



Characterisation of Ga–La–S chalcogenide glass thin-film optical waveguides, fabricated by pulsed laser deposition

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Abstract

The fabrication of stoichiometric thin-film optical waveguides of Ga–La–S via a pulsed laser deposition technique is reported. Stoichiometric films are grown by ablating Ga–La–S bulk glass with a KrF excimer laser ($\lambda = 248$ nm) at an incident laser flux ≥ 3.5 J/cm². The composition of the films is determined by energy-dispersive X-ray analysis and the refractive index is measured by a dark-mode prism coupling technique. Photoinduced structural rearrangement of the as-deposited films leads to a blueshift in the visible absorption edge and a permanent refractive index change, Δn , of -1% . On the basis of these results, grating structures have been written with both blue light, and e-beam addressing, and their suitability for integrated optical structures assessed.

1. Introduction

Chalcogenide glasses are non-oxide materials containing elements from Group VI of the periodic table, namely S, Se and Te. The low vibrational frequencies of the chalcogen bonds allow these materials to transmit over a wide spectral region, from 0.5 to 10 μm in the case of Ga–La–S [1]. As a consequence, these glasses have applications as windows and lenses at infrared wavelengths. The low phonon energy of these bonds also modifies non-

radiative relaxation rates, so that these glasses are suitable as laser host materials. Doping of the Ga–La–S glasses with Ho_2S_3 has yielded fluorescence at 654 nm, with a higher intensity than in the case of tellurite glasses [1].

Photoinduced effects can alter the physical and chemical state of amorphous chalcogenide glasses and films in a number of ways [2]. The two most common phenomena are a reversible red-shift of the absorption edge in well-annealed films/glasses [3] and an irreversible blue-shift for as-deposited films [4] when exposed to light of energy above the band gap of the material. It has been speculated that the irreversible blue-shift for as-deposited films is due to a photopolymerization effect [2]. The surface of the

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as-deposited film consists of incompletely polymerised molecular aggregates which, on illumination, are polymerised and combine with the network. On prolonged exposure, the films have a similar structure to well-annealed films and glasses. Despite the lack of theoretical background, it has been shown experimentally that the induced refractive index change in these materials permits the fabrication of high spatial resolution grating structures using either laser [5] or e-beam [6] addressing, with applications such as mode converters, waveguide couplers and Bragg reflectors in integrated optical devices.

Most work on amorphous chalcogenide materials to date has concentrated on the As–S, Ge–S, Ge–Se and As–Ge–Se compositions. However, all these have a low devitrification temperature so that manufacture of the glass by quenching is difficult. Ga–La–S is easier to prepare because it is more thermally stable with a transition temperature of typically $\approx 600^\circ\text{C}$ [7]. Also it does not suffer from toxicity problems, a factor associated with other chalcogenide materials.

We have previously reported the fabrication of thin-film optical waveguides of Ga–La–S using a pulsed laser deposition technique [8]. In this report we discuss the physical properties and quality of films grown under various deposition conditions, and a more detailed study of the photo-induced effects in these films is presented.

2. Experimental results

Thin films were deposited in a vacuum chamber, at a background pressure of $\approx 10^{-3}$ mbar, as shown in Fig. 1. Ga–La–S glass targets were prepared by standard techniques [9] and ablated with a KrF excimer laser operating at 248 nm, and a pulse duration of ≈ 20 ns. The laser energy per pulse was kept constant at 400 mJ, but the incident laser flux was varied from 2 to 16 J/cm² by changing the beam area on the surface of the target. The ablated plume of material was ejected perpendicular to the target surface and deposited onto a substrate, positioned parallel to the target at a distance of ≈ 6 cm. During the depositions, the effect of substrate temperature on the quality of the films was investigated. The substrates used were Si, CaF₂ and microscope slide

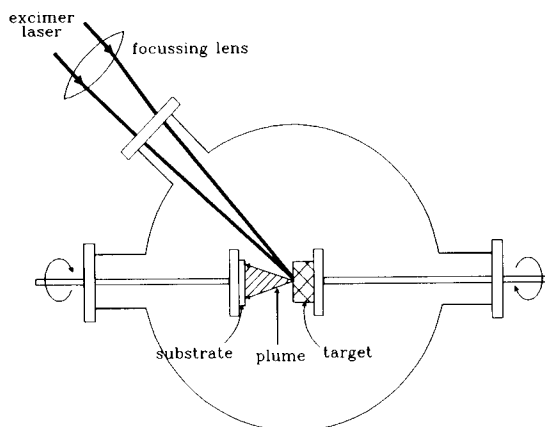


Fig. 1. Experimental arrangement for pulsed laser deposition.

glass which were all rotated slowly during deposition in order to improve the uniformity of the films. Si and CaF₂ are transmissive in the infrared, up to wavelengths of 6 and 100 μm respectively so that transmission spectra of the films in this spectral region could be obtained. Glass substrates enabled absorption spectra in the visible to be taken, using a spectrometer (Perkin–Elmer Lambda 9). All the films were deposited for 20 min at a laser repetition rate of 20 Hz and alpha-step analysis indicated their thickness to be in the region 0.34–1.35 μm .

Fig. 2 demonstrates the effect of substrate temperature on the absorption spectra of the films produced,

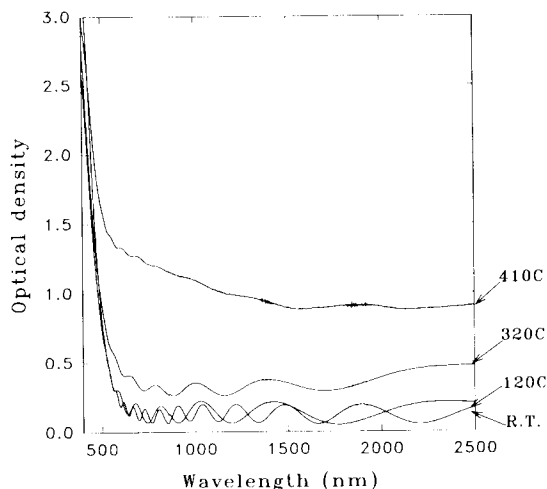


Fig. 2. Absorption spectra of Ga–La–S films deposited at various substrate temperatures.

where the optical density ($\log_{10} 1/T$, T = transmission) is plotted against the wavelength. The periodic modulation observed is an etalon effect due to light interfering from the air/film and film/substrate reflections. Increasing the substrate temperature only served to make the films more opaque at all wavelengths. The most transparent films were obtained by deposition at room temperature. The use of a cooled substrate holder would perhaps improve the transmission properties of the films.

The refractive index and thickness of all the films were determined using a dark-mode prism coupling technique [10] as shown in Fig. 3. The He–Ne beam ($\lambda = 633$ nm) was launched through a rutile prism at an incident angle, ϕ , to the normal. The light was totally internally reflected at the base of the prism and imaged onto a screen. The prism assembly was rotated until a dark line was observed on the screen corresponding to some of the light being coupled into the waveguide. Measurement of the incident angle, ϕ , enabled the effective refractive index, n_{eff} , of the excited mode to be calculated using the equation below, where n_p is the extraordinary refractive index of the prism (2.872), n_a is the refractive index of air (1.0) and α is the angle of the prism (60°):

$$n_{\text{eff}} = n_p \sin \left\{ \alpha + \sin^{-1} \left(\frac{n_a}{n_p} \sin \phi \right) \right\}.$$

Calculations of the effective refractive indices for the TE_0 and TE_1 modes and substitution of these values into the guidance condition for an asymmetric waveguide enabled the refractive index and thickness of

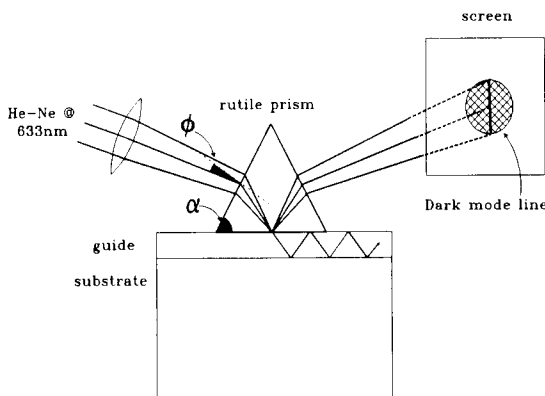


Fig. 3. Experimental arrangement for dark-mode prism coupling.

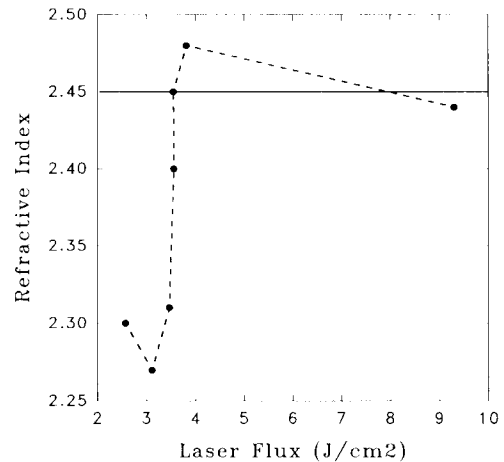


Fig. 4. Refractive index of films deposited at various laser fluxes. The bulk glass has a refractive index of 2.45 as indicated by the solid line.

the films to be evaluated. The dark-mode prism coupling technique has an accuracy in the incident angle, ϕ , readings of $\pm 0.2^\circ$ which results in an error in the refractive index of the thin film of only ± 0.002 .

Fig. 4 shows the refractive indices deduced for the films deposited at various laser fluxes. Those films deposited using a laser flux ≥ 3.5 J/cm² had a refractive index value, $n \approx 2.45$. Using data in Ref. [7], we extrapolated the value of refractive index at $\lambda = 633$ nm, for a Ga/S ratio of 0.7, and find that $n = 2.45$. Hence a good agreement exists between the film and bulk glass refractive indices. Films grown at a laser flux less than this value had a lower index, $n \approx 2.3$. Similar results emerged from analysis of the transmission spectra of these films. The cut-off wavelengths of the films and bulk glass were evaluated by extrapolating the Urbach edge to the abscissa on the spectrum and measuring the corresponding wavelength. The bulk glass had a cut-off wavelength at 480 nm (indicated by the solid line in Fig. 5). Films deposited with laser fluxes above 3.5 J/cm² had a similar transmission spectrum, whereas films deposited with laser fluxes below 3.5 J/cm² were more transparent with a cut-off wavelength at ≈ 350 nm.

Energy dispersive X-ray analysis (EDX) was performed on all the films. The X-ray yield was calibrated against known standards of Ga and S. The

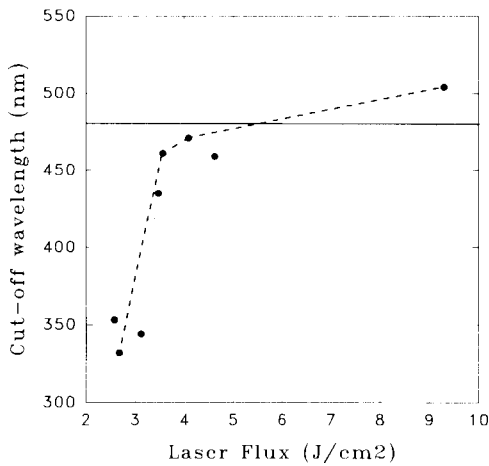


Fig. 5. Cut-off wavelength of films deposited at various laser fluxes. The solid line corresponds to the bulk glass value.

analysis revealed that the films which had similar physical properties to the bulk glass (refractive index, transmission spectra) had a similar elemental composition with a Ga/S ratio of ≈ 0.7 compared with 0.69 for the bulk glass. The films with a refractive index value, $n \approx 2.30$ were non-stoichiometric, with a Ga/S ratio varying from 0.4 to 0.6; the films were sulphur-rich. This condition is in agreement with previous reports on As-S [10] and As-Se-S-Ge [11] in which an increase of sulphur in the composition leads to more transparent films and a reduction in the refractive index. Unfortunately the films grown at high laser fluxes often had undesirable, $\approx 1 \mu\text{m}$ sized spherical droplets deposited on the surface. These droplets are possibly due to a subsurface heating effect on the target, which then ejects clusters of atoms [12].

The homogeneity of such films has been investigated by carrying out EDX analysis at 12 points on the surface of a film. The results showed that the mean atomic weight percents (\pm the standard deviation) for the gallium, lanthanum and sulphur components were 26.82% (± 2.86), 15.24% (± 2.52) and 50.45% (± 5.56), respectively, showing that the film had a good homogeneity across its surface.

All of the films produced were investigated for photostimulated changes. The as-deposited stoichiometric films were illuminated with light from an argon ion laser operating at 488 nm, with a laser flux of 600 mW/cm^2 . This radiation produced a shift in

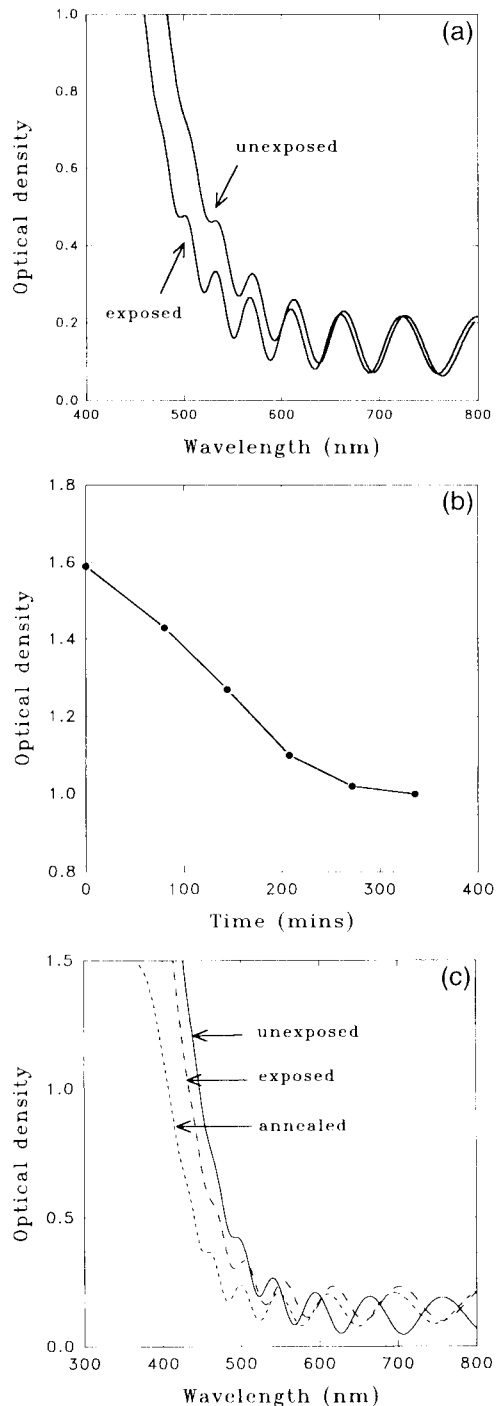


Fig. 6. (a) Photobleaching of a stoichiometric film by illumination from an argon ion laser beam with a flux of 600 mW/cm^2 . (b) Saturation of the photobleaching effect at a wavelength of 460 nm. (c) Annealing of the sample at 250°C for 3 h demonstrating the irreversibility of the photobleaching effect.

the absorption edge to shorter wavelengths (Fig. 6(a)). A time dependence analysis indicated that the process took 5 h to become constant at a wavelength of 460 nm, as in Fig. 6(b). The effect was not reversed by annealing of the sample for 3 h at a temperature of 250°C, which produced a further shift in the absorption edge to shorter wavelengths (Fig. 6(c)). The change in the refractive index resulting from this structural rearrangement was again determined by prism coupling into an area of the film that had a sharp boundary between bleached and unbleached regions. The dark-mode lines for the unbleached area were imaged onto a screen and manipulation of the He–Ne source onto the bleached area (without changing the incident angle, ϕ) shifted the mode lines to the right. This shift corresponds to a negative refractive index change, $\Delta n = -0.02$ (i.e., $\approx 1\%$). The non-stoichiometric films were stable to photoinduced effects, and illumination at several wavelengths $\leq 488\text{nm}$ yielded no shift in the absorption edge. A similar result has been observed for sulphur-rich As–S compositions [10].

3. Discussion and applications

We used the results of the photoinduced properties of the thin films to investigate the strength of grating structures which can be produced in these materials. Diffractive grating structures were written by the interference of two beams from a helium–cadmium laser operating at 442 nm, illuminating the film. Each beam was incident on the surface of a stoichiometric film at an angle of 30°. A low-powered He–Ne laser (4.5 mW) was diffracted via the induced grating and the first-order diffraction efficiency, η , and first-order diffraction angle, θ , measured. These had values of 0.05% and 21.75°, respectively, so using the equation below [13], where d is the thickness of the film (1.15 μm), we calculate an induced Δn :

$$\Delta n = \frac{\lambda \cos \theta}{2\pi d} \cos^{-1}(1 - 2\eta) = 3.6 \times 10^{-3}.$$

This value is much smaller than the saturation value (0.02) deduced earlier. This change is almost certainly due to the fringe instabilities that were present in the interferometric set-up. The induced Δn can be

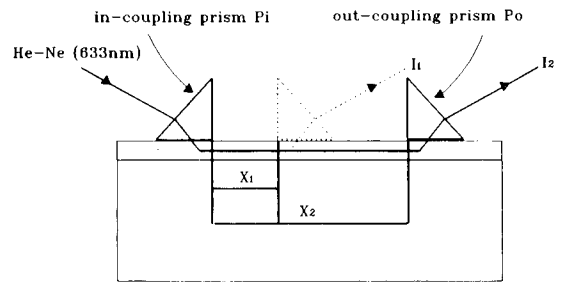


Fig. 7. Experimental set-up for waveguide loss measurements. The output power, I_2 , is measured as a function of the separation, x_2 , between the in-coupling prism, P_i , and the out-coupling prism, P_o .

improved using either a vibrationally stabilised set-up or an electron beam to write the gratings. The latter method was implemented using a 20 keV e-beam rastered across the surface of the film with a pitch of 4 μm . Once again He–Ne laser light was diffracted through the structure and η measured. This measurement gave $\Delta n = 0.015$.

In parallel with the diffraction efficiency studies, we measured the waveguide losses in the films using a prism-sliding method [10] as outlined in Fig. 7. A He–Ne laser (at 633 nm with a power of 25 mW) was guided into the TE_0 mode using a right-angled rutile prism (P_i). The output rutile prism (P_o) was positioned at varying distances from the launch prism and the corresponding output intensity, I , monitored. Using the expression below, a plot of $\log I$ versus the distance, x , was used to yield a loss value, β , for the film:

$$\beta = \frac{10}{(X_2 - X_1)} \ln \frac{I_1}{I_2}.$$

The prism-sliding method proved difficult owing to the small dimensions and fragility of the samples and we must consider our results (shown in Fig. 8) as an estimate for the loss measurement only. The error-bar in the figure was derived from the uncertainty in the output intensity, I , due to the irregular coupling pressure on the output prism, P_o . The sharp decrease in output intensity at a prism separation between 1 and 2 mm (indicated by line BC in Fig. 8) is probably due to scattering of light from a particle or scratch on the surface of the film. The loss measurement can be evaluated by determining the gradient of either lines AB or CD, but since a greater number of

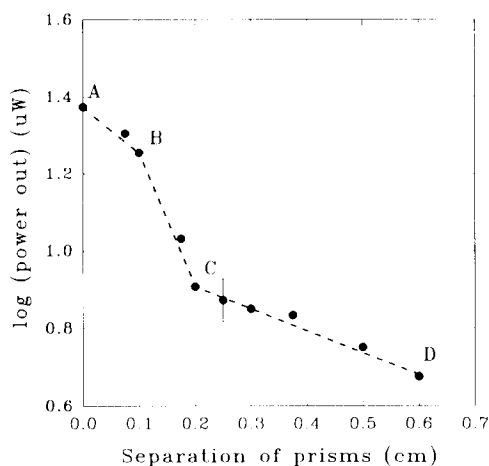


Fig. 8. Waveguide loss measurement using the prism-sliding method. The error-bar represents the typical uncertainty in measuring the output power from the waveguide.

points have been determined for line CD, this would give the more accurate loss value. The resulting loss of ≈ 6 dB/cm is high but can easily be decreased by a number of techniques. If the experiment was repeated at IR wavelengths which have much lower intrinsic absorption losses, being far from the Urbach edge, the losses would be significantly lower [10]. Also, the introduction of a cladding layer on the surface of the films would increase the reduction. An ideal substance for this cladding would be the sulphur-rich Ga–La–S composition which has a lower refractive index, good transmission properties, and is inert to argon ion radiation. The deposition of this material would be simple and convenient since it is possible to perform in situ over-growth by variation of the excimer laser flux used.

4. Conclusion

In conclusion, we have fabricated a variety of thin films of the Ga–La–S composition, by changing the laser flux or substrate temperature during the deposition. Stoichiometric films have been deposited at room temperature and a laser flux ≥ 3.5 J/cm². The films have similar physical properties (transmission spectra, refractive index) to bulk glass and have

photostructural effects which produce a negative refractive index change. Sulphur-rich films have been obtained at low laser flux which do not undergo any photoinduced structural effects. The ease of fabrication of gratings in the stoichiometric Ga–La–S amorphous films using both laser and e-beam addressing makes them an attractive material for applications in integrated optics.

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