Refractive-index changes in fused silica produced by heavy-ion implantation followed by photobleaching

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The changes in refractive index, optical absorption, and volume of synthetic fused silica resulting from the implantation of germanium and silicon ions at energies of 3 and 5 MeV are reported. Implantation changes the density and generates ultraviolet color centers in the silica, which increases the refractive index at visible wavelengths by ~1%. Irradiation of the implanted samples with 249-nm light from a KrF excimer laser photobleaches the color centers and reduces the index by more than 0.1%. Photobleaching is used to write a 4.3-μm pitch diffraction grating in the implanted silica.

The effects of various types of radiation on fused silica have been extensively studied over the years. In particular, heavy-ion irradiation is known to induce optical absorption bands in the UV end of the spectrum[1] and refractive-index changes at all optical wavelengths, thereby an optical waveguide is formed.[2] On the other hand, exposure of silica to high-intensity UV light also results in permanent changes to the optical absorption spectrum and refractive index, i.e., to photosensitivity.[3] The typical index change values are of the order of 10^{-2} in the first case but only 10^{-5} in the second case. This research was initiated to determine whether implantation increases the photosensitivity of silica. The rationale is that photosensitivity is due to color centers in the UV and that the implantation produces these centers in large numbers. In a previous paper[4] we have shown that Ge implantation in fused silica leads to the formation of strong UV absorption bands and to an increase in refractive index of $\sim 10^{-2}$ near the surface. We have also shown that UV irradiation at a wavelength close to one of the induced absorption bands (light from a KrF excimer laser at 249 nm) bleaches the absorption and reduces the index by $\sim 10^{-3}$. By comparison, a report was recently published of a related experiment in which x rays were used to generate color centers in silica, followed by bleaching with 488-nm argon laser light, which resulted in a maximum index change of 10^{-5}.[5] It is important to note that photosensitivity in Ge-doped silica fibers[6] is a similar phenomenon, being due to color centers generated during the preform fabrication and pulling of the fiber. However, we believe that the density of centers achievable is much greater with implantation.

In this Letter we relate the measured refractive-index changes to absorption and structural changes in our implanted samples and demonstrate the use of photobleaching to fabricate a diffraction grating. The relatively large photosensitivity that we obtain in a planar configuration opens up a whole range of applications in integrated-optical circuits; phase gratings may be written with a suitably controlled beam of short-wavelength light for diffracting signals into or out of an optical waveguide, which leads to various signal-processing applications.

The details of the implantation have been described elsewhere.[4] Suffice to say here that doses of 10^{12} to 5×10^{14} ions/cm^2 of Ge and Si have been implanted in planar substrates of synthetic fused silica (Suprasil 2) with energies between 3 and 5 MeV. We found no significant differences between Si and Ge implantations, apart from the fact that the lighter Si ions led to smaller changes in all quantities measured (the difference is of the same order of magnitude as the mass ratio of Si to Ge). This rules out chemical doping by GeO_2 as the cause of the effects observed. The implanted area covered approximately 1 cm × 2 cm. The absorption measurements were carried out from 190 to 900 nm by using a Cary spectrophotometer, and the refractive indices were measured

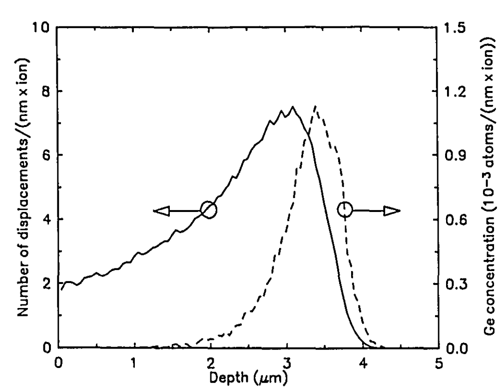

Fig. 1. TRIM simulation of dopant ion concentration and induced displacements for 5-MeV Ge implantation in synthetic fused silica.

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Table 1. Summary of Measurements and of TRIM Results

Conditions			TRIM Results		Measurements		
Ion	Energy (MeV)	Dose (ions/cm^2)	Range (μm)	Displacement per Ion	$\Delta N_{\text{eff}}(\pm 0.001)$	$\Delta h(\pm 2)$ (nm)	Δh/range
Ge	3	10^{13}	2.6	13,600	0.006	−35	−1.4%
Ge	3	10^{14}	2.6	13,600	0.012	−110	−4.2%
Ge	5	10^{13}	3.7	15,500	0.007	−40	−1.1%
Ge	5	10^{14}	3.7	15,500	0.013	−135	−3.7%
Si	5	10^{13}	3.6	3990	0.001		
Si	5	10^{14}	3.6	3990	0.009		

at 589 nm by using guided-mode spectroscopy in the planar optical waveguide formed by the implantation. An Abbe refractometer was used in lieu of a prism coupler, with an accuracy of 10^{-4}. In most cases, the optical waveguides are monomode, and the effective mode index is used as an estimate for the average refractive index in the guiding layer.

In order to gain information about the physical effects of implantation on the silica, we used a Monte Carlo simulation package called TRIM,[7] in which incident ions are followed individually through their collisions in the material. Some results of the simulation are shown in Fig. 1 for a typical case (the noise on the curves comes from the limited number of ions tried). First, the implanted ions are deposited in a 1-μm-thick layer lying 3.5 μm below the surface (the dashed curve). For the doses used in this research (10^{12}–10^{14} ions/cm^2), the peak volume concentration of Ge atoms in silica reaches 10^{18}/cm^3 or 0.01 mol. %. This concentration is 3 orders of magnitude too small to explain the observed index increase (10^{-2}) by the doping effect of Ge. To account for the full index increase, one must consider other effects of the implantation. In particular, each incident ion produces a large number of atomic displacements through collisions in the host material. The solid curve in Fig. 1 shows the distribution and number of these displacements. The profile of the increase in refractive index is believed to follow somewhat the profile of displacements,[2] which extends from the surface down to the end of the ion range. In the following we use measured quantities and TRIM estimates (Table 1) to explain the changes in optical properties observed after both ion implantation and UV bleaching.

In the spectrum of the implantation-induced optical absorption (solid curve of Fig. 2), the prominent features are the so-called B_2 band (244 nm) originating from a doubly charged, diamagnetic oxygen vacancy,[1] the silica E' band (212 nm) also associated with an oxygen vacancy but with adjacent Si atoms asymmetrically relaxed into charged and neutral trivalent coordinations,[8] and a VUV band whose peak is past 190 nm. Recently, a VUV band at 7.6 eV (163 nm) was reported to arise from the same oxygen vacancy with which the B_2 band is associated.[9] The appearance of strong absorption bands in the UV has been known for some time to be associated with damage processes occurring with heavy-ion implantation.[1] The TRIM calculation indicates that each Ge ion produces approximately 1.5×10^4 atomic displacements along its track (4×10^3 for Si). Thus an ion dose of 10^{14}/cm^2 results in 10^{18} displacements/cm^2, corresponding to a peak volume density approaching 10^{22}/cm^3. We assume that many of these displacements result in defects and, ultimately, color centers by trapping a hole or an electron. For comparison, photosensitivity in Ge-doped silica fibers is attributed to extrinsic centers associated with Ge impurities. The concentration of Ge atoms in standard fibers is of the order of 10^{21}/cm^3 (for 10 mol. % doping), and only a fraction of these impurities result in color centers.[10] This difference in the densities of color center precursors may explain why implanted silica is approximately 100 times more photosensitive than Ge-doped silica fibers.[11]

The other optical effect of the implantation is an increase in refractive index (Δn) ranging from 1.5×10^{-3} to 1.4×10^{-2} depending on dose and energy (see Table 1). This increase in index arises from changes in polarizability and density.[12] In our case the relationship is given by

$$\Delta n = \Delta n_\alpha - [(n^2 - 1)(n^2 + 2)/6n](\Delta V/V).$$

In this equation, Δn_α is the index change that is due to polarizability effects, and the density contribution is expressed as a relative volume change $\Delta V/V$, which should be equal to the relative thickness change $\Delta h/h$ for areas large compared with the implanted thickness. The contribution of polarizability changes, Δn_α, may be obtained from a

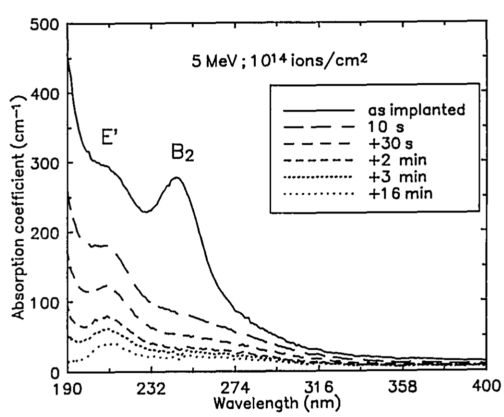

Fig. 2. Typical UV absorption spectrum induced by the implantation (solid curve) and after several stages of optical bleaching with 110-mJ/cm^2 pulses at 50 pulses/s.

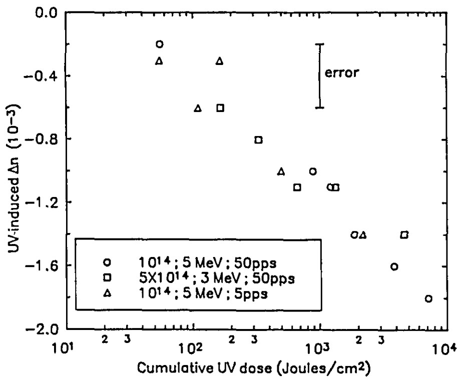

Fig. 3. Evolution of Δn in implanted samples during UV exposure.

Kramers–Krönig analysis[13] of the absorption spectrum of an implanted sample. In the case of Fig. 2, we get $\Delta n_\alpha = 0.0015$, out of a total measured index increase of 0.013. In order to account for the total increase, a relative volume change of −2.2% (i.e., a compaction) is needed. This result is not unreasonable since EerNisse[14] observed that compaction in silica induced by implantation of 500-keV Ar ions saturates at ~2.7% for a dose of 10^{14} ions/cm^2. In our samples we measured the volume change by profiling the surface height discontinuity at the boundary of an area masked during the implantation. Depending on the dose and energy, the surface of the implanted glass was found to lie between 35 and 135 nm below that of the unimplanted area (see Table 1). In the case of Fig. 2, the height change divided by the range yields an average compaction of 3.7%. A closer quantitative agreement would require a better knowledge of the depth profiles of index change, color centers, and compaction, including possible saturation effects (which may also explain why the average compaction is smaller for the 5-MeV cases).

Bleaching of the UV absorption was carried out with a KrF excimer laser that delivered intensities of 110 mJ/cm^2 per 20-ns pulse at repetition rates of as much as 50 pulses/s (pps) and a wavelength of 249 nm. Figure 2 shows the UV absorption spectrum of the implanted layer after several stages of bleaching. The most efficient bleaching occurs for the B_2 band, along with the VUV band, while the E' band shows a remarkable resistance to complete bleaching. Associated with the changes in absorption, significant changes in refractive index were measured. Figure 3 shows, for three different cases, the effect of UV light on Δn: a decrease reaching almost -2×10^{-3}. One of the curves was obtained by bleaching at 5 pps, and the other two were obtained at 50 pps. No notable difference is seen in the rate of index change between the two UV dose rates, which rules out average thermal effects. In this case (bleaching), the measured Δn follows the Kramers–Krönig transformation of the changes in the UV spectrum (Δn_α) within a factor of 2. Lack of data in the VUV spectrum prevents a more accurate determination of this relationship for now.

Finally, to demonstrate the device fabrication possibilities, a 4.3-μm period grating was written in a silica sample (initially implanted with 10^{14} Ge/cm^2 at 5 MeV) by exposing selected areas to a UV dose of 1600 J/cm^2, using an intensity of 400 mW/cm^2. This exposure lasted more than 1 h, confirming that heating cannot be responsible for the index bleaching because thermal diffusion would have smeared out such a short period grating. The grating efficiency was measured by shining a 632.8-nm beam of light from a 5-mW He–Ne laser perpendicularly through the plane of the sample. Three diffracted orders on each side of the transmitted main beam were visible, with a diffraction efficiency $\eta = 2 \times 10^{-5}$ in each of the two first-order beams. This efficiency corresponds to an index modulation of 0.0002 according to the formula $\Delta n = \lambda\sqrt{\eta}/(\pi d)$,[5] where d is taken to be the range of the implants. The difference between the size of the index modulation and the Δn expected from the results of Fig. 3 for this UV dose (−0.001 at 1.6×10^3 J/cm^2) is not understood at present and may be due to the technique used to define the grating (a proximity shadow mask). For total bleaching ($\Delta n \sim 0.002$) the efficiency could reach 0.1%.

In summary, we have shown how structural rearrangements (ΔV) and polarizability changes (Δn_α) in an implanted silica layer add up to allow waveguide formation ($\Delta n > 0.01$) and how UV exposure bleaches out only Δn_α ($\approx$0.002) through the photosensitive effect. The photoinduced refractive index changes obtained here are among the largest reported so far in fused silica and are sufficient for several applications in integrated optics. A 4.3-μm period grating was written to demonstrate the feasibility of device fabrication.

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