

Photorefractive index gratings in SnO₂:SiO₂ optical fibres

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Abstract

Permanent photorefractive gratings with considerable refractive index modulations ($\sim 3 \cdot 10^{-4}$) were written in silica optical fibres doped with very low levels of SnO₂ (~ 0.15 mol %) using ultraviolet (UV) laser radiation at 248 nm. The photoinduced refractive index change does not show any sign of saturation even for long exposure times (i.e. total fluence $> 20 \text{ kJ/cm}^2$). A comparison with GeO₂:SiO₂ fibres shows that, under similar UV intensities, saturation takes place for shorter exposure time and comparable refractive index changes are obtainable for GeO₂ concentrations ~ 10 mol %.

Bragg gratings based on ultraviolet (UV) photosensitivity of optical fibres have attracted much attention since their first demonstration because of their many applications, such as sensors, dispersion compensators and laser mirrors. Telecom optical fibres which have low content of GeO₂ (~3%) show small refractive index changes when exposed to UV radiation. It is thus necessary to increase the photosensitivity of optical fibres [1] through post-fabrication methods (such as hydrogen loading and flame brushing) and co-doping (B₂O₃, SnO₂ and rare earths). Compared to other techniques, the use of SnO₂ keeps the absorption in the third telecom window at 1.5 μm low, is less time consuming and potentially cheaper. SnO₂ also provides better temperature stability of the grating. Up to now SnO₂ has been used as a codopant to increase the photosensitivity of germanosilicate [2,3] and phosphosilicate [4] optical fibres, resulting in numerical apertures (NA) between 0.23 and 0.29 and refractive index modulations (Δn_{mod}) of $\sim 10^{-3}$ [2,4]. To our knowledge pure SnO₂ doped silicate fibres have never been investigated. A major problem with tin silicate fibres is the difficulty of their fabrication, considering also the fact that crystallization occurs for SnO₂ concentration of ~1 mol %. In this work we show that small concentrations (~0.15 mol %) of SnO₂ in the silica network, without the need of adding any other codopant (e.g. GeO₂, P₂O₅), give permanent refractive index changes with a high degree of photosensitivity. A comparison with SiO₂:GeO₂ fibres shows that GeO₂ concentrations nearly two orders of magnitude higher are needed to produce the same photosensitivity under similar UV intensities (although for shorter exposure times). The results indicate that concentrations of ~1 mol % of SnO₂ could potentially lead to the production of SnO₂: SiO₂ optical fibres with high enough photosensitivity and at the same time lower NA (<0.2) than SnO₂ codoped germanosilicate and phosphosilicate fibres. Lower NA is desirable for compatibility with standard telecom fibres.

The SiO₂:SnO₂ fibres used in these experiments were produced via MCVD (modified chemical vapour deposition) by depositing a soot rich in SnO₂ at 1300 °C and then consolidating the sintered particles at 1800 °C. During the collapse the temperature was kept under 2200 °C to avoid massive SnO₂ volatilization. The fibre produced had NA ~ 0.095 and cut-off wavelength $\lambda_c \sim 1.3 \mu\text{m}$. Gratings with high reflectivity at ~1543 nm were written using a KrF excimer laser (wavelength 248 nm, pulse duration ~20 ns, pulse fluence $I_p \sim 80 \text{ mJ/cm}^2$ and repetition rate 20 Hz) and a phase-mask to create the interference pattern.

Fig. 1 shows the evolution of Δn_{mod} as a function of exposure time. Δn_{mod} was calculated by fitting the reflectivity curves (i.e. reflectivity R as a function of wavelength λ) using the following formulas:

$$R = \left(1 + \left(kL \text{sinc} \left(kL \sqrt{\delta^2 - 1} \right) \right)^{-2} \right)^{-1} \quad (1)$$

$$k = \frac{\pi \Delta n_{\text{mod}}}{\lambda}$$

$$\delta = \frac{-2n_{\text{av}}}{\Delta n_{\text{mod}} \lambda_B} (\lambda - \lambda_B)$$

where L is the grating length, n_{av} the average refractive index, and λ_B the Bragg wavelength. The maximum Δn_{mod} achieved in these preliminary experiments was $\sim 2.8 \cdot 10^{-4}$ after an exposure of 3.7 hours, corresponding to a reflectivity largely greater than 90% for ~4 mm long gratings. Measurements at different UV laser intensities were carried out in order to understand whether the photosensitivity in our experiment is based on one-photon or multi-photon process. If the initial growth of Δn_{mod} is considered to be proportional to $I_p^\beta \cdot t$ (t is the exposure time, β a numerical coefficient), the slope of a log-log plot of the growth rate

$d(\Delta n_{\text{mod}})/dt$ vs I_p gives the exponent β . Values of β close to 1 suggest a photochemical reaction driven by one-photon process. From fig. 2 we estimate β to be ~ 0.99 , indicating that the photosensitivity at 248 nm in our SnO₂:SiO₂ fibres is governed by one photon absorption process [5].

Similar Δn_{mod} under the same experimental conditions has been obtained in GeO₂:SiO₂ optical fibres with ~ 10 mol % of GeO₂ [6,7] and also when a shorter UV writing wavelength (193 nm) was used in a 8 mol % GeO₂ fibre [5]. Standard telecom fibres (about 4 mol % of GeO₂) produced index changes one order of magnitude lower ($\sim 2.6 \cdot 10^{-5}$) [8]. It has also to be remarked that the grating dynamic is different. The growth of the grating in germanosilicate fibres is faster than in our experiment. In fact, as clearly seen from Fig. 1, saturation was not achieved even after very long exposures at a considerable I_p . In ref. 2 the photosensitivity of silica fibres with ~ 1 mol % of SnO₂ (i.e. 5-6 times greater concentration than in our fibres) and ~ 10 mol % of GeO₂ was studied and $\Delta n_{\text{mod}} \sim 10^{-3}$ was obtained. Assuming that SnO₂ and GeO₂ act independently on photosensitivity and Δn_{mod} has a linear dependence on dopant concentration, our results on SnO₂ SiO₂ fibre (~ 0.15 mol %) suggest that the photosensitivity of the fibres in ref. 2 (~ 1 mol %) was mostly due to SnO₂ contribution.

In order to understand better SnO₂:SiO₂ photosensitivity, we carried out absorption measurements before and after UV exposure on slices obtained from the same preform we used to produce the fibre. The preform slice was polished on both sides down to 60 μm . It is clear from figure 3 that the spectrum of the unexposed sample is similar to that of a GeO₂:SiO₂ glass, with values comparable to those with 8% mol of GeO₂ [8]. Note that the

main peak is shifted toward slightly longer wavelengths (~252 nm), in agreement with the fact that Sn has a lower band-gap than Ge. In GeO₂:SiO₂ glasses the exposure to UV radiation induces bleaching of the peak at 242 nm (assigned to germanium-oxygen deficient centres) and an increase in the rest of the spectrum. Similarly, in the SnO₂:SiO₂ glass the ~252 nm band is bleached and there is an increase in absorption at longer wavelengths. Recent measurements showed the possible substitutional role of Sn in the tetrahedral site of the SiO₂ network and the increase in the concentration of three-fold coordinated Sn sites (SnE') after X-ray exposure [9]. In analogy with germanosilicate glasses, the observed bleaching at ~252 nm can be explained with the bleaching of Sn-Oxygen deficient centres to produce SnE' centres. Below 210 nm the absorption change in our SnO₂:SiO₂ preforms is negative whereas a positive change was observed in GeO₂:SiO₂ between 160 and ~230 nm [6-8]. A positive absorption change in the considered UV range was also observed in SnO₂ codoped germanosilicate and phosphosilicate fibres [2,4].

Kramers-Kronig performed on the absorption changes measured in thin, low concentration, GeO₂:SiO₂ preform slices accounts for the refractive index changes in the optical fibres [6-8], indicating that similar processes take place both in the fibre and in the bulk preform sample when exposed to UV radiation. In our experiments the absorption change in preform slices seems to be significantly smaller and mostly negative (at least at wavelengths longer than 190 nm) although the refractive index change in the fibre is positive. Although measurements below 190 nm should be performed for a complete Kramers-Kronig calculation the results seem to indicate that the photosensitivity in SnO₂:SiO₂ fibres may be related to the fibre itself (fabrication, geometry, stress...) and not only a consequence of

material properties. Further investigations are required to understand the spectrum changes after UV exposure, the role of Sn-associated defects and fibre fabrication.

In summary, significant photosensitivity has been achieved in SnO₂:SiO₂ optical fibres, even at very low concentration of SnO₂. A comparison with SiO₂:GeO₂ fibres shows that dopant concentrations nearly two orders of magnitude higher are needed to produce the same photosensitivity under similar UV intensities (although for shorter exposure times). Measurements at different intensities indicate that the refractive index change is typical of one-photon process at 248nm. Future work should lead to a better understanding of how SnO₂ enhances the photosensitivity, fibres with greater SnO₂ concentrations and thus higher index modulations. It is hoped that this research will lead to the production of highly photosensitive optical fibres with low loss at 1.5 μm and compatible with standard telecom fibre (similar NA).

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Figure captions

1. Growth of Δn_{mod} resulting from exposure to KrF laser at 20 pulses/s with pulse fluence $I_p \sim 80 \text{ mJ/cm}^2$, grating length 4 mm). Inset: reflection spectrum for 3.7 hours' exposure.
2. Initial modulation growth rate as a function of KrF laser fluence per pulse. The continuous line is the best linear fit. The resulting slope is ~ 0.99 .
3. UV absorption spectra of a SiO₂:SnO₂ optical preform slice ($\sim 60 \text{ }\mu\text{m}$ thick) vs KrF excimer laser exposure (repetition rate 20 Hz, pulse fluence $I_p \sim 100 \text{ mJ/cm}^2$). Inset: UV induced absorption changes.

Fig. 1

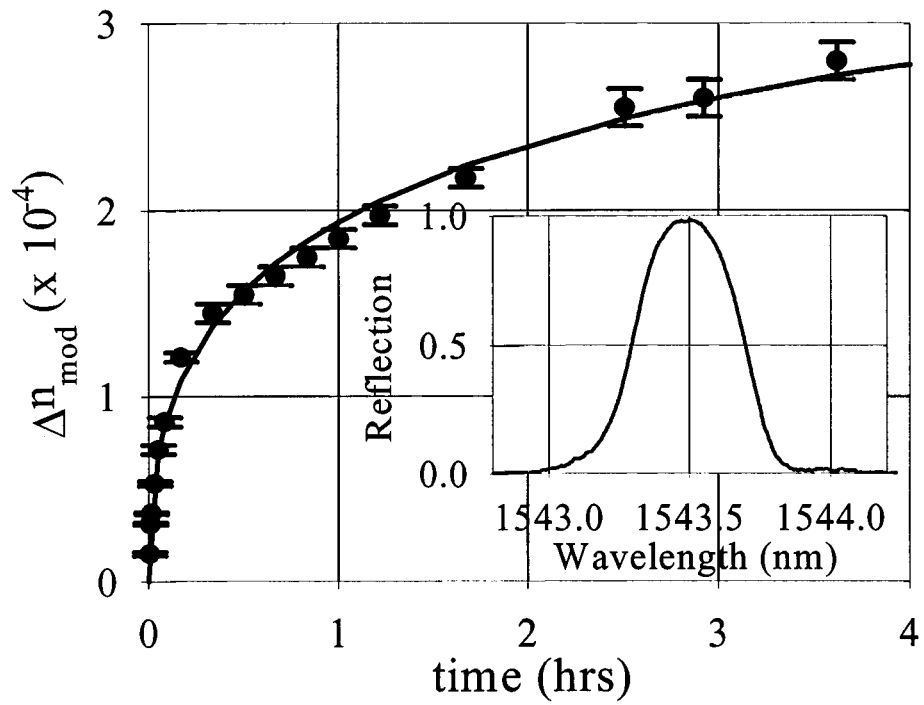


Fig. 2

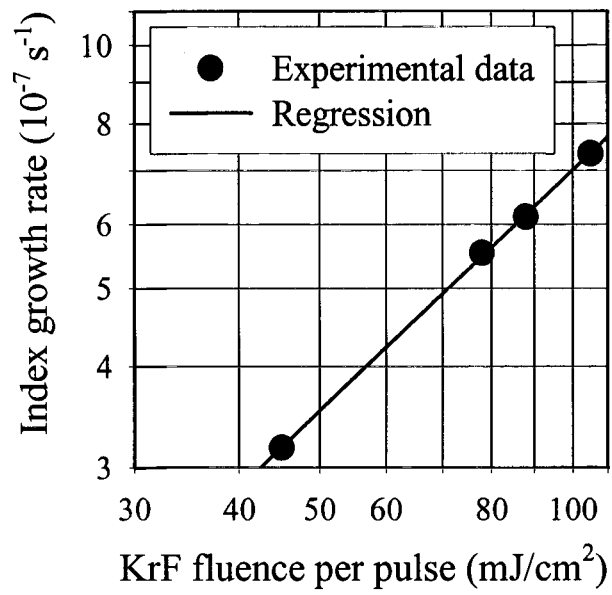


Fig. 3

