UV induced refractive index changes in lead germanate glass waveguides grown by pulsed laser deposition

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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.

Introduction

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 value of n=1.83, which is also attractive for non-linear 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.

Results

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 paper however, we report mainly 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 193nm and 248nm. The composition of the target material in mole % was: $55GeO_2$-20PbO-10 BaO-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). 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 :

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

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 thickness, 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 onto 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 of $13.3\mu m^{-1}$. We thus, set d_{eff} =75nm. Also shown in fig.1 is the characteristic absorption band centred at ~240nm which is accessed with 244nm 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 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. A small angle of incidence of ~16° ensured that diffracted light could enter the substrate, and the intensity could thereby be measured as depicted in figure 2(b).

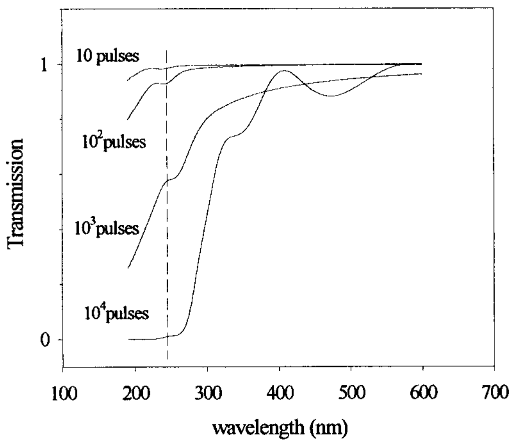


Fig.1:Transmission at varying film thickness. note absorption band and, in thicker film, etalon effect

For writing laser powers of 60mW, at power densities of 0.5 Wcm^{-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 1×10^{-2} mbar to 6×10^{-2} mbar. Oxygen pressures of less than 1×10^{-2} mbar produced films that 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.

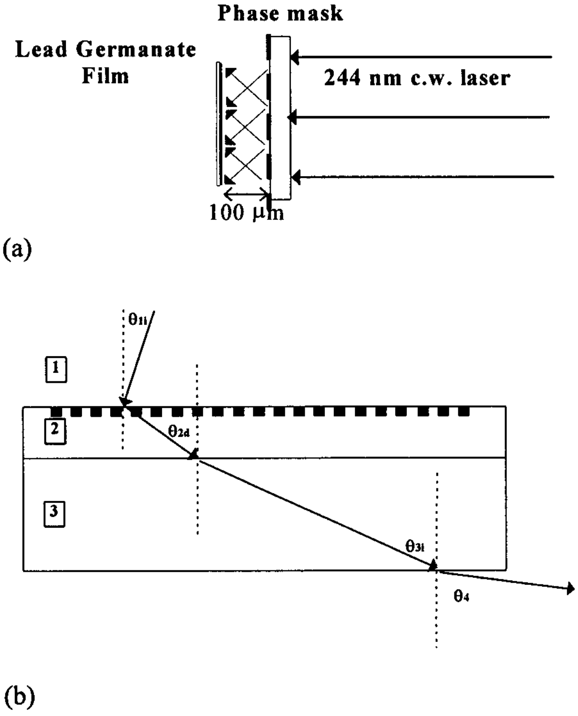
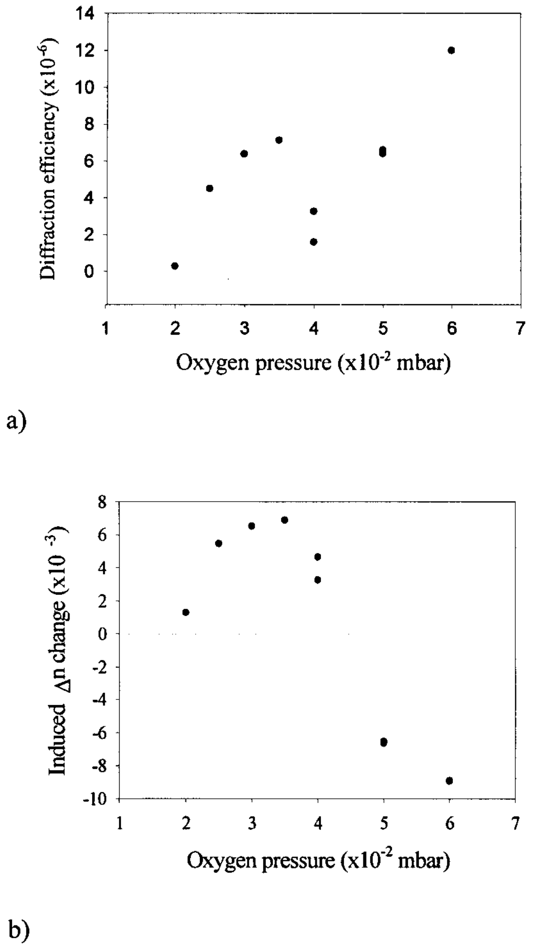


Fig.2: Experimental set-up

It is known that the GeO defect is responsible for the photosensitivity of germanosilicate materials [5,6], so the oxygen stoichiometry in 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) represents 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 a pressure of 4×10^{-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 in it's magnitude. As discussed below we believe 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, to date, partly verified the above argument since they have shown that in the high oxygen pressure region ($>4\times10^{-2}$ mbar) the dominant refractive index change is negative. Negative refractive index changes are frequently associated with surface relief patterns due to expansion of the material after illumination. This is also the case for the films grown at high oxygen partial pressures since a surface relief grating was detected by atomic force microscope observations. The low oxygen pressure ($<4\times10^{-2}$ mbar) region is currently being investigated and will be discussed during the talk. Gratings written using 193 and 248 pulsed excimer lasers have also shown evidence of competing mechanisms. Monitoring of the diffraction efficiency *directly* after exposure have shown an increase in magnitude of Δn for certain fluences. This can be explained by two competing processes (positive and negative Δn) with different saturation values and response/decay times. Using the information of the sign of the refractive index change, the data in figure 3(a) can be replotted to show both magnituse and sign of Δn. This is shown in figure 3(b) where the transition from positive to negative index changes is clearly shown.



a)

b)

Fig.3: effect of O_2 pressure on photosensitivity

Conclusion

Very high photoinduced refractive index changes 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 pressure during growth. The largest refractive index change was observed in the negative regime with a calculated value from the raw diffraction efficiency data being $\Delta n=-9\times10^{-3}$. However, the readout geometry, depicted in figure 2, suggests a correction must be applied for Fresnel losses. For an incidence angle of $\theta_i=16^{\circ}$ the refractive index change corrected for Fresnel loss becomes $\Delta n=-1.06\times10^{-2}$.

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