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Photosensitivity of lead germanate glass waveguides grown by pulsed laser deposition.

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Abstract

We report very large photoinduced refractive index changes, Δn, of order $\sim 10^{-2}$, in lead germanate glass waveguides grown by pulsed laser deposition. The magnitude of Δn was derived from measurements of diffraction efficiency for gratings written by exposure with 244 nm light through a phase mask, while the sign of Δn was determined from ellipsometric data. Results are shown for films grown under oxygen pressures ranging from 1×10^{-2} to 6×10^{-2} mbar.

Lead germanate glasses are important low phonon energy laser hosts, that combine a range of desirable optical properties. Efficient lasing in the infrared spectral region has been demonstrated, for glasses with Tm^{-} doping [1], and the intrinsic infrared transmission can extend to beyond 5 μm [2]. The index of refraction of lead germanate glasses is high, with a bulk value of n=1.83, which is also attractive for nonlinear optical applications involving $\chi^{(3)}$ processes. Additionally however, the host glass can exhibit pronounced photosensitivity. When thin film (~1μm) optical waveguides are fabricated using pulsed laser deposition (PLD) for example [3], the material can be photomodified using appropriate UV laser wavelengths, enabling efficient channel waveguides, and associated grating structures to be written for waveguide laser applications.

Similar behaviour has recently been observed in GeO_2 - SiO_2 sputter deposited glass films [4], where gratings were written using pulsed excimer laser exposure. In this letter however, we report on the photosensitivity of lead germanate glasses grown by PLD, induced by c.w. irradiation at a wavelength of 244 nm, from a frequency doubled Ar ion laser.

The lead germanate glass waveguides were grown from a bulk lead germanate glass target on to borosilicate glass (microscope slides) and fused silica substrates, using excimer laser irradiation at wavelengths of 193 nm and 248 nm. The composition of the target material in mole % was: $55GeO_2$-20PbO-10BaO-10ZnO-$5K_2O$. Deposition was carried out in a background oxygen atmosphere at pressures of between 10^{-2} mbar and 10^{-1} mbar: the resultant refractive index change (magnitude and sign) was found to be critically dependent on the actual value used. Further details on growth and morphology can be found in [3].

The thin film glass waveguides were found to be photosensitive across a wide spectral region, spanning wavelengths of 193nm, 248nm (pulsed excimer), 244nm (c.w. frequency doubled Ar ion) and 325nm (c.w. He-Cd). Only the photosensitivity at 244 nm is considered in this paper however. Gratings were written using a silica phase mask, with period of 1077nm, (QPS technology Inc, USA), which was optimised for use at 244 nm, and had a residual zero order intensity of 0.8%.

It is straightforward to calculate the value of Δn achieved for films of known thickness, using the usual diffraction grating expression :

$$\eta = \tanh^2 (\Delta n \, \pi \, d / \lambda \cos \theta),$$

where η is diffraction efficiency, d is the film thickness, and λ is the wavelength of the diffracted light. If, however, the absorption depth of the film at the writing wavelength is appreciably smaller than the actual film thickness, then an effective thickness, d_{eff}, must be used, as it is only this reduced thickness that contributes to the observed diffraction effects. To establish this value of d_{eff}, films were grown with progressively decreasing thicknesses, covering the range ~350nm to ~0.3 nm, by limiting the number of laser pulses used for deposition.

Figure 1 shows spectrophotometer traces for several such films grown on fused silica substrates to enable recording of UV transmission spectra. The number of laser pulses used for these films was 10, 10^2, 10^3, and 10^4 respectively. Alphastep surface profile measurements indicated a film thickness of ~350 nm for 10,000 laser pulses, (equivalent to 0.035 nm per pulse). A log plot of film transmission versus thickness yields a 1/e absorption depth of ~75nm at a wavelength of

244 nm, equivalent to an absorption constant α of 13.3μm^{-1}. We thus set d_{eff}=75nm. Also shown in figure 1 is the characteristic absorption band centred at ~240nm which is accessed via 244 nm exposure.

Figure 2(a) shows the recording geometry adopted. A low power He-Ne laser (632.8nm) was used to monitor diffraction efficiency during grating recording for glass films that were positioned in close proximity to the phase mask, spaced off by 100μm thick glass cover slips. Under such recording conditions, the light intensity pattern has a fundamental period in the near field (Fresnel diffraction regime) which is half that of the phase mask. Using normal incidence readout for the He-Ne laser. light diffracted from this 538.5nm period recorded grating was trapped within the waveguide layer, due to total internal reflection at both film/substrate, and film/air boundaries. An angle of incidence of ~16° ensured that the diffracted light could enter the substrate, and the intensity could thereby be measured as depicted in figure 2(b)

For writing laser powers of 60mW, at power densities of 0.5 W/ cm^{-2}, the diffraction efficiency saturated within 120 seconds. A standard writing time of 4 min was therefore adopted for all subsequent films examined. Figure 3 shows the calculated values of induced index change, Δn, as a function of the oxygen pressure used during film growth, over the range 1 x 10^{-2} mbar to 6 x 10^{-2} mbar. Oxygen pressures of less than 1 x 10^{-2} mbar produced films which were dark in colour compared to the clear pale yellow at higher pressures. At pressures approaching 10^{-1} mbar, the films were cloudy, or opaque, and had poor transmission at 633nm.

It is known that the Ge-O defect is responsible for the photosensitivity of germanosilicate

materials [5,6], so the oxygen content and co-ordination within the films, induced via variable oxygen pressure during growth, is having a clear effect on the resultant photosensitivity as shown in figure 3.

Figure 3(a) shows a plot of the Δn values, obtained by the diffraction efficiency formula, and using d_{eff}, as a function of the oxygen pressure during the growth. As shown in the plot, the refractive index change values present a sharp minimum for an oxygen pressure of $4x10^{-2}$ mbar. These results can be interpreted in terms of positive and negative refractive index changes. Diffraction efficiency measurements are not sensitive to the sign of the refractive index change but only to its magnitude. As discussed below, we believe that the minimum observed in the plot represents the point of change between two competing processes that leads to refractive index changes with different signs. This type of behaviour is not uncommon, and has been seen before in photosensitivity measurements where the variable quantity is cumulative UV fluence, for example [7], rather than the variable oxygen content reported here.

Ellipsometer measurements have been performed on films grown at oxygen pressures of 3×10^{-2} and 6×10^{-2} mbar. Regions of 5 mm square were exposed to an expanded 244 nm laser beam, for periods up to 1 hour, to ensure a saturated exposure. The ellipsometer results for the film grown at 6×10^{-2} mbar indicate the presence of a lowered refractive index, accompanied by a volume expansion. The best fit values obtained for this lowered refractive index are ~1.80. Atomic force microscope (AFM) scans of the regions exposed through the phase mask show clear evidence of surface relief gratings induced via material expansion in regions of high light intensity. Conversely, ellipsometer data for the film grown at a pressure of 3×10^{-2} mbar, indicates a

refractive index increase. No relief gratings have been observed in AFM scans of exposed films grown at this pressure however.

Using such ellipsometer data, we can replot the Δn versus oxygen pressure curves, as shown in figure 3(b). This result is also supported by other studies using excimer laser pulses at 193nm to write gratings in these films, where the diffraction efficiency, monitored both during and after exposure, shows the characteristics of competition between two different (increasing and decreasing) refractive index modifying processes. Results of this work will be published elsewhere.

For the film grown at a pressure of 6×10^{-2} mbar therefore, the measured diffraction efficiency, using d_{eff}=75 nm, yields a large Δn of -9×10^{-3}. When Fresnel reflections are taken into account, this yields a corrected value of -1.06×10^{-2}, which we believe is a rather high value. So far no attempts have been made to either hydrogen load these films, or conduct any post-annealing studies. Both of these will be tried, as well as using longer wavelength light (325 and 351 nm) to generate index changes that penetrate deeper into the film, thereby enabling channels to be written in these planar guides.

In conclusion, very high photoinduced refractive index changes, in the order of $|\Delta n| = 0.9 \times 10^{-2}$, were observed in pulsed laser deposited lead germanate glass waveguides after c.w. frequency doubled Ar+ laser (244nm) illumination. The induced refractive index changes can be either positive or negative depending on the oxygen partial pressure during growth.

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References

1. J. R. Lincoln, W. S. Brocklesby, C. J. Mackechnie, J. Wang, R. S. Deol, D. C. Hanna, D. N. Payne, Electron. Letts., **28**, 1021, (1992).
2. W. H. Dumbaugh, Proc SPIE, **297**, 80, (1981).
3. S. Mailis, C. Riziotis, J. Wang, E. Taylor, A. A. Anderson, S. J. Barrington, H. N. Rutt, R. W. Eason, N. A. Vainos, C. Grivas, Accepted by Optical Materials, June 1998.
4. J. Nishii, H. Yamanaka, H. Hosono, H. Kawazoe, Opt. Letts., **21**, 1360, (1996).
5. R. J. Campbell, R. Kashyap, Int. J. of Optoelectronics, **9**, 33 (1994)
6. A. V. Amossov, A. O. Rybaltovsky, J. Non-Crystalline Solids, **179**, 75 (1994)
7. M.V.Bazylenko, D.Moss, J.Canning. Opt. Letts., **23**, 697, (1998).

Figure Captions.

Figure.1. Absorption spectra of lead germanate films, of various thickness grown on fused silica substrates. The vertical dotted line indicates the absorption band around 240 nm

Figure.2. a) Outline of the grating recording setup, incorporating a 244nm optimized phase mask. b) Schematic of the readout geometry. [1]= air, [2]= lead germanate film, [3]=glass substrate.

Figure.3. a) Plot of the absolute values of the refractive index changes (not corrected for Fresnel losses) as a function of the oxygen pressure during growth. b) Replot of the calculated values taking account of the sign.

Fig 1

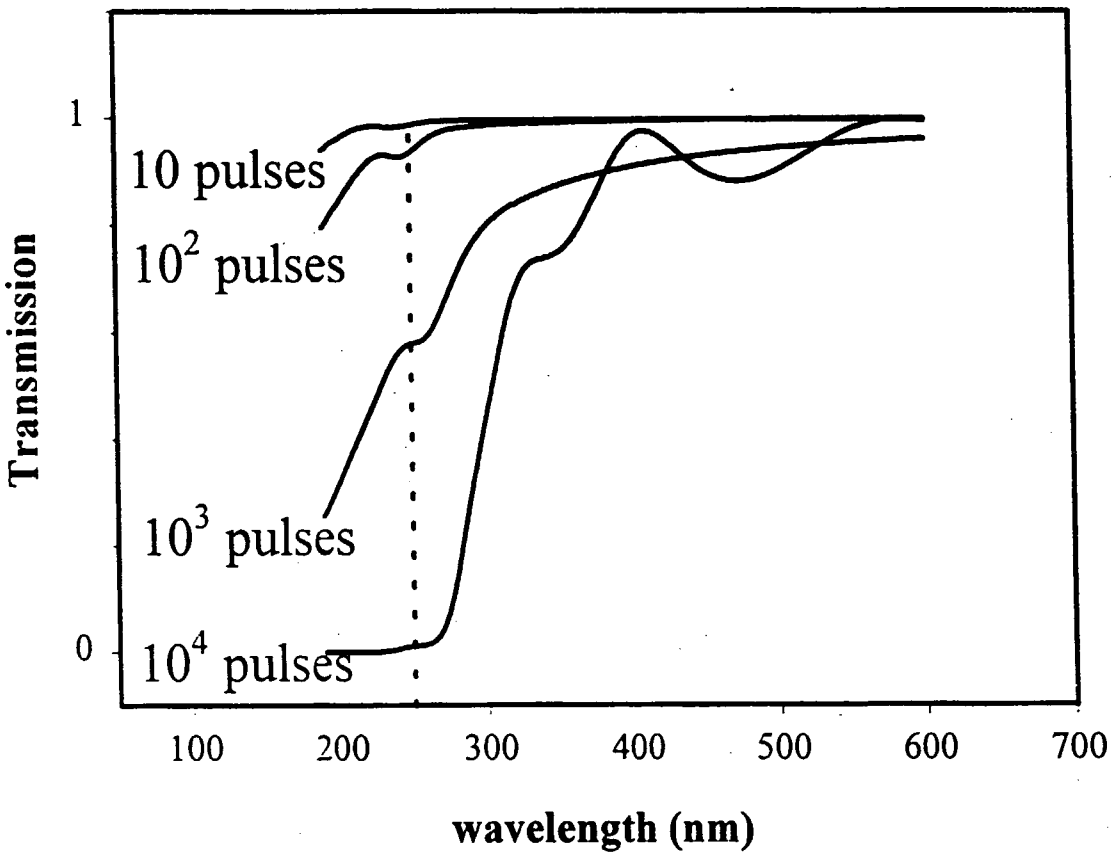
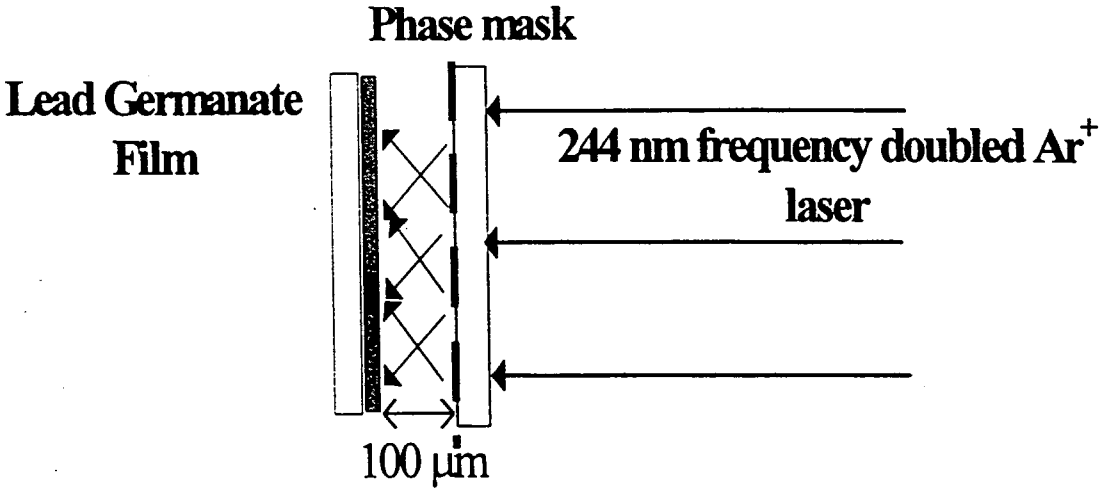

1
0
Transmission
10 pulses
10^2 pulses
10^3 pulses
10^4 pulses
100
200
300
400
500
600
700
wavelength (nm)

fig 2

a)


Phase mask
Lead Germanate Film
244 nm frequency doubled Ar^+ laser
100 μm

b)

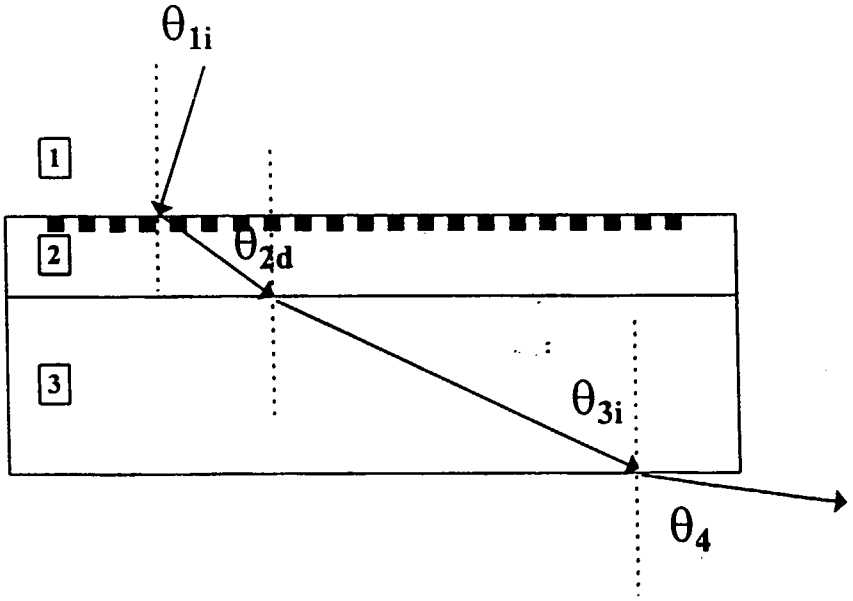
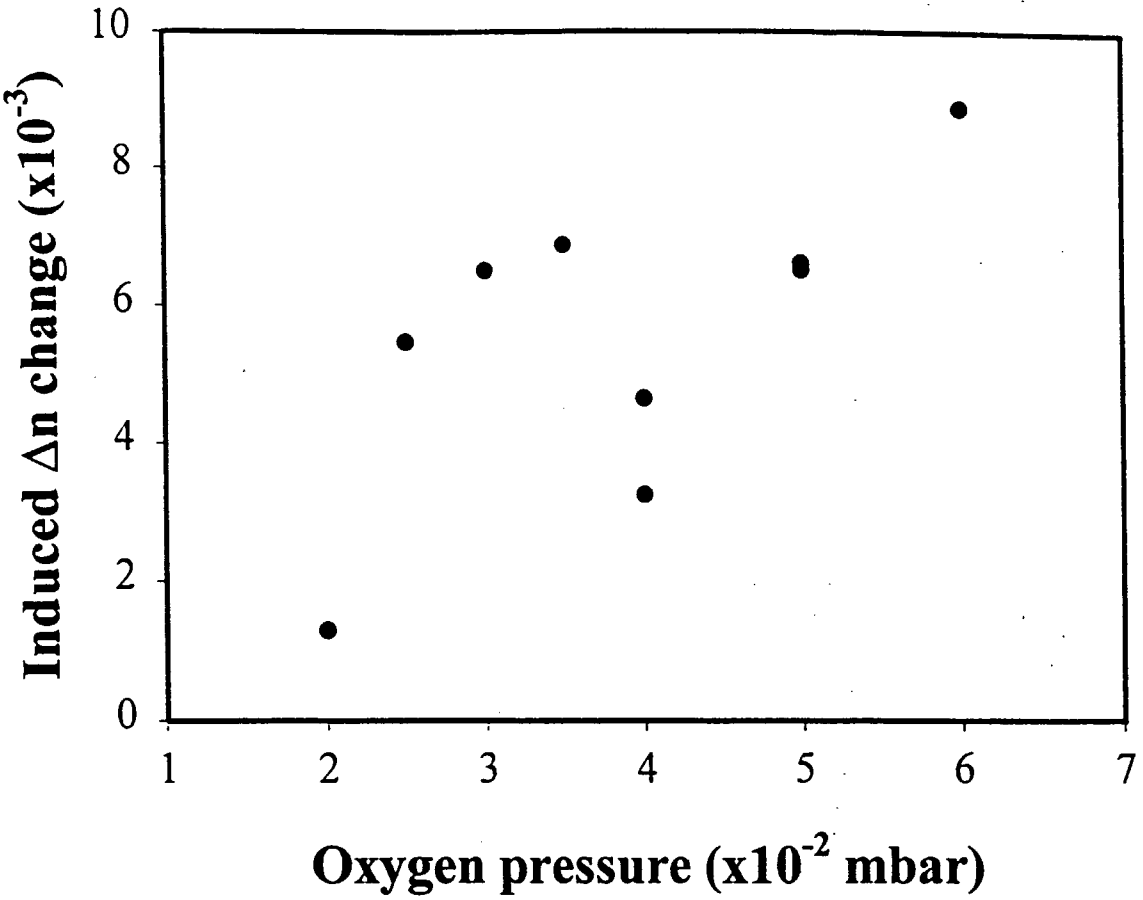
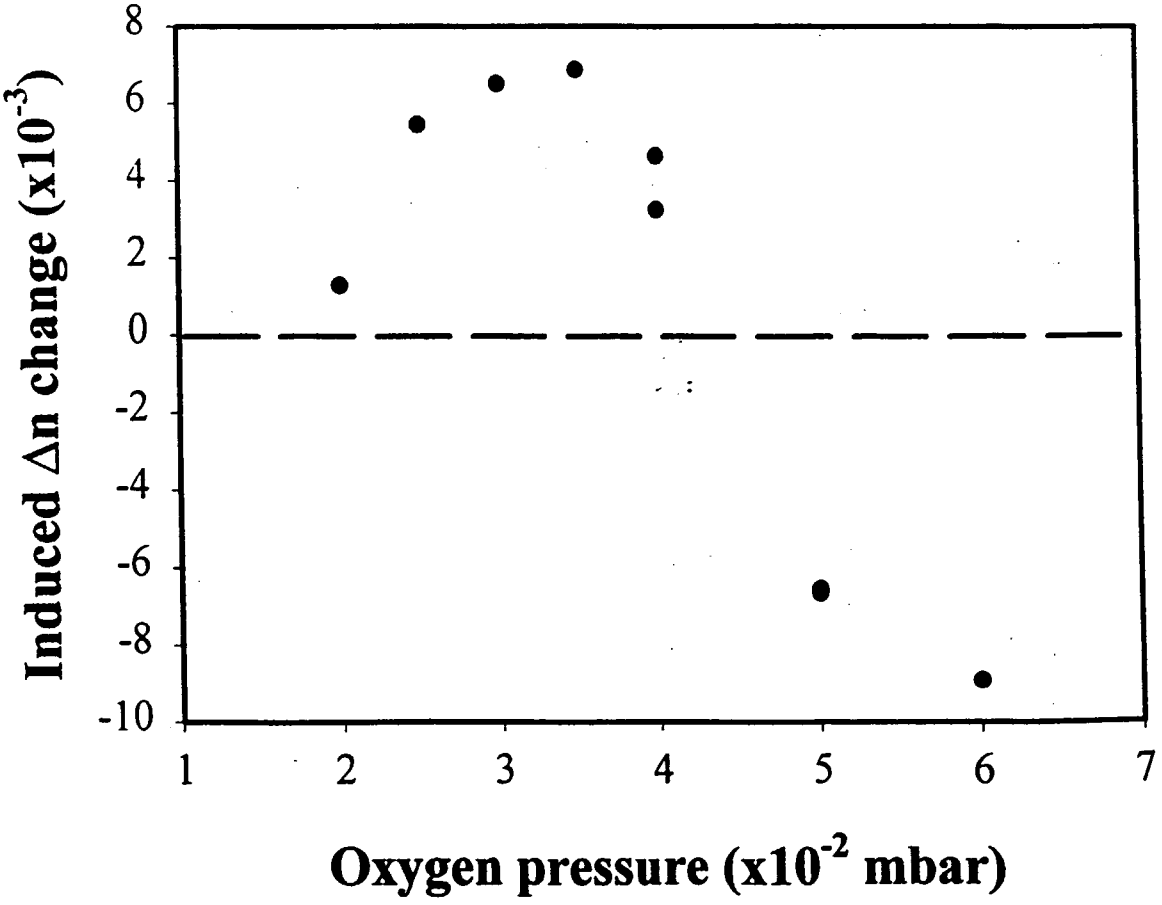

θ_{1i}
1
2
θ_{2d}
3
θ_{3i}
θ_4

fig 3

a)


Induced Δn change (x10-3)
10
8
6
4
2
0
1
2
3
4
5
6
7
Oxygen pressure (x10-2 mbar)

b)


Induced Δn change (x10-3)
8
6
4
2
0
-2
-4
-6
-8
-10
1
2
3
4
5
6
7
Oxygen pressure (x10-2 mbar)