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Enhanced photosensitivity in germanosilicate fibres exposed to CO_2 laser radiation

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Abstract

We report a novel method to increase the UV photosensitivity of GeO_2:SiO_2 optical fibres based on exposure to CO_2 laser irradiation before grating writing. Fibres treated with a CO_2 laser can produce gratings with refractive index modulation two times greater and a Bragg wavelength that can be 2 nm longer than untreated fibres. Experiments carried out on GeO_2:SiO_2 preform samples, treated with a CO_2 laser in a similar way to the fibres, showed a marked increase of the 242 nm absorption band. This is associated with an increase of the germanium oxygen deficient centres (GODC) and is believed to be responsible for the higher photorefractive response.

Since the discovery of photosensitivity in optical fibres by Hill and co-workers in 1978 [1], many in-fibre optical devices based on Bragg gratings have been produced, such as dispersion compensators, filters, fibre lasers, cavity mirrors and optical fibre sensors. Several methods have been used to increase the photosensitivity of germanosilicate fibres [2]: post-fabrication processes and codoping are the most common, especially for standard telecom fibres that would otherwise have an insufficient degree of photosensitivity. Among the post-fabrication methods are hydrogen loading [3] and flame brushing [4], whereas codoping can be realised by adding B [5], Sn [6] and rare earths [7] to the silica matrix. Both hydrogen loading and flame brushing are based on the reaction of hydrogen molecules with a common Ge-O-Si site to produce OH groups and bleachable GODC. Although this process enhances fibre photosensitivity, it should be remarked that the absorption in the third telecom window 1.55 μm is increased because of the formation of absorption bands at 1.39 μm (Si-OH) and 1.41 μm (Ge-OH). It is therefore desirable to find new techniques to increase the photorefractive response of germanosilicate fibres which are less time consuming, cheaper and give lower optical loss at 1.5 μm. Thermal treatment using CO_2 laser radiation was proposed to modify the photosensitivity of hydrogenated fibre *during* grating writing so that the periodic modification in Δn results in apodisation [8]. Here we propose and investigate a novel post-fabrication technique to increase the photorefractivity of germanosilicate fibres. The fibres (not hydrogenated) were exposed to intense CO_2 laser radiation *before* the gratings were written, using *high* intensity UV laser. A significant increase in the refractive index modulation and average refractive index (i.e. reflectivity and Bragg wavelength respectively) has been detected and related to CO_2 laser induced thermal effects. Measurements on bulk samples showed that the GODC population increases with increasing CO_2 exposure, this probably being the reason for the higher photorefractive response. In addition, a dependence of the photosensitive enhancement on UV intensity has been observed and suggests the presence of two different defects, one of which is bleachable through multiphoton absorption.

The fibre used in the experiment was produced via modified chemical vapour deposition (MCVD) and had an external diameter of 120 μm, numerical aperture (NA) of ~0.27 and cut-off wavelength (λ_c) of ~1.36 μm. The fibre was side-exposed to ~13.5 W continuous wave CO_2 laser for 15 seconds and subsequently rapidly cooled down with liquid nitrogen. The photosensitivity was tested via grating writing. The gratings were written with a phase-mask exposing the treated fibre for 100 s to 248 nm Kr-F excimer pulses at 20 Hz and 300 mJ/cm^2 per pulse. The reflectivity response of the grating written in the fibre exposed to a CO_2 laser intensity of ~350 W/cm^2 is shown in fig. 1 together with the reflectivity spectrum of the untreated fibre. Compared to the untreated fibre grating, the treated fibre grating provides higher reflectivity and a longer Bragg-wavelength (shift of ~1.4 nm). The modulations in the refractive index (Δn_{mod}) of the fibre gratings were estimated from the reflection curves to be $1.6\cdot10^{-4}$ and $2.27\cdot10^{-4}$ for the untreated and treated samples respectively.

Other samples from the same fibre were exposed for 3 seconds at different levels of CO_2 intensity; the cooling of these samples was either in liquid N_2 or in air. The values of Δn_{mod} estimated from the reflection spectrum are presented in fig. 2 indicating significant increase for increasing CO_2 intensity; no meaningful increase in the photorefractivity is due to liquid nitrogen treatment. In addition, large shifts in Bragg-wavelength were detected for gratings written in treated fibres. In type I gratings, if refractive index changes take place only during grating inscription, one would expect an average refractive index change (Δn_{ave}) ~ $\Delta n_{mod}/2$. The data presented in fig. 2 show that Δn_{ave} induced in the treated fibres is much larger than $\Delta n_{mod}/2$, indicating a contribution strictly related only to CO_2 treatment. Moreover, the deviation of Δn_{ave} from $\Delta n_{mod}/2$ is more significant at high CO_2 intensity levels. The photorefractivity seems also to be dependent on the UV intensity: at low UV intensities (<50 mJ/cm^2 per pulse) there are negligible differences between the fibre treated with CO_2 laser and the untreated one, whereas at high UV intensities (>200 mJ/cm^2 per pulse) Δn_{mod} of the fibre exposed to CO_2 laser radiation is approximately two times larger than that of the untreated fibre. It was suggested that both in silica [9] and germanosilicate fibres [10-11] two types of defects contribute to the 242 ÷ 248 nm absorption peak. Since the difference between gratings written in treated and untreated fibres increases with increasing UV intensity, our results seem to be consistent with a model implying two types of GODC defects with different bleaching dependence on UV intensity; one of these defects, whose concentration increases after CO_2 treatment, can be bleached only at high UV intensities, probably through multi-photon absorption. This model is supported by the fact that the photosensitive effects in the untreated fibre are linear with UV intensity.

To understand the observed behaviour, we have investigated the effects on the absorption spectrum of thin preform samples, treated in a similar way to the fibres that showed photosensitivity enhancement. Samples ~170 μm thick were cut from the same preform we used to draw the aforementioned fibre and subsequently polished to optical quality. The samples were exposed to a CO_2 laser beam (340 W/cm^2) for 15 s and absorption spectra were recorded before and after irradiation. The absorption of 242 nm GODC band increased more than 3 times and was beyond the maximum level detectable by the spectrophotometer. Unfortunately it was not possible to reduce the sample thickness below 100 μm because the sample became very brittle and the temperature reached melting values during CO_2 exposure. For these reasons we chose to repeat the experiments using a preform with lower numerical aperture (NA ~0.2) and exposed the samples to lower CO_2 powers. Fig. 3 shows the absorption spectra of the sample exposed to the CO_2 laser beam (210 W/cm^2) for subsequent exposures of 9 s (corresponding total exposure time is indicated in the figure). It is evident that the absorption of GODC at 242 nm increases continuously and reaches a saturation level after long exposures (see inset of fig. 3). Therefore it is reasonable to assume that the large increase in the photorefractivity of the fibre can be correlated to the increment of the number of oxygen-related defects observed in the UV spectrum.

The time evolution of GODC concentration during CO_2 exposure was detected in situ by using a frequency doubled Ar^+ laser and a silicon photodiode. The transmission of the germanosilicate preform slide at 244 nm (fig. 4) shows a weak growth when the CO_2 laser is turned on, followed by a strong reduction that quickly reaches saturation. When the laser is turned off the transmission promptly increases and then reduces, settling down to a level lower than the initial level (before the CO_2 laser was turned on); this final level, as well as the saturation level before the laser is turned off, decreases for increasing CO_2 laser power. Since the absorption at 244 nm is proportional to GODC concentration, the observed transmission evolution can be explained on the basis of thermodynamic equilibrium of defects, the proportions of which depend on two competing reactions. At low temperature the GODC reduction due to GeE' generation [11] is dominant over the GODC generation from ≡Ge-O-Si≡ sites, whereas at high temperatures the opposite is true. In this way, the increase in transmission (peaks 1 and 2 in fig. 4) with respect to room temperature, observed for few hundreds of milliseconds after the laser is switched on and off, can be explained considering that the temperature during these periods is below a few hundred ^{0}C and the GODC reduction due to GeE' generation dominates. After a few hundred milliseconds the CO_2 laser is switched on, the sample reaches temperatures where defect generation is much higher than reduction, so the transmission drops. With increasing CO_2 power, the temperature reaches higher values and the defect generation increases, thus decreasing the steady state UV transmission. The photosensitive enhancement after this CO_2 laser induced thermal cycle is explained by the part of the defects that remain in the silica network and is responsible for transmission decrease.

In order to clarify the thermal effect on fibre photosensitivity associated with CO_2 laser exposure, we treated two different fibres with the same thermal cycle by using the CO_2 laser and the furnace used during fibre drawing. The fibre was warmed up to 1800 ^{0}C in 1 minute, kept at this temperature for 1 minute, cooled down to 1100 ^{0}C in 75 seconds and finally cooled to room temperature by natural convection. Gratings, written as previously, show that the increase in photosensitivity due to CO_2 exposure is closely related to temperature effects - the reflection increase is almost the same in the two fibres differently treated, as is the induced Δn_{mod}. However, one clear difference is that the grating written in the fibre which was heated in the furnace shows a small Bragg wavelength shift, Δn_{ave} being thus consistent with the induced Δn_{mod} (i.e. $\Delta n_{ave} \sim \Delta n_{mod}/2$), while, as previously pointed out, for gratings written in the fibre exposed to CO_2 laser radiation $\Delta n_{ave} >> \Delta n_{mod}/2$. In addition, for the fibres treated with the CO_2 laser, a considerable Bragg wavelength shift is also detected when the grating is written with low excimer laser powers, corresponding to which Δn_{mod} is negligible. The reason why such average refractive index variation occurs in the fibre treated with the CO_2 laser and not in the thermally treated fibre is still under investigation.

In summary, the exposure of germanosilicate fibres to CO_2 laser radiation before grating inscription significantly increases the photosensitivity. This has been related to an observed increase of GODC defects due to thermal effects. The defects, responsible for the enhanced UV photosensitivity, can be bleached only at high UV laser intensities, suggesting that multi-photon absorption takes place. Although the increase in photorefractivity is still far from the maximum values obtained in the past ($\Delta n=10^{-3}-10^{-2}$), to the best of our knowledge, the Δn is the highest for type I gratings achieved in pure germanosilicate fibres without hydrogenation. Further improvements are expected by optimisation of the exposure parameters and fibre composition. Such a technique could be exploited for apodisation and chirping of fibre gratings.

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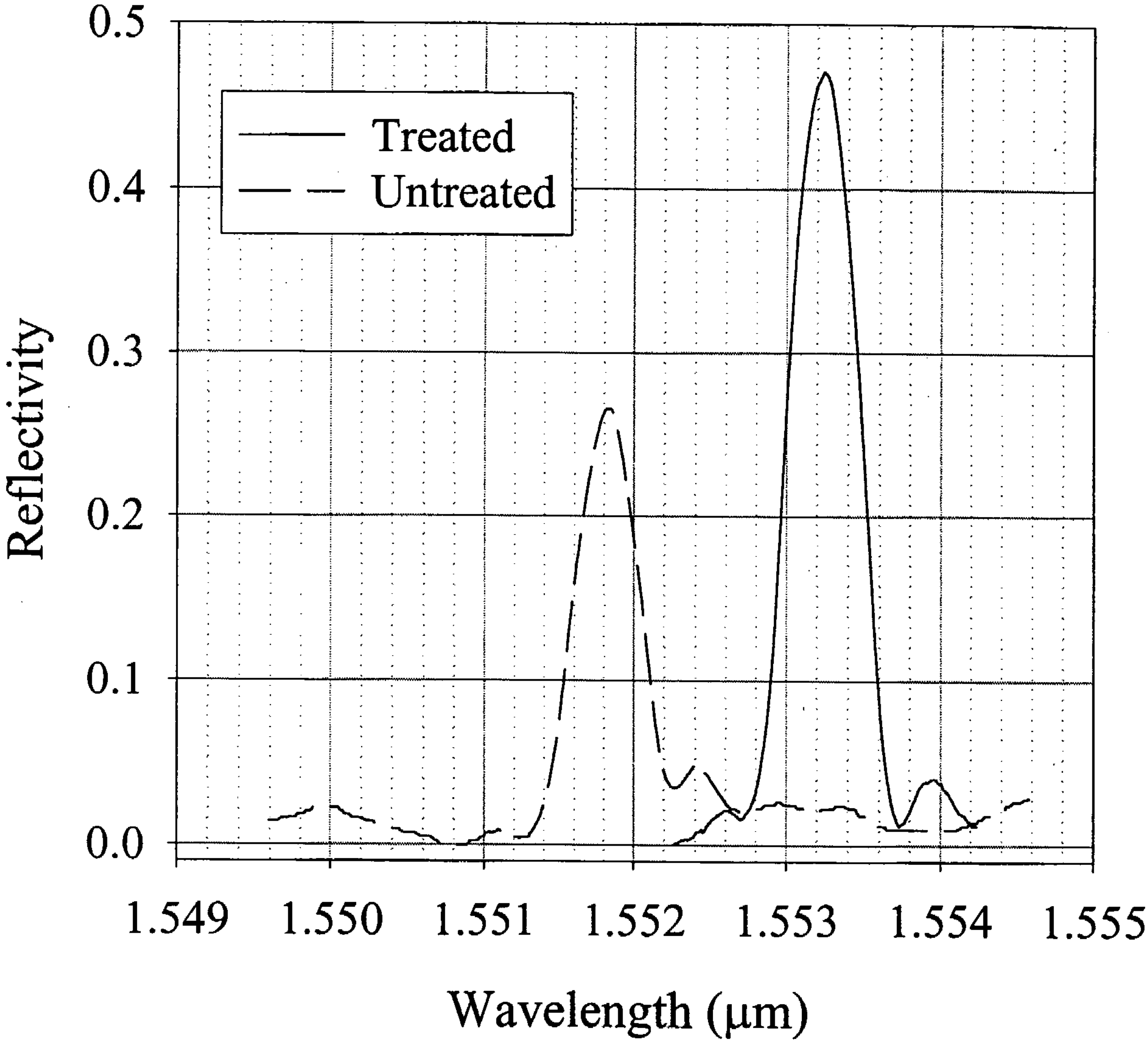
Figure Captions

1. Reflection spectra of the gratings written in fibre exposed to the CO_2 laser for 15 s (intensity: 350 W/cm^2) and in the untreated fibre. NA and external diameter of the fibre are 0.28 and 120 μm respectively, UV pulse energy and frequency 200 mJ/cm^2 and 20 Hz.

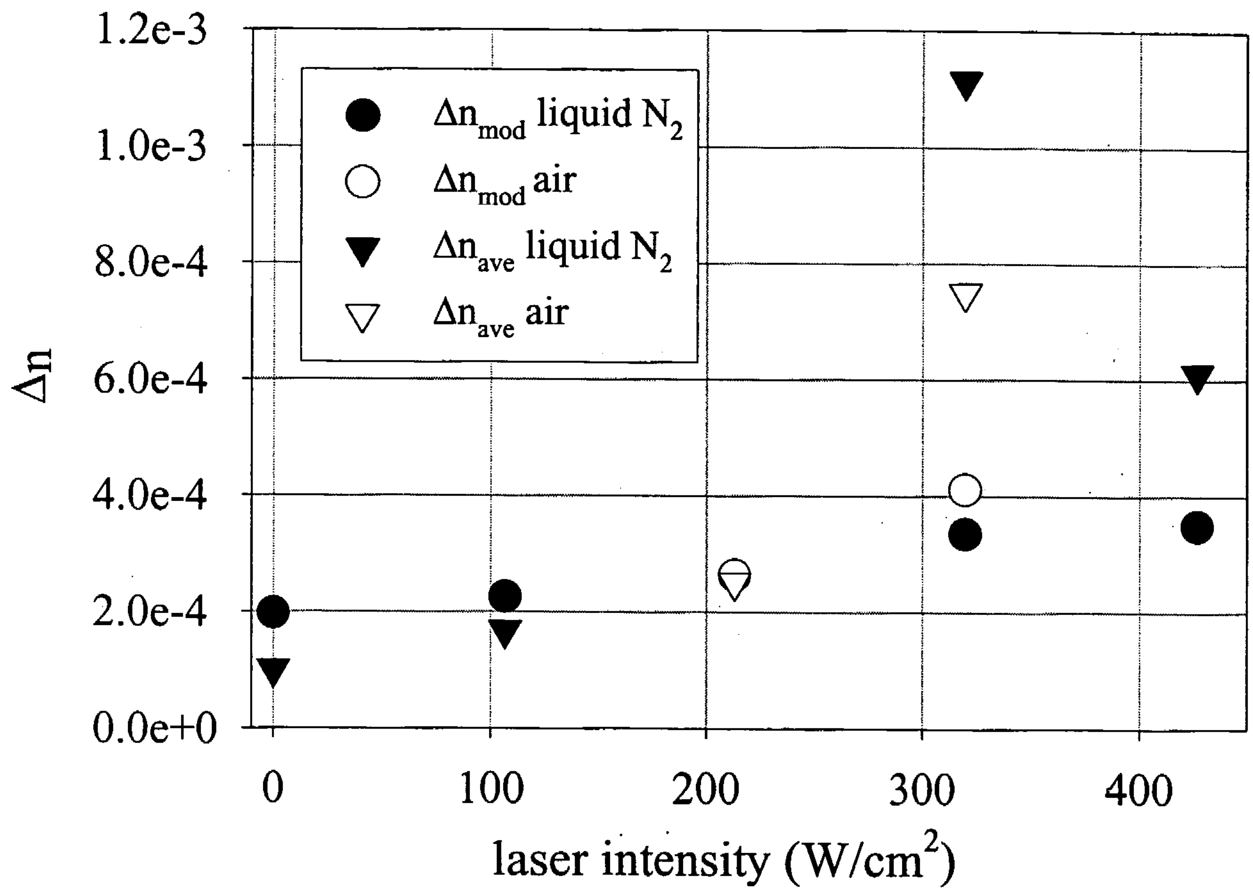
2. Dependence of the induced Δn on CO_2 laser intensity. Filled symbols represent fibres heated up by CO_2 laser and cooled by liquid N_2, open symbols represent fibres only treated with CO_2 laser. Δn_{mod} are deduced from reflection spectra, Δn_{ave} from Bragg-wavelength shift. Gratings were written by exposing fibres to pulsed excimer laser (pulse energy 300 mJ/cm^2, frequency 20 Hz, pulse duration 20 ns).

3. Absorption spectra of preform slide exposed to the CO_2 laser radiation (intensity: 210 W/cm^2). The inset shows the dependence of the 242 nm peak absorption on cumulative CO_2 laser exposure time; the fitted curve is a stretched exponential: $A=7.56+12\cdot(1-\exp(-0.0282\cdot t^{0.72}))$.

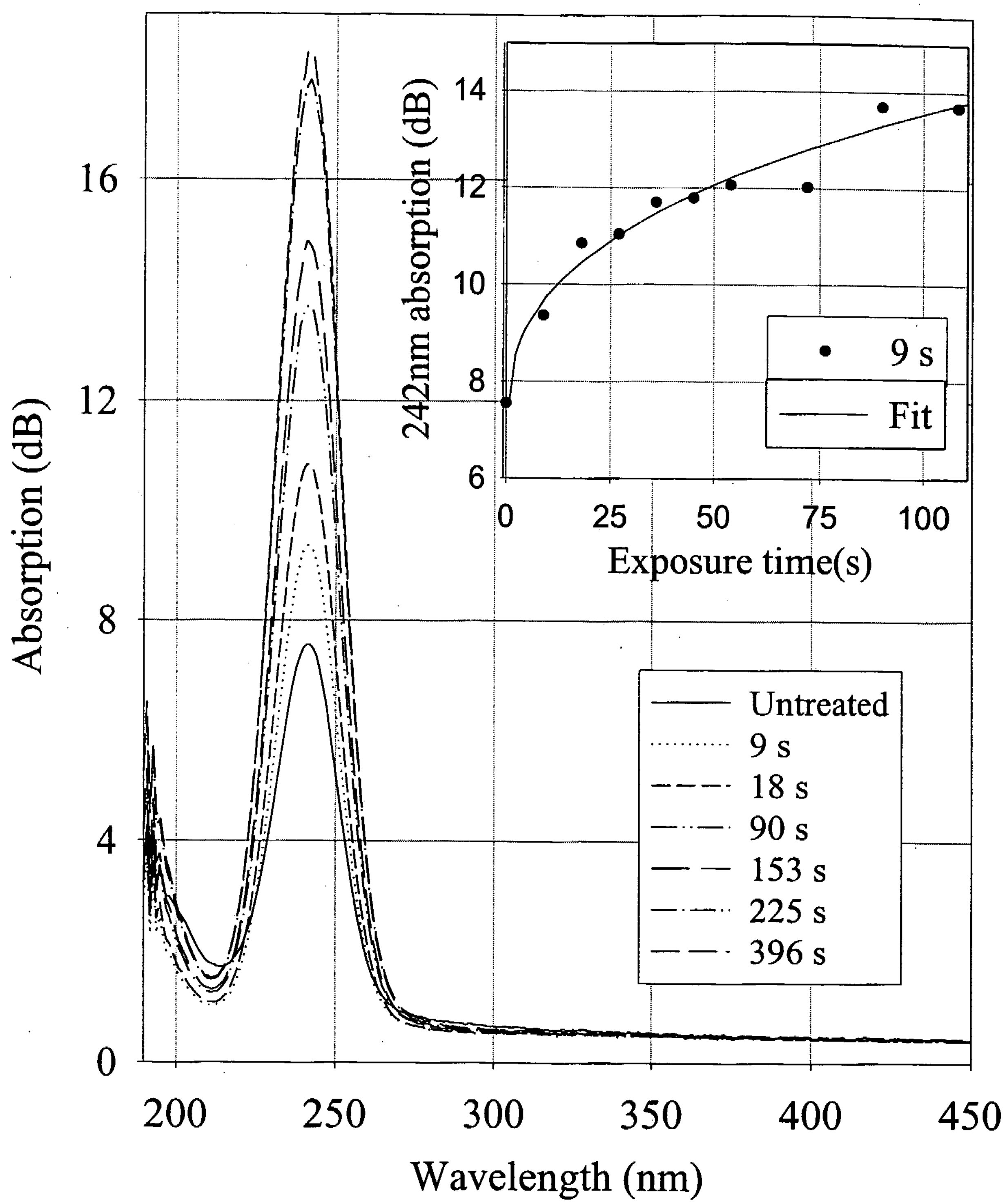
4. Intensity of 244 nm laser transmitted through a preform slide ~140 μm thick as a function of time. The CO_2 laser (P=280 W/cm^2) is turned on at t=5 s and switched off at t=12 s. Regions labelled with 1 and 2 are ranges of time where the temperature is below 300-500 ^{0}C and GODC reduction dominates over GODC generation.



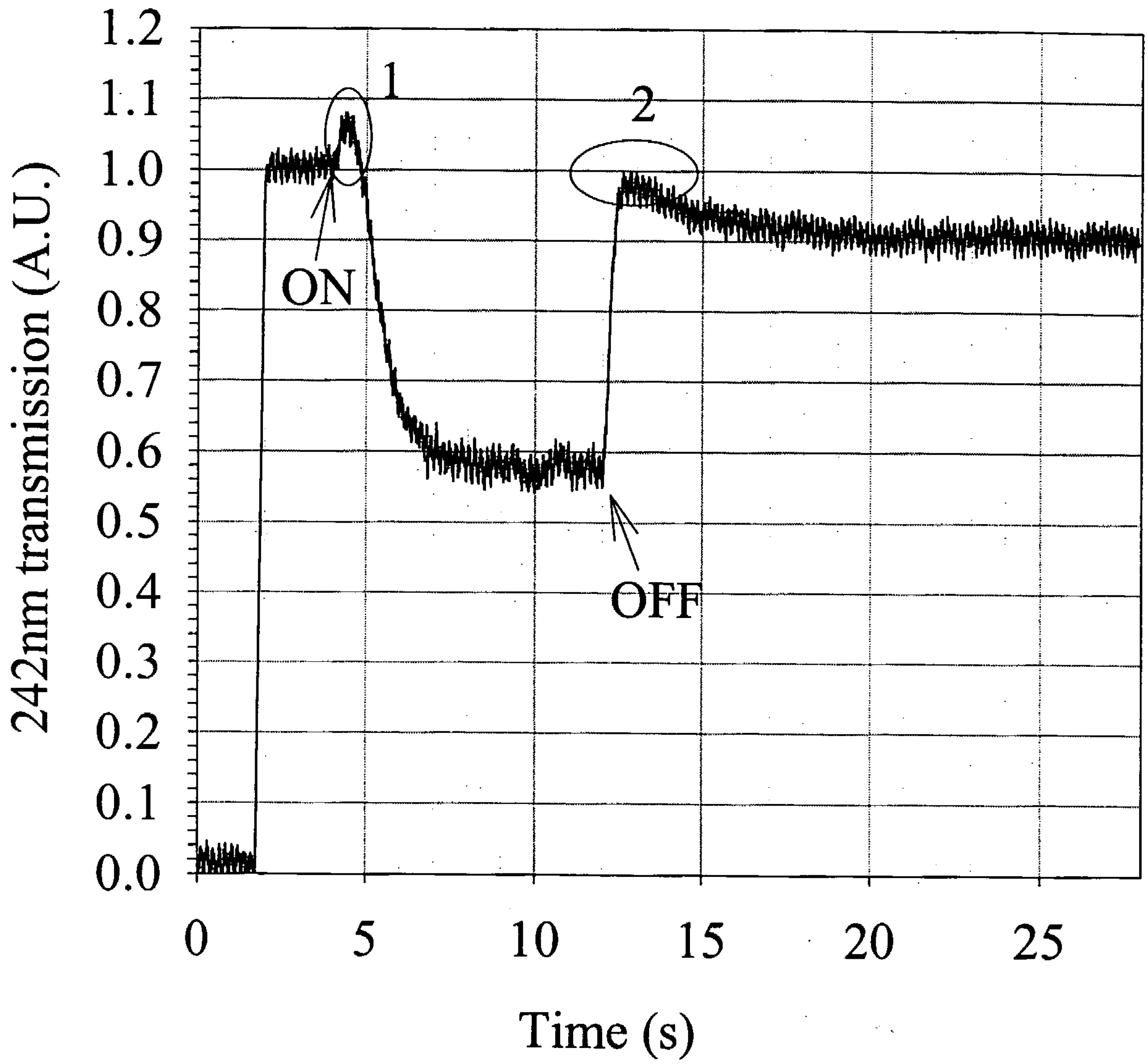
Treated
Untreated
Reflectivity
0.5
0.4
0.3
0.2
0.1
0.0
1.549
1.550
1.551
1.552
1.553
1.554
1.555
Wavelength (µm)



1.2e-3
1.0e-3
8.0e-4
6.0e-4
4.0e-4
2.0e-4
0.0e+0
Δn
0
100
200
300
400
laser intensity (W/cm^2)
Δn_{mod} liquid N_2
Δn_{mod} air
Δn_{ave} liquid N_2
Δn_{ave} air



Absorption (dB)
16
12
8
4
0
200
250
300
350
400
450
Wavelength (nm)
Untreated
9 s
18 s
90 s
153 s
225 s
396 s
242nm absorption (dB)
14
12
10
8
6
0
25
50
75
100
Exposure time(s)
9 s
Fit


1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
242nm transmission (A.U.)
1
2
ON
OFF
0
5
10
15
20
25
Time (s)