these materials to transmit over a very wide spectral region, from the mid-visible, 0.5μm, to beyond 10 μm in some cases. The consequence of this low phonon energy is that chalcogenides are finding increasing potential as infrared laser hosts, particularly in the region spanning 3-5μm, where alternative solid-state laser sources are scarce.

Additionally, chalcogenides are of interest in the area of nonlinear optics. Using optical or electron-beam addressing, it is possible to modify the structure of the glass to produce regions of altered transmission and refractive index, and hence directly write diffractive structures in bulk samples, and more importantly, thin films, for use in integrated optical devices. The nature of the photo-induced structural rearrangement is quite complicated, and is not fully understood in all materials, but the atomic and molecular reconfigurations can influence the refractive index by very large amounts, in some cases up to 20% [1,2].

Up till now, the chalcogenides that have received most attention are those based on the As-S, Ge-Sb-Se, and Ge-As-Se material systems. Problems occur however with these glasses, as the constituents are often toxic, and there are difficulties with ease of mechanical working, and low devitrification temperatures. The newer Ga-La-S composition [3] has not yet, to our knowledge, been prepared in thin film form, and hence our interest in laser ablative deposition of such films. One of our clear goals is to use these photoinduced changes to produce optical waveguide structures via a direct-write process, and hence optimise the guide parameters for particular wavelengths in both the visible and infrared regions.

DEPOSITION DETAILS

The deposition chamber used was a standard turbo-pumped system capable of base pressures of $\sim 10^{-4}$ mbar. The target was a 12 mm sample of the Ga-La-S glass of nominal composition $7Ga_2S_3.3La_2S_3$ ($LaGa_{2.3}S_5$), which was prepared using standard techniques [4]. The laser used was a KrF laser operating at 40 Hz, and the beam was scanned vertically across the target surface, to optimise uniformity of deposition. Normally, when target size permits, rotational and translational scanning is used, but in this case the simpler method of step-wise scanning was adopted. The laser was focussed to an average flux of 4 J cm^{-2}, and the substrate was positioned at a distance of ~ 5 cm from the target. After deposition, the chamber and the film produced had a strong sulphurous smell, indicative of the loss of sulphur that was characteristic of the films. The likelihood is that the sulphur in the plume had reacted with some hydrocarbon impurity in the vacuum chamber, producing the unpleasant smelling sulphur compounds. Future depositions will occur in a chamber with a base pressure of $\sim 10^{-7}$ mbar, which hopefully will remove this undesirable problem.

The substrates used were discs and slabs of ordinary microscope glass of refractive index 1.52, and also, for use in infrared characterisation measurements, CaF_2, which has an index of 1.434, and which is transparent out to 10 μm. For optical waveguide applications, it is necessary to use substrates with an index which is lower than the film being deposited; for the case of Ga-La-S the index is ~ 2.5, so, unlike the case of epitaxial crystal growth which requires both lattice matching and lower index for the substrate, the constraints are more relaxed.

The deposited films had the same characteristic pale yellow colour as the target material, and spectrophotometer traces showed very similar transmission characteristics to those of the bulk glass. The surface uniformity was very good, and under SEM examination showed very few of the droplets and particles often reported for other materials grown via laser ablation. The thicknesses were in the 1-4 μm region for growth times of 15-60 mins, corresponding to a growth rate of 0.03 nm per pulse.

ANALYSIS OF FILM CHARACTERISTICS

The films were analysed using Rutherford backscattering (RBS), and EDX analysis, to investigate the potential loss of sulphur indicated by the smell remaining in the chamber after deposition. Figure 1 shows the RBS results, together with a computer simulation of a film of thickness 1.2 μm, and a composition of $LaGa_{2.2}S_{3.8}$. Although the La/Ga ratio is as expected, the sulphur content is clearly $\sim$ 25% light in the film. The EDX results are in close agreement, yielding a composition of $LaGa_{2.3}S_{3.7}$.

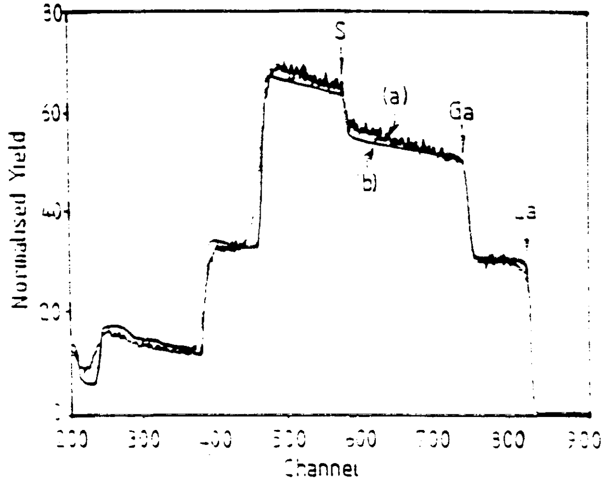

Figure 1. RBS spectrum from a typical film.
(a) experimental data.(b) simulation for 1.2μm film.

Despite the non-stoichiometric nature of the deposition, the photo-structural effects that were sought from these films did not appear to be appreciably influenced. Future deposition work will use a double target technique for correcting the sulphur deficiency, by inclusion of a separate sulphur target, in addition to the existing bulk sample.

PHOTOSTRUCTURAL STUDIES

Photo-bleaching experiments were carried out by exposing the film at a comparatively low irradiance of 0.16 W cm^{-2} using light from an Ar$^+$ laser at a wavelength of 514.5 nm, for a period of 5 hours. The transmission changes were not constantly monitored during this exposure, but a transmission spectrum was recorded after the 5 hour period. It is likely that the bleaching observed is not due to the integrated exposure, and therefore the transmission change observed cannot be related to exposure time directly. Further experiments are needed to examine the nonlinear nature of the bleaching process. Results are shown in figure 2 for film transmission before (a), and after (b), exposure. The periodic ripples seen in the spectrum are due to parasitic etalon effects, and do not represent the true transmission spectrum of the film; the change in transmission was clearly visible by eye. Annealing the film at a temperature of 250°C for 2 hours returned the transmission to its original value.

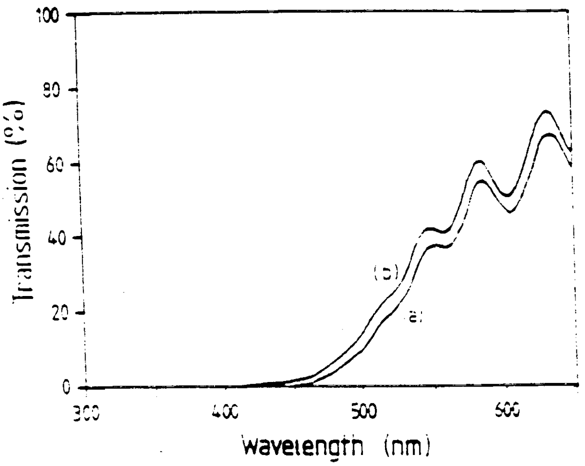

Figure 2. Transmission spectra of deposited film (a) before and (b) after photo-bleaching experiments.

The induced transmission, and possibly refractive index, changes were further investigated via holographic grating writing. Two laser beams at 514.5 nm overlapped on the film at an angle of 36°. The resultant interference pattern wrote a modulation into the film which was simultaneously monitored via a secondary He-Ne laser. The diffracted light was measured over a period of approximately 5 minutes, from which the final value of diffraction efficiency, η, of 0.01%, allowed an estimate of the modulation of index, Δn, achieved in the ~ $1\mu m$ thick film, via the expression[5],

$$\Delta n = \frac{\lambda \cos\theta}{2\pi d} \cosh^{-1}\left(\frac{1}{1-2\eta}\right) \qquad (1)$$

where d is the $1\mu m$ thickness of the film, and θ is the external writing angle (36°). The diffraction result implied a Δn value of 2.10^{-3}, which is smaller than the values reported for other chalcogenides, but is encouraging considering the interferometric set-up was not vibrationally stabilised, and the film was not stoichiometric in it's sulphur content. Further work will focus on more accurate measurements using films grown via the double target geometry.

Photo-diffusion studies were also performed on a film that had been overcoated with a thin (10nm) layer of silver. The composite structure was exposed for a 30 minute period, through the substrate, at an irradiance of 2 W cm^{-2}, using 514.5 nm laser light. After removal of the residual silver layer in a solution of $Fe(NO_3)_3$, EDX analysis showed that 0.3 atomic % of silver was present in the regions that had been exposed, and that none was present in the unexposed regions, indicating that photodiffusion had occurred in those regions exposed to laser light. This result is particularly important to the current interest in laser writing of guides, as the regions with a silver in-diffusion will have a modified refractive index, and hence support guided waves either directly if the index is increased, or via the writing of side walls for a decreased index. Other work[6] has also shown a preferential etch rate for undoped regions containing no silver, via a NaOH etch, but the results for this Ga-La-S material were inconclusive.

Finally a small piece of the film was exposed to 20 keV electron-beam addressing in a SEM. A 1mm^2 square area was exposed to a raster scanned beam writing a grating with a 4 μm pitch. After removal from the SEM, a grid pattern was clearly discernable, which diffracted an incident He-Ne beam into several orders, the intensity of which indicated a value of $\Delta n = 1.5 \times 10^{-2}$ for the exposed regions.

All the above photostructural effects are of particular importance in waveguide applications, for which the uniformity of growth, thickness, homogeneity and hence waveguide loss is of prime importance. Currently the films produced have not yielded a definitive loss measurement, but prism coupling has allowed the determination of the effective indices of the first few TE modes, via examination of the angular position of the 'dark' modes. Using a 60° rutile prism, 4 TE and 3 TM modes were observed, from which the refractive index of the film was calculated to be 2.53, which is in close agreement with the expected value for the bulk glass sample. Loss measurements will be obtained on future films which are grown under more optimum conditions.

FUTURE DIRECTIONS AND CONCLUSIONS

The most important development is obtaining improved quality growth, and to this end, a redesigned chamber with two independent targets is now available. The schematic is shown in figure 3, in which two separate excimer beams are incident on two different targets. Although this introduces a further degree of complexity into the deposition process, it also introduces another degree of freedom, which in the case of chalcogenide growth should allow the sulphur deficiency to be corrected. The deposition of such glassy materials is also more tolerant to slight variations in growth conditions than those that are required for epitaxy, and it is anticipated that glass growth of a range of other materials will shortly be pursued, which also show such photostructural effects.

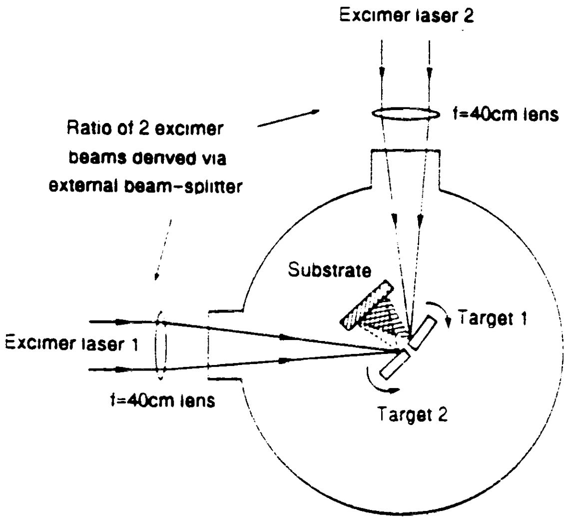

Figure 3. Double beam chamber with independent target control.

ACKNOWLEDGEMENTS

The authors are grateful to P.J.Chandler of Sussex University for the RBS analysis, and the Science and Engineering Research Council for sponsorship, and financial support.

REFERENCES

1. A.E.Owen. A.P.Firth and P.J.S.Ewen, Philosophic. Magazine **B 52**, 347 (1985).

2. A.M.Andriesh, Y.A.Bykovsky, E.P.Kolomeiko, A.V.Makovkin, V.L.Smirnov and A.V.Shmalko, Sov.J.Quantum Electron. 7, 347 (1977).

3. S.Benazeth, M.H.Tuilier, A.M.Loireau-Lozach, H.Dexpert, P.Logarde and J.Flahaut, J.Non-Cryst. Sol. **110**, 89, (1989).

4. A.M.Loireau-Lozac'h, M.Guittard, J.Flahaut., Mat.Res.Bull. **11**,1489 (1976).

5. E.Kratzig, O.F.Schirmer, Photorefractive Materials and their Application 1, 150, (Springer-Verlag,Berlin,1988).

6. B.Mednikarov, Solid State Technology, 177 (1984).