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Large photoinduced refractive index changes in pulsed laser deposited lead germanate glass waveguides with controllable refractive index sign change.

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Abstract

Photosensitive lead germanate glass optical waveguides have been grown by pulsed laser deposition. The deposited waveguides are photosensitive over a broad ultraviolet spectral range (325 nm- 193 nm). Positive and/or negative refractive index changes have been observed depending on the intensity of the ultraviolet radiation as well as on the deposition conditions. Absolute refractive index change values up to $|\Delta n|=1.06\text{x}10^{-2}$ have been measured.

PACS: 42.70.Ce, 42.70.Gi, 42.49.Gn

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Submitted
Applied Physics A.
July 99

Introduction

Photosensitive glasses represent a fruitful area for potential applications in optical communications and photonics. The most investigated case of light induced refractive index changes is the case of germanium doped silica and today photosensitive fibres and planar waveguides are currently used for the fabrication of many devices used by telecommunications industry. However, the small refractive index changes which can be obtained in untreated (non hydrogenated) silica glasses may limit the performance of such devices such as direct u.v. written optical circuits. The demand for larger refractive index changes is ever present and hence the research for new glass materials having the desired optical and chemical properties is increasing. Germanate glasses can be good candidates as highly photosensitive materials mainly because of their large absorption in the ultra violet (u.v.) spectral region as well as for their excellent transmission characteristics in the infra red spectral region [1]. They can also be used to form active devices since their low phonon energy enables them to become excellent hosts for laser active dopants and laser action in the infra-red spectral region has been already reported [2]. Growth of such lead germanate optical waveguides has been realised by using pulsed laser deposition (PLD) [3].

In this paper a study of the photosensitivity exhibited by PLD grown lead germanate thin films as a function of exciting wavelength and growth conditions is presented. Both continuous wave (c.w.) and pulsed lasers have been used for the investigation of their photosensitivity and very high refractive index changes (positive and/or negative depending on the growth conditions and recording intensity) have been observed in as-grown materials.

1. Fabrication

Lead germanate thin films were grown from a bulk lead germanate glass target on to borosilicate glass (microscope slides) and fused silica substrates, using excimer lasers at wavelengths of 193 nm (ArF) and 248 nm (KrF). The target glass composition in mole% is $55GeO_2$ - 20PbO-10BaO- 10ZnO - $5K_2O$, with some glasses having a partial substitution of Al^{3+} for Zn^{2+}. The large refractive index difference between the films (n_F = 1.812 ± 0.005) and the substrates (n_S=1.5) enables the formation of optical waveguides and a study of their characteristics has been investigated in [3]. The optical properties such as absorption) of the films depend on the growth conditions and more specifically on the partial pressure of oxygen which was present during growth. In figure 1a, a plot of the absorption coefficient measured at 400 nm for films grown using a KrF excimer laser at different oxygen partial pressure is depicted, showing an increase of the optical absorption with increasing oxygen pressures. The choice of 400 nm was due to this wavelength falling conveniently between regions of high absorption and high transparency. The same shift was observed also in ArF excimer laser grown films, suggesting that both methods produced films of similar optical properties. Post annealing of films grown at relatively high partial pressures of oxygen caused a blue shift of the absorption edge as shown in figure 1b, suggesting bleaching of the defects responsible for the previously observed increased absorption.

EDX (Energy Dispersive X-ray analysis) measurements provided semi-quantitative indications of changes in the stoichiometry of the material under varying oxygen pressure, indicating the expected increase in oxygen content with increasing oxygen partial pressure during growth. This, together with the fact that the background oxygen pressure affects the dynamics of the plasma plume, can explain the variation in the optical properties of films grown at different oxygen pressures.

2. Photosensitivity

The method used for the quantitative measurement of the photoinduced refractive index changes Δn was the measurement of the diffraction efficiency for diffraction gratings recorded in the material as further discussed below. The diffraction efficiency measurements enabled the calculation of the absolute induced refractive index change, assuming the small argument approximation of the thin grating diffraction efficiency formula:

$$\eta \approx (\pi d \Delta n/\lambda)^2$$

Where: d is the thickness of the grating Δn the refractive index change and λ the probe wavelength

2.1. Experimental procedure

Grating recording was achieved either by using an interferometric arrangement or a π-phase mask, depending on the spatial-temporal coherence characteristics of the sources used for recording. The use of a π-phase mask enables grating recording using sources of poor spatial-temporal coherence such as excimer lasers.

A schematic of the two recording methods is shown in figure 2. Figure 2a shows the outline of the interferometric recording arrangement including a HeNe probe beam transmitted through the exposed area and diffracted off the recorded grating. Monitoring the diffracted part of the HeNe beam using an optical power meter gives both the diffraction efficiency value and the recording-decay dynamics. Figure 2b shows a schematic of the π-phase mask method. The sample is brought into close proximity to the phase mask (~100 μm) using appropriate spacers in order to take advantage of the near field Fresnel diffraction intensity pattern.

The diffraction efficiency measurements in the case of the phase mask recording were performed after the exposure and removal of the phase mask by using a HeNe probe beam and measuring the diffracted power.

3. Results and discussion

The extended absorption of the PLD grown samples throughout the u.v. spectral region suggests an extended photosensitivity in the same spectral region in the same way as it occurs for photosensitive Ge-doped silica fibres [4] and as expected photoinduced refractive index changes were observed in a wide range of u.v. wavelengths from 325 nm to 193 nm using both c.w. and pulsed sources.

Efficient recording has been observed for 325 nm (HeCd laser) illumination of lead germanate samples using the interferometric setup. With the power output available (5 mW) at 325 nm the grating strength saturates after ~800 sec. After the exposure and decay of all transient components of the grating, the measured steady state value of diffraction efficiency corresponds to the final permanent refractive index change and typical measured values were of the order of 10^{-4}.

Larger Δn values up to 1% were observed using a frequency doubled Ar^+ (FRED) laser at 244 nm. The absorption band around 240 nm of the as-grown samples is very high due to the presence of the Ge-O defect as shown in figure 3 where transmission spectra of identically grown samples of different thicknesses are depicted. The dip in the transmission observed in the thin samples around 240 nm corresponds to the absorption band of the Ge-O defect responsible for the photosensitivity of Ge doped silicate fibres. From the transmission data the absorption length of the films at 244nm was estimated to be ~75 nm. Using this value for the effective thickness of the grating, the photoinduced refractive index change was calculated for films grown under different oxygen partial pressures. In figure 4a the calculated Δn data are depicted as a function of the oxygen partial pressure. In order to explain the behaviour of Δn around 4×10^{-2} mbar ellipsometric measurements were performed to identify the sign of the photoinduced refractive index change. The ellipsometric measurements showed a positive change for pressures below 4×10^{-2} mbar and a negative change for pressures over 4×10^{-2} mbar and the plot of Δn as a function of oxygen partial pressure, with corrected sign, is depicted in figure 4b. This behaviour is not uncommon and it has been observed before in Ge-doped silica not as a function of growth conditions but as a function of accumulative optical fluence [5]. Surface relief patterns were also observed, in atomic force microscope scans, on films exhibiting high negative Δn values and this is in agreement with reports of material expansion in negative photoinduced refractive index changes in germanium doped silica optical fibres [4].

A comparison between c.w. and pulsed recording has been undertaken by using two different pulsed u.v. sources. Grating recording on films grown under different conditions has been performed using KrF (248 nm) excimer laser delivering pulses of 20 nsec or 0.5 psec duration, and an ArF (193 nm) delivering pulses of 20 nsec duration. The exposure of the films was kept well below the multi pulse ablation threshold which was determined beforehand for each wavelength and pulse duration. The recording was mainly performed by using appropriate phase masks due to the poor coherence characteristics of the above mentioned lasers. Typical exposure values were of the order of 0.3 J/cm^2-0.4 J/cm^2 and peak powers of 0.4 MW for the 20 nsec sources to 12 MW for the 0.5 psec source. Since the relaxation of the gratings occurred over the time scale of minutes, the time evolution of the gratings could be monitored after removing the phase mask at a constant time delay (15 sec) after the last recording pulse.

The dependence of the refractive index change induced by the 20 nsec excimer laser exposure on the oxygen partial pressure used during growth seems to follow the same trend as in the c.w. case showing a dip around $3x10^{-2}$-$4x10^{-4}$ mbar and an increase by almost an order of magnitude for higher oxygen pressure suggesting the same mechanism for recording (using the Ge-O defect absorption band situated around 240 nm). However, the diffraction efficiency of the gratings becomes saturated at lower levels than the ones recorded with the c.w. FRED laser. A possible explanation for this can be the simultaneous excitation of positive and negative refractive index changes with significant steady state residues as a result of the six orders of magnitude higher intensity of the pulsed recording. The two, opposite sign, refractive index changes partially cancel each other and eventually decrease the overall refractive index change . Evidence for simultaneous excitation of two competing refractive index distributions was given also by monitoring the diffraction efficiency development, after recording. The relaxation of the recorded gratings leads to an overall increase of the diffraction efficiency which is the signature of two refractive index distributions with opposite sign which decay with different time constants [6]. In order to study the effect of intensity on the photosensitivity for the lead germanate samples, gratings were recorded with the 0.5 psec excimer laser using a phase mask arrangement. The saturation level of the induced refractive index change was further decreased in this case and it also showed a marked insensitivity to the growth conditions, a fact that further supports the intensity dependence hypothesis. Plots of the photoinduced refractive index changes as a function of the oxygen partial pressure during growth are depicted in figure 5a for 20 nsec KrF recording and figure 5b for 0.5 psec recording.

The photosensitivity of the films was also examined at 193 nm using an ArF excimer laser with both phase mask and interferometric arrangement. This wavelength gives access to the second absorption band of the Ge-O defect which peaks at 195 nm [4]. The samples showed an increase of the refractive index change with increasing oxygen partial pressure although the overall saturated refractive index change did not exceed 10^{-4}. The inefficiency of the 193 nm recording is again attributed to the simultaneous recording of two competing, opposite sign, refractive index distributions.

Finally the refractive index change results are summarized in table I where the method used, the u.v. sources, and the calculated Δn are indicated.

4. Conclusions

A study of the u.v. photosensitivity of pulsed laser deposited led germanate glasses has been carried out. The material is photosensitive throughout the ultra violet spectral region and refractive index changes of the order of 1% have been measured. The photoinduced refractive index change can be either positive or negative depending on the growth conditions and the recording intensity.

5. Acknowledgements

We would like to acknowledge the *Engineering and Physical Sciences Research Council* (EPSRC) for research funding under grant no. GR/L28722. Ji Wang and Elizabeth Taylor, Bill Brocklesby and Bob Greef are gratefully acknowledged for glass target fabrication, AFM use, ellipsometer use and fruitful discussions. Part of this work was supported within the framework of the *Ultraviolet Laser Facility* at the *Foundation for Research and Technology-Hellas, Institute of Electronic Structure and Laser.*

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Figure captions

Figure.1	a) Absorption coefficient measured at 400 nm versus oxygen partial pressure during growth for films grown with KrF excimer laser. b) Absorption spectra of a lead germanate film before annealing (solid line) and after (dashed line).
Figure.2	Experimental arrangement for a) interferometric recording and b) π-phase mask recording
Figure.3	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.4	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.
Figure.5	Plot of the absolute value of the photoinduced refractive index change versus oxygen partial pressure by a) 20 nsec KrF excimer laser b) by 0.5 psec KrF excimer laser.

Table captions

Table I. Summary of the grating recording methods, lasers used, exposures and measured refractive index changes.

Figure 1

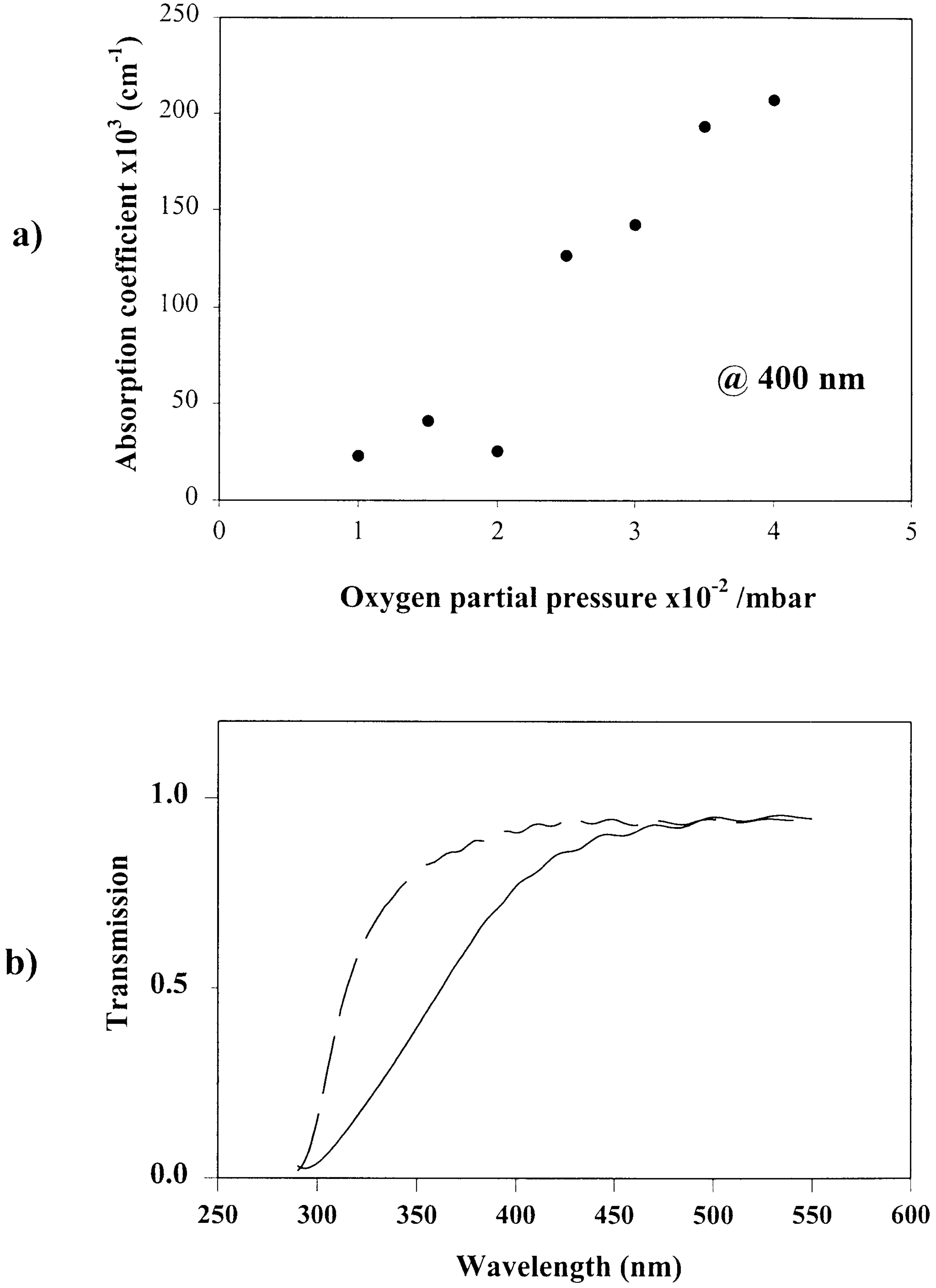
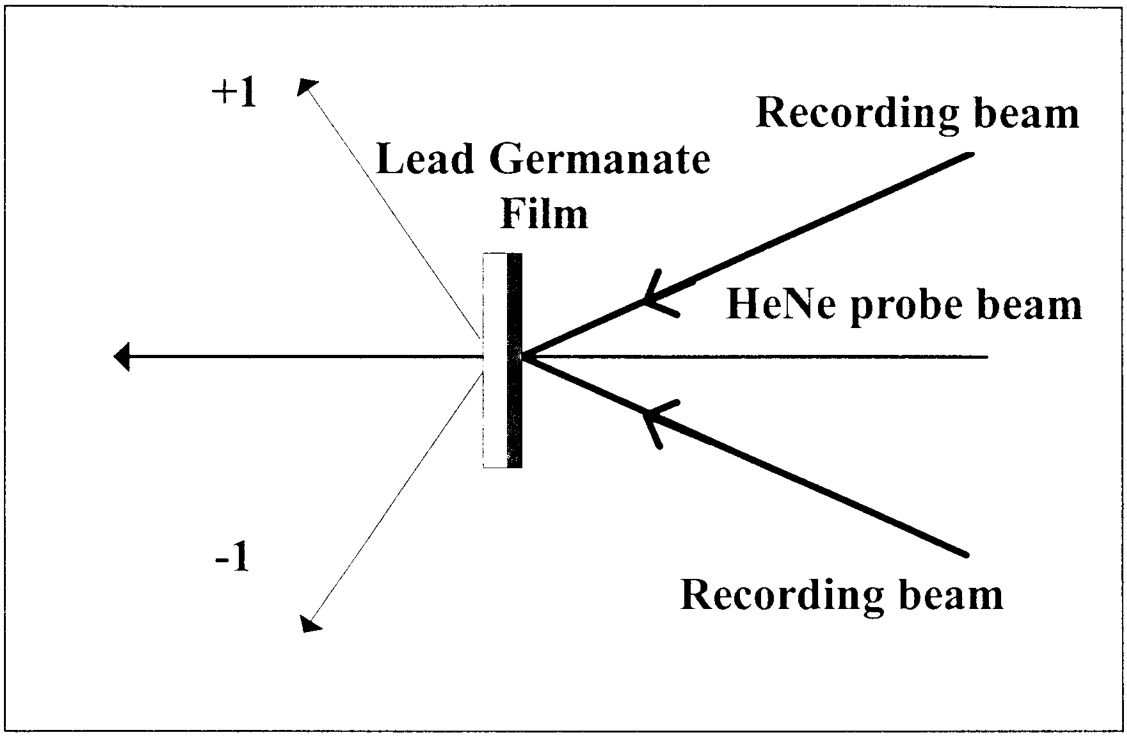

a)
Absorption coefficient x10^3 (cm^{-1})
250
200
150
100
50
0
@ 400 nm
0
1
2
3
4
5
Oxygen partial pressure x10^{-2} /mbar
b)
Transmission
1.0
0.5
0.0
250
300
350
400
450
500
550
600
Wavelength (nm)

Figure 2

a)


+1
Lead Germanate
Film
Recording beam
HeNe probe beam
-1
Recording beam

b)

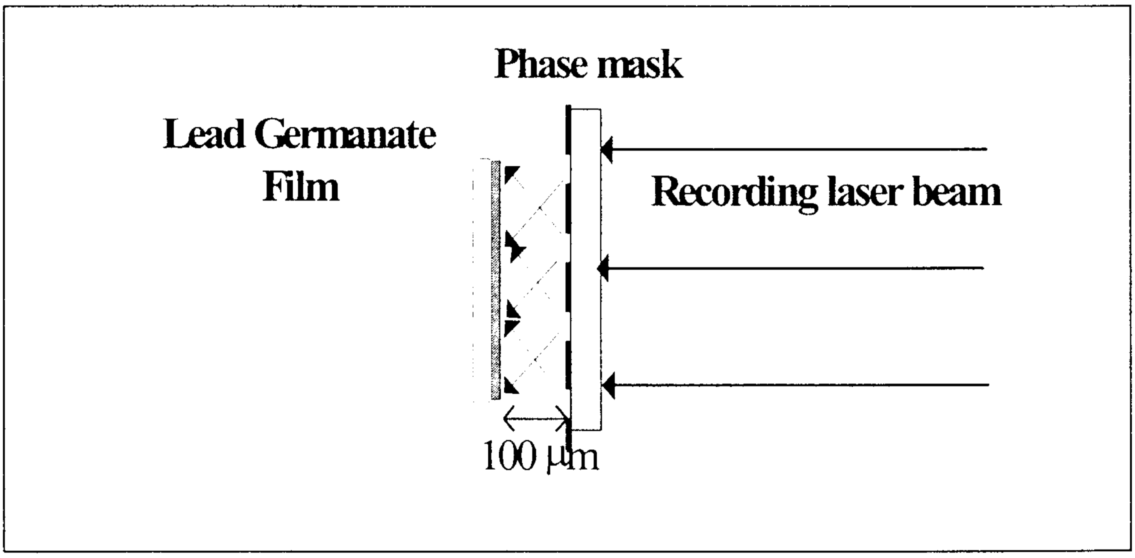

Phase mask
Lead Germanate
Film
Recording laser beam
100 μm

Figure 3

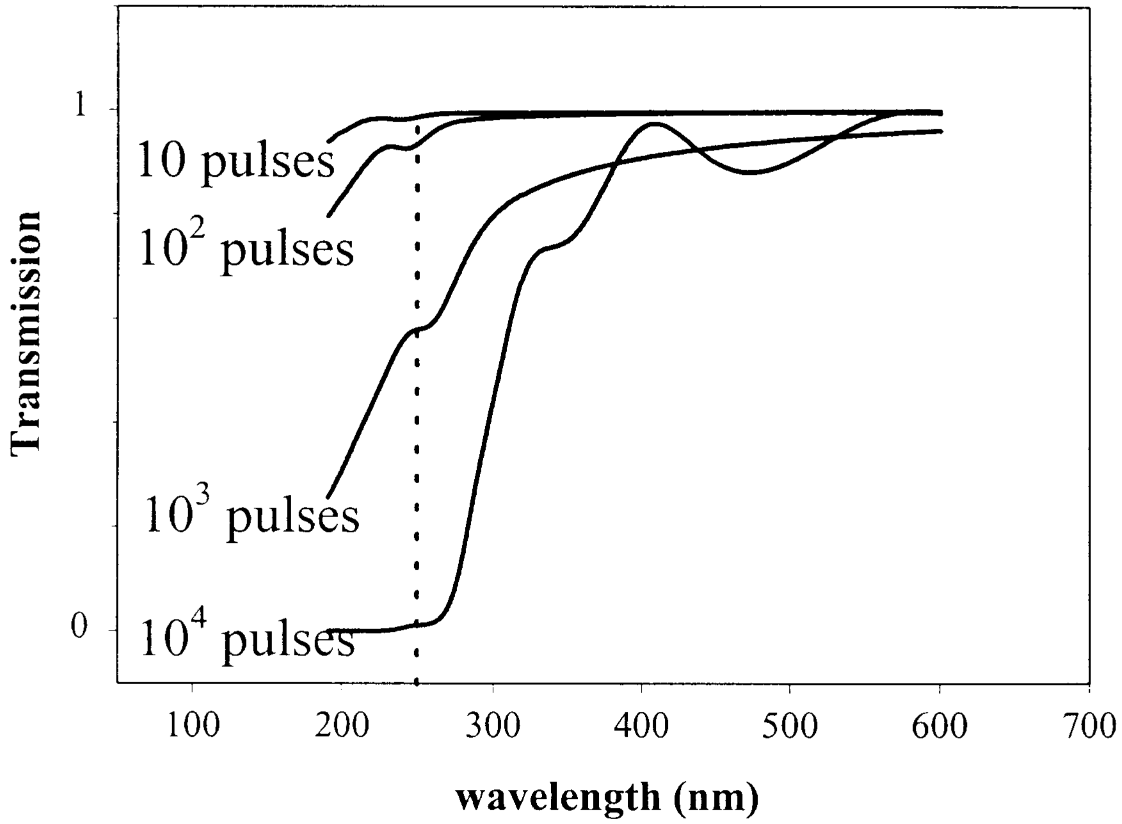

1
0
Transmission
10 pulses
10^2 pulses
10^3 pulses
10^4 pulses
100
200
300
400
500
600
700
wavelength (nm)

Figure 4

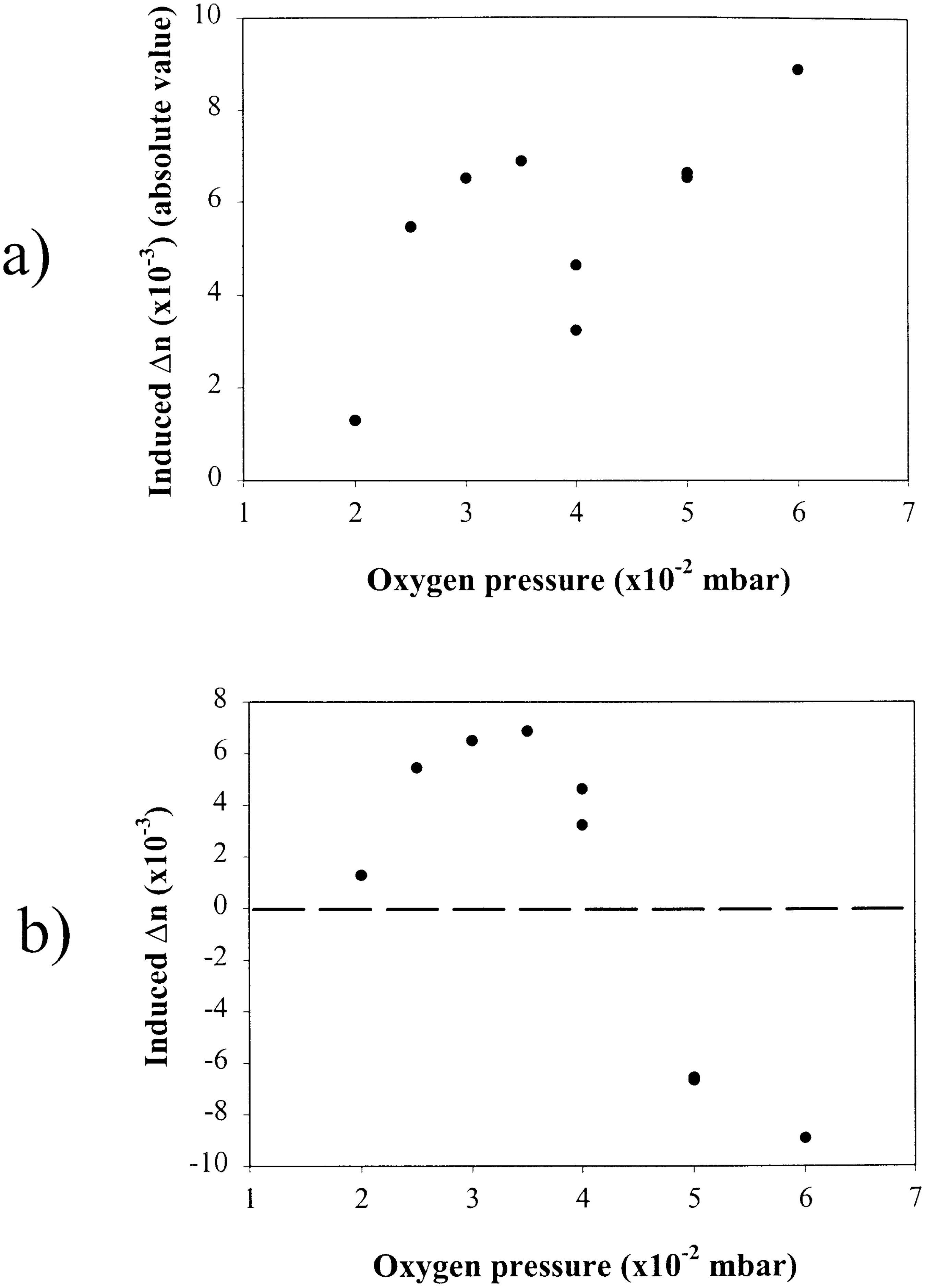

a)
Induced Δn (x10^{-3}) (absolute value)
10
8
6
4
2
0
1
2
3
4
5
6
7
Oxygen pressure (x10^{-2} mbar)
b)
Induced Δn (x10^{-3})
8
6
4
2
0
-2
-4
-6
-8
-10
1
2
3
4
5
6
7
Oxygen pressure (x10^{-2} mbar)

Figure 5

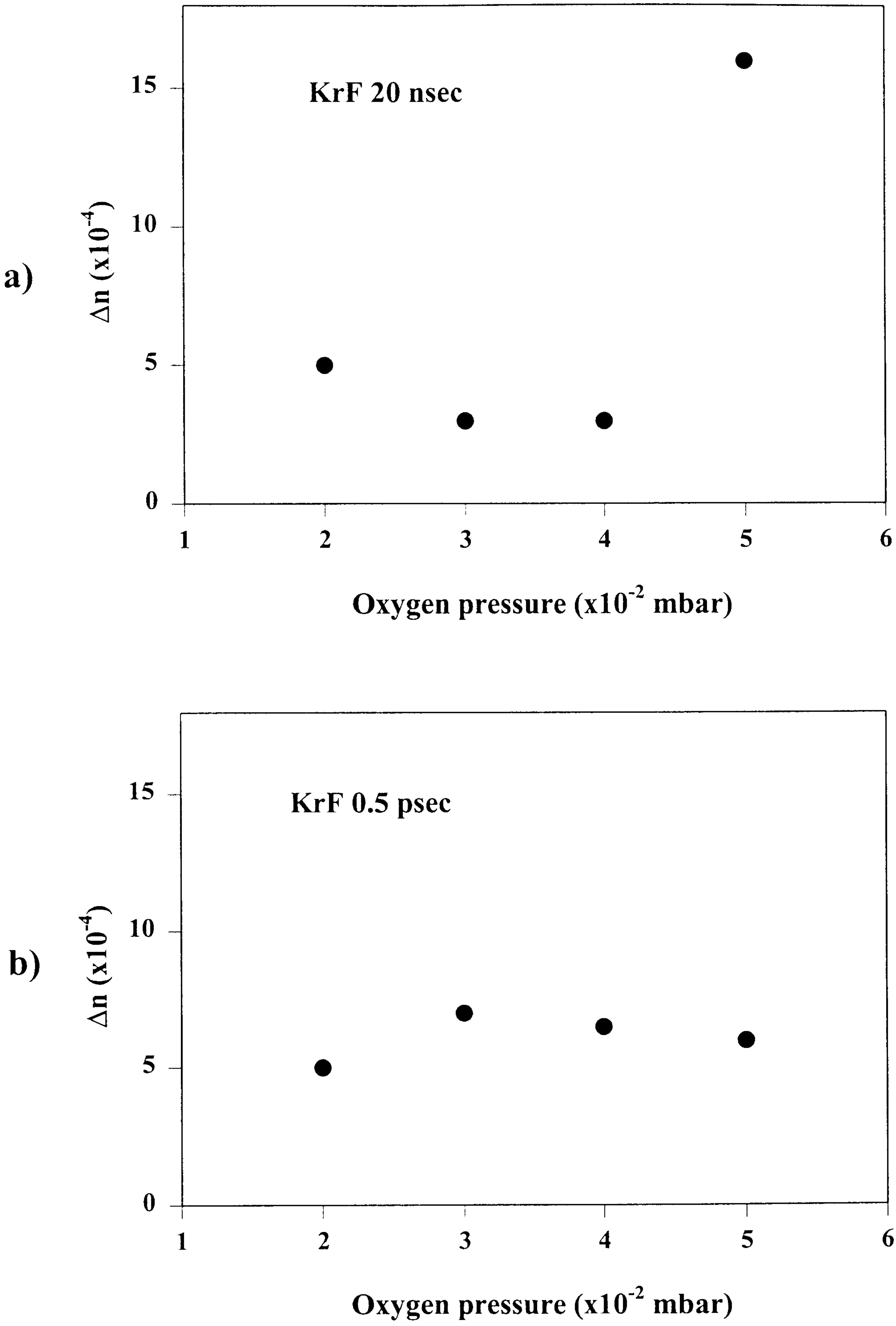

a)
KrF 20 nsec
Δn (x10^-4)
0
5
10
15
1
2
3
4
5
6
Oxygen pressure (x10^-2 mbar)
b)
KrF 0.5 psec
Δn (x10^-4)
0
5
10
15
1
2
3
4
5
6
Oxygen pressure (x10^-2 mbar)

Table I

Laser	**Method**	**Exposure J/cm^2**	$\|\Delta n\|$
HeCd (c.w. @325nm)	Interferometer	500	10^{-4}
FRED (c.w. @244nm)	Phase mask	110	10^{-3}-10^{-2}
KrF (pulsed @ 248nm) 20 nsec	Phase mask	0.3	10^{-3}
KrF (pulsed @ 248nm) 0.5 psec	Phase mask	0.3	10^{-3}-10^{-4}
ArF (pulsed @ 193nm) 20 nsec	Interferometer & phase mask	0.4	10^{-4}