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Characterisation of compositional photosensitivity dependence of Ga-La-S thin films fabricated by pulsed laser deposition

(Submitted for ULF-LENS annual report 1994/95)

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1. Introduction

Thin films of chalcogenide glasses of Ga-La-S composition (GLS) have recently been grown via the technique of pulsed laser deposition (PLD)[1,2]. These non-oxide glasses have many attractive features including a wide transmission range which extends from visible wavelengths up to $\simeq 10\mu m$, and low phonon energies, which drastically reduce non-radiative relaxation rates, thus making them interesting candidates for infra-red laser hosts. Furthermore, under irradiation with light in the blue/uv wavelength region, these glasses can exhibit several photostructural effects including photobleaching[2], photodoping, and more complicated reconfiguration behaviour, in which refractive index variations of the order of 1% can easily be produced. The exact cause of such index changes is uncertain[3], but the possibility of writing diffractive grating structures with sub-micron resolution in waveguide GLS structures holds out much potential for distributed feedback integrated optical devices. Previous results on both laser and e-beam grating writing[2] have revealed the ease with which gratings can be produced in GLS films, but so far, no systematic study has been undertaken on how the induced refractive index change depends on exact compositional properties of the GLS glasses.

2. Thin film growth characteristics

All the thin films, (thicknesses in the range 0.5 - 4.0μm) were grown via PLD in a vacuum chamber as shown in figure 1. The background pressure prior to ablation was in the region of 10^{-4} mbar. Target materials were prepared at Southampton University from Ga_2S_3/La_2S_3 starting materials, in the ratio of 60/40 and 70/30, and took the form of glass discs of ~ 20mm diameter. As indicated in figure 1, both target and substrate were rotated during growth, to ensure uniformity of plasma characteristics and uniformity of deposition respectively. The laser used was an LPX KrF excimer laser, operating at $\lambda = 248$ nm. The substrate rotation produced films that were radially very uniform, so that measurements could be made on photosensitivity at various radial positions, in an attempt to correlate the results with subsequent stoichiometric analysis performed at equivalent positions on the film.

Laser energies in the range 150 mJ to 500 mJ per shot were used, at energy densities between 3 Jcm^{-2} and 12 Jcm^{-2}. The distance between substrate and target could also be varied between 3 cm and 9 cm. All depositions were carried out using ordinary glass microscope slides as the substrate, and room temperature growth only was performed. The large size (75 mm x 25 mm) of the slides used immediately revealed that film properties such as colour and texture were a function of radial position. Some depositions produced films that were red/brown colour at the centre of the substrate (d = 0), but yellow/white at the edge (d = 37.5 cm). The exact colour depended on several factors, notably energy density used and target-substrate distance; large energy densities and small distances produced films that showed large radial variations in colour.

3. Photosensitivity measurements

From the $\simeq 50$ films produced several were selected for preliminary evaluation of their photosensitivity. A 50 mW He-Cd laser operating at 442 nm was used to write gratings in a holographic set-up as shown in figure 2. During the writing process, which took between 5 minutes and 20 minutes, the diffraction efficiency of the grating was continually monitored, at 1 minute intervals, by closing shutter S, and measuring the diffracted light intensity from incident beam 1, on the photodiode as shown. Care was taken to shield the photodiode from stray light, by suitable positioning of apertures. As the experiment in figure 2 is clearly sensitive to vibrational instabilities and hence inconsistent grating efficiency results, two precautions were taken during the measurements. Firstly the equipment was vibrationally and thermally isolated using a floating table and thermal enclosure, and secondly fringe stability was monitored at the plane where the GLS film sample was positioned. It was observed that after laser warm-up, holographic fringe movements of no more than $\pm 10\%$ occurred during a typical writing period of up to 20 minutes.

For quantitative results, a film was chosen (film#49) that showed a high degree of radial uniformity, a progressive colour change from orange/brown at the centre, to yellow at the edge, and a centre thickness sufficient to record large diffracted intensities. The growth conditions of this film were: laser energy = 200 mJ, substrate-target distance = 7 cm, laser repetition rate = 27 Hz, and deposition time = 50 minutes. These conditions produced a film with a centre thickness of ~ 3 μm, and an edge thickness of ~ 1 μm.

4. Results and discussion

Figure 3 shows a typical diffraction efficiency measurement obtained from film #49. The experimental points were recorded every minute, and the diffraction efficiency values are defined as I(diffracted)/I(transmitted), thus correcting for background absorption in the film. The solid line is a theoretical curve based on the assumption that the refractive index change produced is a saturating function of time, given by

$$\Delta n(t) = \Delta n\ (t = \infty)\ [1 - e^{-t/\tau}]$$

where $\Delta n\ (t = \infty)$ is the saturated index change, τ is the characteristic response time, and $\Delta n(t)$ are the values deduced from the measured diffraction efficiencies $\eta(t)$, as given by[4]

$$\eta(t) = \tanh^2 \left[\frac{\Delta n(t)\, \ell\, \pi}{\lambda \cos\theta} \right]$$

Where the gratings are written at a wavelength λ, with a sample of thickness ℓ, at a beam half-angle of θ as shown in figure 2.

The theoretical fits were necessary to deduce both $\Delta n\ (t = \infty)$ and τ for each point on the film, as saturated diffraction efficiency results would have required measurements to be taken for times greatly exceeding τ, thus increasing the likelihood of systematic errors through instabilities in grating writing. As can be seen from figure 3, the fit is good between measured values and computed results, using only $\Delta n\ (t = \infty)$ and τ as fit parameters

The variation of film colour with radial distance indicates a compositional change across the film. Although PLD is capable of faithful stoichiometric transfer between target and substrate, there can be systematic variations at incorrect distances, and for deposition at appreciable angles off the normal. The film was therefore sent for quantitative EDX analysis, to compare the ratio of Ga:La:S at each position where a Δn measurement has been made. In total 11 points were measured across the film, covering a range of ~25 mm from the central area.

Initial EDX results from Southampton University were complemented by an extended EDX analysis performed at Cambridge University. The results showed that both the sulphur and gallium content of the film systematically increased as a function of radial distance from the central area, while the lanthanum content did the opposite. Figure 4 shows this trend with a straight line fit added. The lanthanum content has been normalised here, by dividing the x-ray count for lanthanum by the total amount for all three elements. The value here is therefore a normalised count rate, rather than either an atomic or weight per cent value. The trend however is clear. Similarly, the fitted value of τ, the response time, has been plotted as a function of the radial distance in figure 5. Again the trend is sensible, as the film is thicker at the centre than further out, hence more time is required at constant laser power, to modify the film refractive index.

The final graph, figure 6, shows the correlation between normalised lanthanum content and deduced value of Δn at $t = \infty$. Other fits of Δn versus normalised gallium or sulphur content show very similar, but opposite gradient, trends.

It seems clear therefore that the measured photosensitivity is a function of specific elemental ratio. The inferred value of Δn ($t = \infty$) over this limited elemental variation of $\pm 10\%$ is of order 1%, which is sufficiently high for writing efficient distributed feedback gratings in planar waveguide structures. Of more importance perhaps is the ability to predict the Δn achievable for a range of glass compositions. PLD enables growth of materials with precise properties, so that fabrication of gratings with non-sinusoidal index profiles is possible, knowing the results from e.g. figure 6.

Further studies likely with GLS involve investigation of some of the darker films produced, which have shown photosensitivity at wavelengths extending to the red (λ = 633 nm). Excimer laser pulsed grating writing is also possible, and we have made preliminary studies of this behaviour.

References

1. K.E. Youden, T. Grevatt, R.W. Eason, H.N. Rutt, R.S. Deol, G. Wylangowski. Appl. Phys. Lett. **63**, p.1601-1603, (1993).

2. D.S. Gill, R.W. Eason, C. Zaldo, H.N. Rutt, N.A. Vainos. J. Non-Cryst.Sol. Accepted for publication Feb. (1995).

3. S.R. Elliott, J. Non-Cryst. Sol. **81**, p.71, (1986).

4. E. Kratzig, O.F. Shirmer, 'Photorefractive Materials and their applications I,' Springer-Verlag, Berlin, p.50, (1988).

Figure Captions

1. Schematic of laser ablation chamber.

2. Experimental arrangement for measuring diffraction efficiency from GLS films.

3. Typical data obtained for diffraction efficiency a, a function of time, with computer generated best fit.

4. Normalised lanthanum content versus radial position on film #49.

5. Deduced response time, τ, versus radial position on film #49.

6. Correlation between deduced value for Δn at $t = \infty$, and normalised lanthanum content for film #49.

Acknowledgements

The authors are pleased to acknowledge Professor Costas Fotakis, and all the staff at FORTH- IESL for their help and assistance during the course of these experiments. Thanks also go to Brian Ault, and Barbara Cressey at Southampton University, and Stephen Reed at Cambridge University for EDX analysis of film composition.

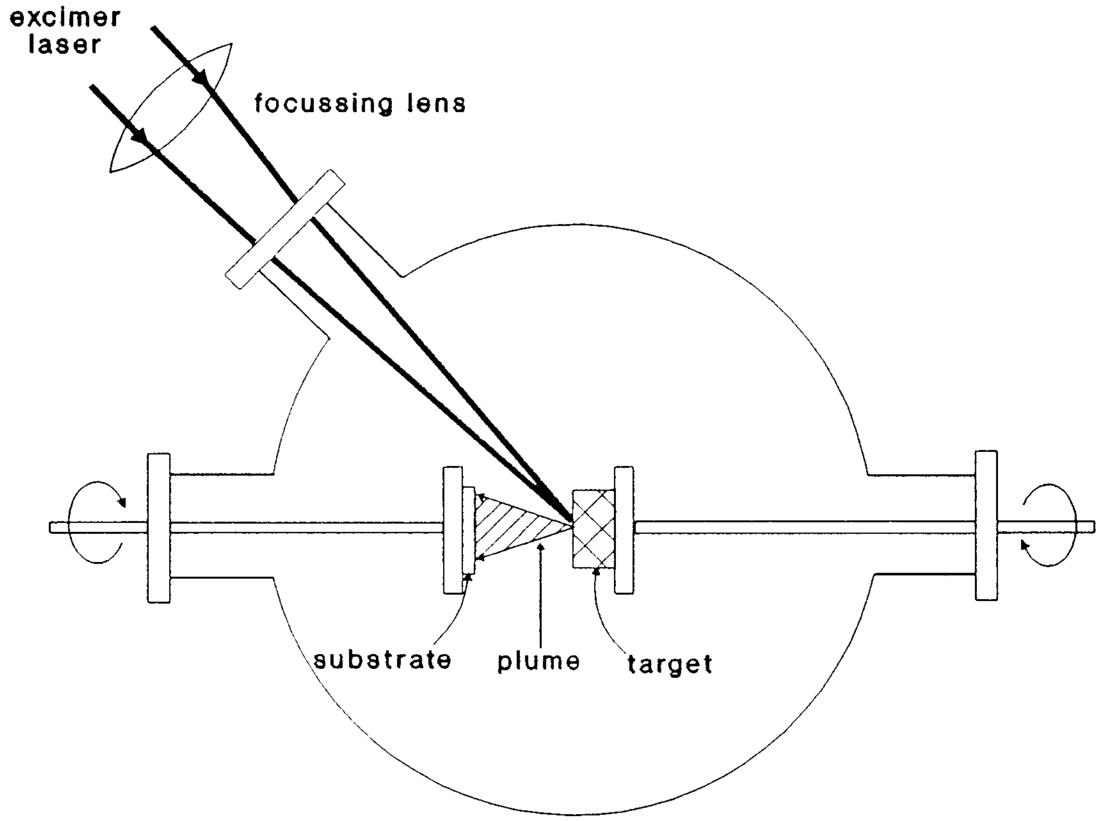
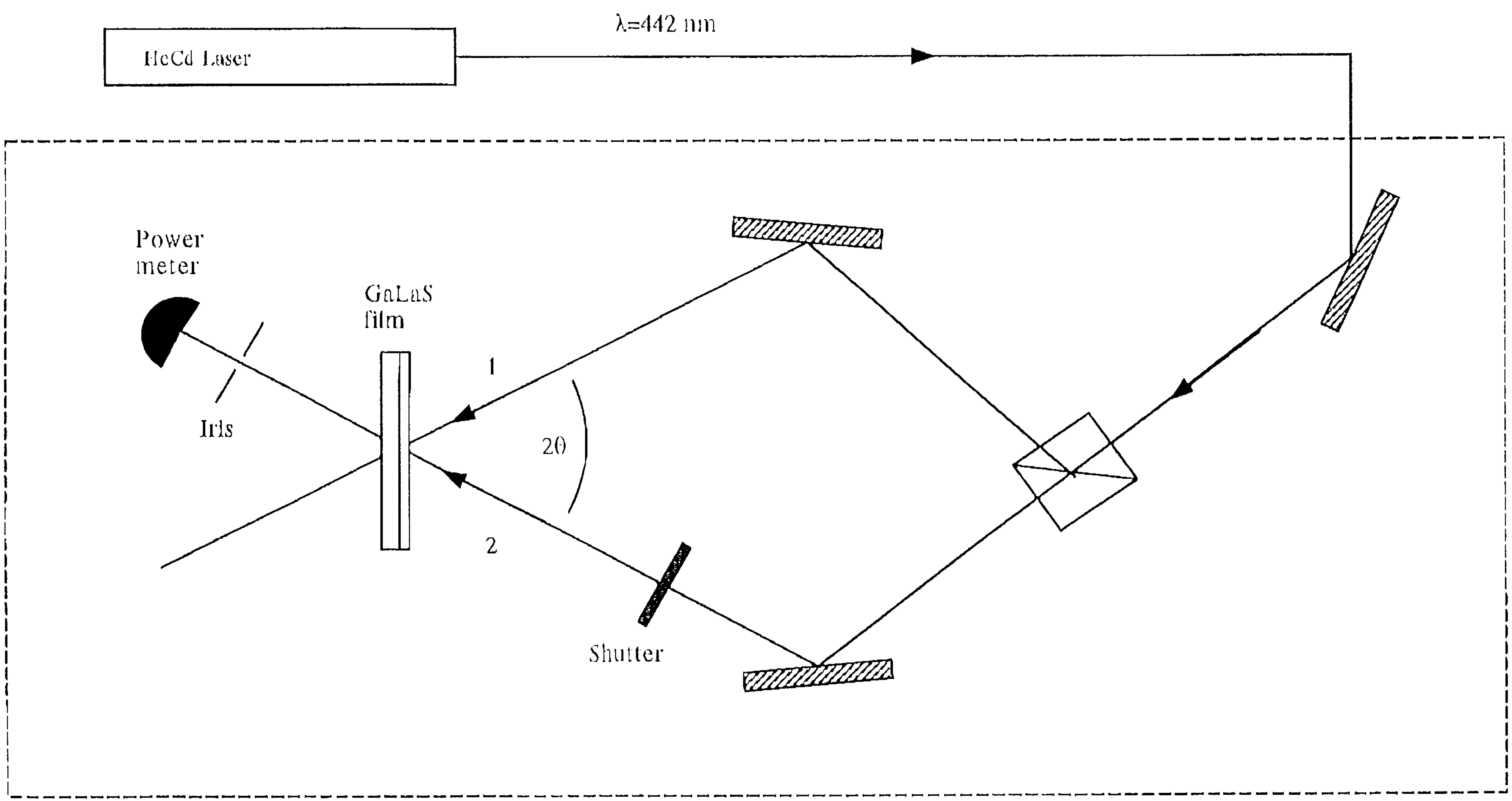


fig 1



(Not original)

fig 2

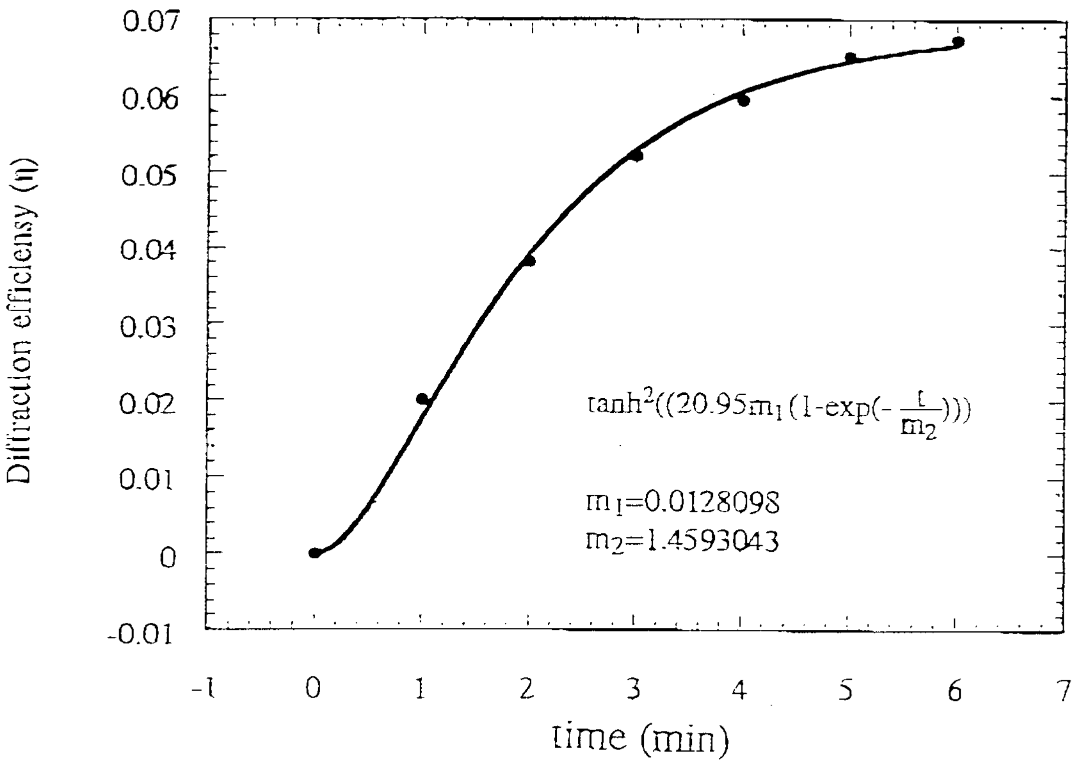


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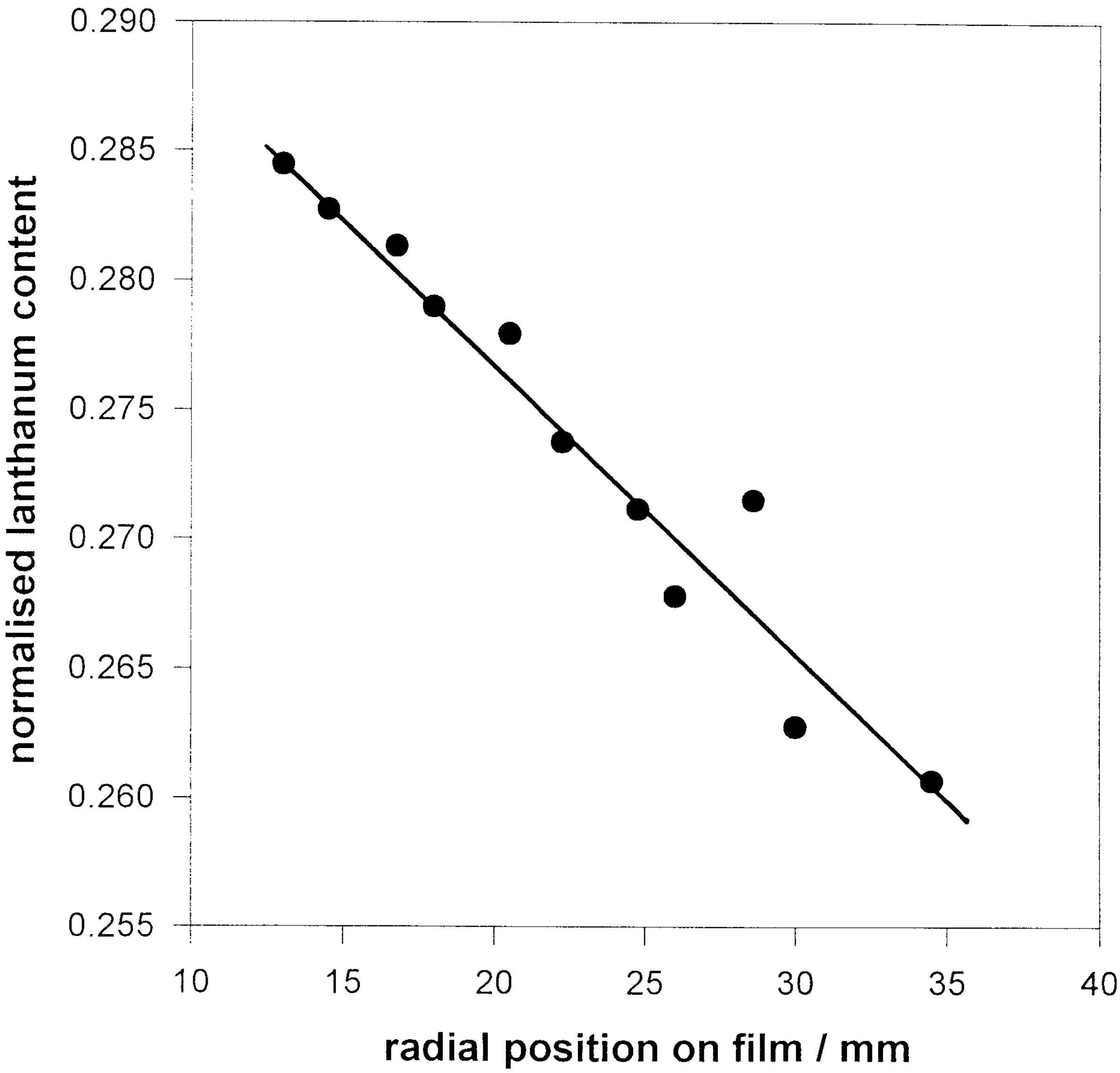
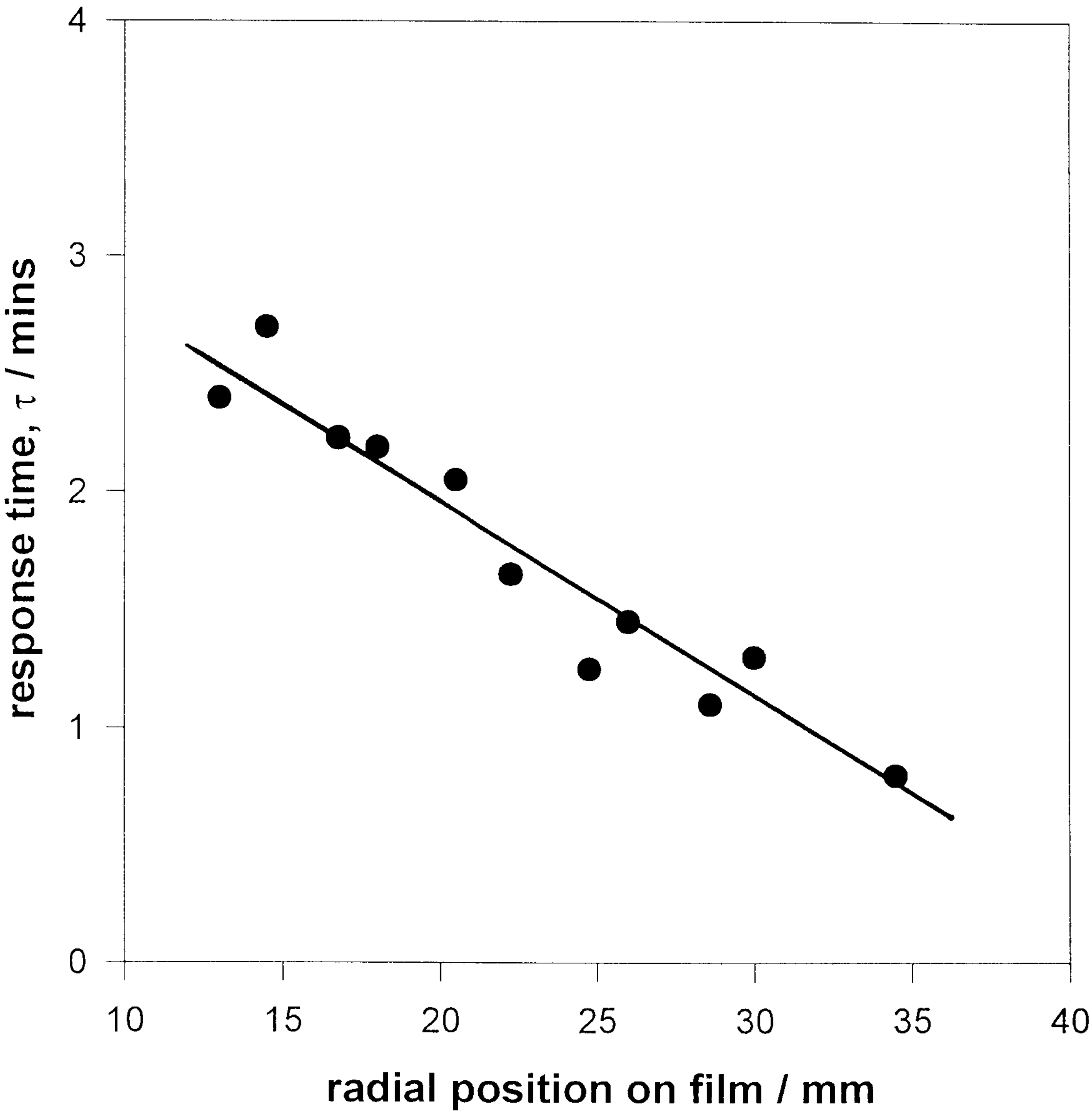
Fig 3



0.290
0.285
0.280
0.275
0.270
0.265
0.260
0.255
normalised lanthanum content
10
15
20
25
30
35
40
radial position on film / mm

fig 4



4
3
2
1
0
10
15
20
25
30
35
40
response time, τ / mins
radial position on film / mm

fig 5

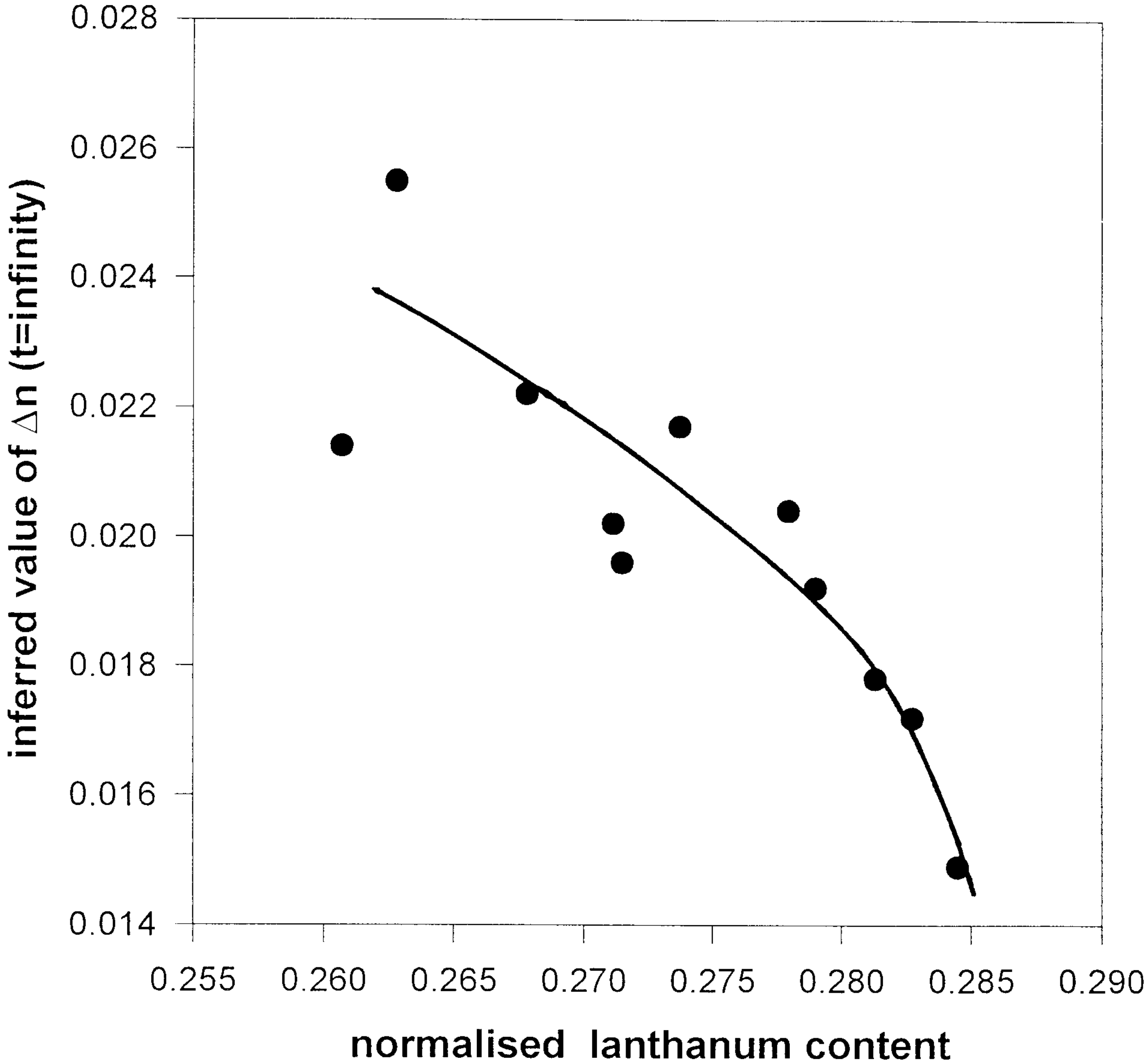

0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
inferred value of Δn (t=infinity)
0.255
0.260
0.265
0.270
0.275
0.280
0.285
0.290
normalised lanthanum content

Fig 6.