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Formation and bleaching of strong ultraviolet absorption bands in germanium implanted synthetic fused silica

J. Albert, K. O. Hill, B. Malo, and D. C. Johnson
Communications Research Centre, P. O. Box 11490, Station H, Ottawa, Ontario K2H 8S2, Canada

J. L. Brebner, Y. B. Trudeau, and G. Kajrys
Groupe des Couches Minces, Université de Montréal, Montréal, Québec, H3C 3J7 Canada

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Germanium ions have been implanted in fused silica using ion beams having energies of 3 and 5 MeV and doses ranging from 1×10^{12} to 5×10^{14} ions/cm^2. For wavelengths shorter than 400 nm, the optical absorption increases strongly with two absorption bands appearing at 244 and 212 nm. The ion-induced optical absorption can be bleached almost completely by irradiation with 249 nm excimer laser light. Ion implantation also increases the refractive index of silica near the substrate surface. At 632.8 nm a refractive index increase of more than 10^{-2} has been measured. This decreases by 4×10^{-3} upon bleaching with 249 nm light.

This work was stimulated by research on photosensitivity in optical fibers. The refractive index of the core of a germanium-doped fiber is observed to change permanently on irradiation by visible or ultraviolet light. The result leads to the conjecture that photosensitivity may also occur in bulk silica in which the germanium doping is achieved by means of ion implantation.

Photosensitivity in optical fibers was first observed in germanium-doped fibers through the creation of a Bragg index grating in a fiber carrying coherent 488 nm argon laser light.[1] Subsequently, irradiation of the optical fiber from the side by ultraviolet light was shown to change the core refractive index, enabling the writing of in-core Bragg reflectors using a holographic technique,[2] and mode converter gratings using a point-by-point technique.[3] Although photosensitivity has been observed primarily in Ge-doped fiber, it has also recently been observed in a Ge-free optical fiber.[4]

The phenomenon of photosensitivity in fibers is of great practical interest since it can be used to fabricate in-core fiber devices for optical communications and sensors. Devices such as Bragg reflection gratings,[1–2] intermodal couplers,[3,5,6] and reflectors for fiber lasers[7] have been demonstrated. The physical mechanisms underlying the process are not well understood. The increase in refractive index in the long wavelength region is related to the absorption of light in the ultraviolet wavelength region due to color centers in the glass but the details of the physical processes are not known. Reference 8 reviews some of the possible mechanisms involved.

In this letter, we report the first observation of photosensitivity in bulk silica which has been doped by ion implantation. The result may lead to a greater understanding of the photosensitivity phenomenon and have practical application in the fabrication of passive integrated optical waveguide devices.

Suprasil 2 synthetic fused silica substrates (available from Heraeus Amersil) were coated with 10–20 nm of aluminum to provide ground contact and avoid charging during the implantation. The implantations were carried out using the Université de Montréal 6 MV Tandem accelerator. The beam current of Ge^{3+} ions was typically 150 nA with a beam spot 3 mm in diameter scanned over an area of 4 cm^2 on the sample. The doses ranged from 1×10^{12} to 5×10^{14} ions/cm^2 at two energies, 3 and 5 MeV. The samples were maintained at room temperature during implantation. Under these conditions, TRIM simulations indicate that the germanium ions lie in a layer approximately 0.7 μm thick (full width at half maximum), at a depth of 2.1 μm for the 3 MeV ions and 3.1 μm for the 5 MeV ions.

After the implantation, the aluminum layer was etched away in a solution of 32:2:6 parts of phosphoric acid, nitric acid, and deionized water. No further processing of the substrates was carried out before the measurements (no annealing).

The absorption was measured with a spectrophotometer covering the range of 190–900 nm. No significant features were observed between 400–900 nm in any of the samples. The small thickness of the doped layer allows an accurate measurement of the large absorption coefficients that occur near the intrinsic absorption edge of silica. This measurement is not so easily performed in fibers or bulk doped samples since thin (~1 μm) slices are required.

Implantation of ions in silica forms optical waveguides by increasing the refractive index locally.[9] The refractive index change in the samples in which waveguiding occurs is estimated by measuring the coupling angle of the guided modes with a prism coupler. This measurement yields the effective index for the guided mode and also provides a lower bound for the refractive index in the ion implanted layer (the refractive index of the unimplanted silica at 632.8 nm is 1.457).

Bleaching experiments were carried out with a KrF excimer laser operating a 249 nm. The pulse duration is 12 ns and the energy per pulse is 100 mJ. The light beam has a rectangular cross section of approximately 10×30 mm.

A total of eight samples were implanted. The first result is that an optical waveguide near the surface is detectable only for samples with doses $\geqslant10^{13}$ ions/cm^2. The measured index changes lie between 0.007 (10^{13} dose at 3

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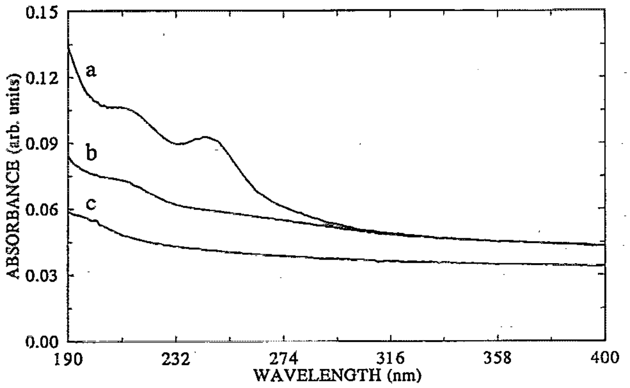

FIG. 1. (a) Absorbance spectrum of fused silica implanted with a dose of 10^{13} germanium ions per cm^2 at 3 MeV; (b) same sample after bleaching for 2 min at 50 pulses/s; (c) unimplanted substrate spectrum.

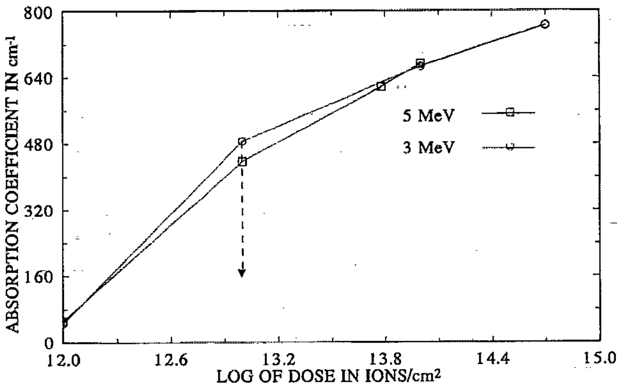

FIG. 2. Absorption coefficient (α) at 244 nm for the different doses and energies used, using $I_t = I_0 \exp(-\alpha d)$. The absorbing thickness d is taken to be 2.46 μm for the 3 MeV data and 3.47 μm for the 5 MeV data. the dashed line shows the effect of bleaching with ultraviolet light.

meV) and 0.015 (10^{14} at 5 MeV). The waveguides are very lossy however, with a bright scattering streak observable for only 15–20 mm past the coupling prism. Observation with a microscope of the implanted region revealed cracks on the sample surface, mainly along the edges of the implanted zone and to a lesser extent in the central region.

Strong absorption bands in the ultraviolet appeared in the silica after the implantation. Figure 1 (curve a) shows the ion induced absorption change in a sample with 10^{13} ions/cm^2 at 3 MeV. For comparison, the absorption spectrum for a blank substrate (curve c) is also shown. The band near 212 nm (5.85 eV) is usually associated with the silica E' defect which is presumed to occur at a charged oxygen vacancy.[10] There are two possibilities for the other band centered near 244 nm (5.1 eV). It has been observed in heavy ion irradiated fused silica (labeled the B_2 band)[11] and tentatively associated with a neutral oxygen vacancy.[12] A 240 nm band also shows up in various commercial fused silicas, and may be due to germanium or aluminum impurities or to electron or hole traps created in the synthesis of the glass.[13] There are many possible defect mechanisms for the increased absorption at wavelengths shorter than 190 nm,[10] we do not attempt an interpretation before more analysis is done on the data. In Fig. 2, we show the dependence of the peak absorption at 244 nm on the implanted dose at the two energies used. The coefficient of absorption is approximated as follows. First, the contribution from the silica substrate is subtracted. Next, the optical density is assumed to be uniform from the surface of the substrate down to the point where the tail of the germanium distribution has fallen to one half its maximum value. Taking the full path of the ions instead of only the thickness of the stopping layer allows to take into account color centers generated in the pure silica by the ions as they slow down. Calculated in this manner, the absorption coefficient does not seem to depend on implantation energy. This brings weight to the interpretation that the 244 nm absorption is due to an intrinsic defect, caused by the implantation but not due to the presence of germanium. It may be worth noting that the maximum density of germanium atoms used in this work (10^{18}/cm^3) is three orders of magnitude smaller than that of typical fibers and preforms. Also, germanium doped silica has a strong peak near 281 nm, due to Ge(1) defects,[14] which is absent in our data.

In order to evaluate the effect of bleaching, we irradiated the silica samples with 249 nm light from an excimer laser operating continuously at 50 pps. For the sample whose absorption curve is in Fig. 1, the ion induced absorption is almost completely eliminated (see curve b) by the laser irradiation. Throughout bleaching, the silica sample emits a strong red fluorescence. After bleaching, there remains a constant difference in absorbance between the bleached and the unimplanted sample as a function of wavelength. Another observable change is that the surface cracks originally concentrated near the edges of the implantation zone now cover it completely and uniformly. The region of the sample where no implantation occurred remained free of damage. A new measurement of refractive index at 632.8 nm yielded a value 0.004 lower than the one measured on this sample before bleaching. This result was obtained even though the waveguide was very lossy because of the surface damage limiting the propagation to a distance of only 1–2 mm. The photoinduced index change is at least ten times larger and of the opposite sign than the one obtained in Ge doped optical fibers.[8]

In this preliminary work on photobleaching of Ge-implanted fused silica, many interesting phenomena have been observed. For wavelengths shorter than 400 nm, strong absorption bands are induced by the implantation which can be bleached out by laser exposure at 249 nm. The implantation also results in a refractive index increase in the visible, and therefore the formation of an optical waveguide. The result is consistent with previous work that shows that implantation of almost any ion in silica increases its index through structural changes.[9] Of more significance is the relatively large decrease in the refractive index at longer wavelengths that occurs on exposure of the waveguide to ultraviolet light. The result that the photoinduced index changes are larger than those in optical fibers may be due to the higher density of color centers created in the implantation process. Finally, surface damage is generated during the implantation. This is consistent with the fact that compaction of the silica network occurs, leading to tensile stresses concentrated near the edges of the implanted area.[15] The increase in damage during bleaching confirms that some structural rearrangements also occur during the exposure.[16] Preliminary experiments show that all the absorption bands, structural damage, and waveguiding layers created during the implantation are removed by an annealing for 20 min at 1200 °C, in spite of the fact that very little germanium diffusion occurs in these conditions.

The strong photosensitivity in these samples provides a potential means for submicron-sized feature definition by exposure to ultraviolet laser light in integrated optic device fabrication. An added benefit of ion implantation is that the changes in optical absorption of thin doped layers are easily measurable in the spectral region of interest for the study of color center dynamics in glasses.

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