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Ion implantation induced photosensitivity in Ge-doped silica: Effect of induced defects on refractive index changes

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Abstract

Planar germanosilicate thin film glasses grown by flame hydrolysis technique on silica substrate have been implanted at 5 MeV with silicon ions to a dose of 10^{14} ions/cm^2. Samples were subsequently exposed to a series of KrF (5 eV) and ArF (6.4 eV) excimer laser irradiation. Optical absorption and electron spin resonance were measured before and after each series of irradiation. We report an important refractive index change that can be correlated with the photobleaching of the ion implantation induced absorption bands. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The photosensitivity of germanosilicate glasses and optical fibers has attracted much attention after the fabrication of index gratings in the fiber core [1]. Direct UV writing in optical waveguides is a promising technology for the fabrication of photonic integrated circuits on planar waveguides. To date, most results of UV writing in planar waveguides have been based on material grown by flame hydrolysis which need preprocessing, such as hydrogen loading, in order to achieve significant UV induced index changes [2]. It was recently observed that photosensitivity can be induced in silica by implantation of silicon ions [3]. This process avoids the use of hydrogen sensitizing treatment and thus yields stable films which retain their predisposition for large photosensitivity for years of storage. Clearly, for the fabrication of optical integrated circuits in planar silica waveguide structures, it is useful to show that gratings can be fabricated in localized areas of samples. Ion implantation is shown here to be an appropriate technique for their production. Ion implantation leads to strong absorption bands which can be bleached with UV light. We have implanted the Ge-doped samples with silicon ions at an energy of 5 MeV and bleached the absorption bands

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with ArF (193 nm) and KrF (248 nm) excimer lasers in order to compare the bleaching efficiency at these two wavelengths. The ion implantation increases the refractive index of the material up to 2% for a dose of 10^{14} ions/cm^2 in a region of 5 μm near the surface. The bleaching of the absorption bands by the UV light leads to a negative variation of the refractive index of the order of 10^{-3}. The estimation of the refractive index change by the Kramers–Kronig analysis is close to that of the measured values. This paper describes the results of a series of experiments undertaken to determine the effects of ion implantation on the photosensitivity of Ge-doped planar silica waveguide structures.

2. Experimental

Samples of Ge-doped, Boron co-doped silica 20 microns thick deposited on silica substrate by using the flame hydrolysis technique from PIRI, are implanted with silicon ions at room temperature in a vacuum of 10^{-7} Torr using the University of Montreal's 6 MV Tandem van de Graaf accelerator. Analysis of these samples before implantation showed the depth profile of the Ge concentration to be constant at 7% and the B concentration to increase from 4% at the surface to more than 10% at a depth of 0.5 microns. The optical absorption measurements in the 190–400 nm wavelength range were carried out using a Cary-5 spectrophotometer and below 190 nm at 10^{-6} Torr using a VM-502 spectrophotometer from Acton Research. No significant features were observed between 400 and 900 nm in any of the samples. The bleaching of the absorption bands was performed by 20 ns excimer laser pulses from a Lumonics 500 operating with either ArF (193 nm, 6.4 eV) or KrF (248 nm, 5.0 eV) gas mixture. The variation of refractive index measurements was performed using an Abbe refractometer at 589 nm by taking the difference of the index values of the implanted and the virgin region. Electron spin resonance (ESR) studies were made on an X-band Bruker ESP-300E spectrometer to evaluate the presence and development of paramagnetic structural defects in the films. Spin concentrations were determined by comparing the double integrated spectra of the samples with that of a strongpitch standard.

3. Results and discussion

Following implantation, the samples were exposed to UV irradiation from the Lumonics KrF and ArF excimer laser operating at 248 and 193 nm, respectively, with up to 100 mJ/cm^2, 20 ns pulses at a repetition rate of 10 Hz. Intermittent UV absorption and room temperature ESR spectra were taken at various times during the irradiation in order to observe the possible bleaching effects of UV light on the variation of the population of the optically active and paramagnetic centers. Figs. 1 and 2 contain representative induced absorption coefficient spectra in the visible and vacuum UV region obtained after implantation of the film at a dose of 10^{14} ions/cm^2 followed by irradiation at different doses of ArF and KrF lasers, respectively. As can be seen, ion implantation induces strong absorption bands in the regions of 5, 6.5 and 7 eV and a weak feature around 4.5 eV, different from what is seen in the pure silica implanted with the same ions [3]. We measured absorbance spectra in the implanted regions and in the non-implanted regions. By subtracting the virgin material spectrum from the implanted one and dividing by the thickness of the implanted region

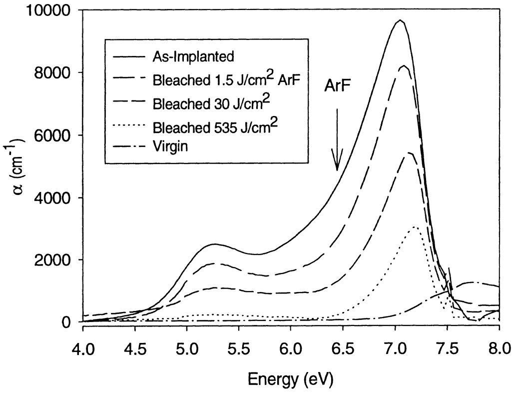

Fig. 1. Absorption coefficient spectra following implantation and irradiation with different doses of ArF (193 nm) laser.

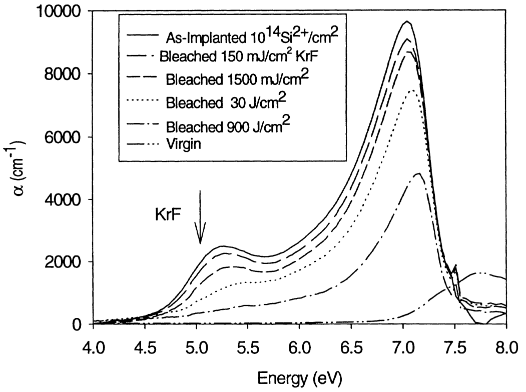

Fig. 2. Absorption coefficient spectra following implantation and irradiation with different doses of KrF (248 nm) laser.

(3.4 μm) we obtained the net absorption coefficient due to the implanted layer only. In doing so, the absorption coefficient is considered to be constant all over the implanted region. This represents an approximation since creation of defects by heavy ion irradiation is not uniform along the ion track. In order to determine the presence of more absorption bands overlapped by the broad visible ones, we have investigated the paramagnetic defects by measuring ESR signals. Fig. 3 shows the presence of GEC (Germanium electron center) and GeE′ signals in the as-implanted samples. Since it is known that GEC's defects have absorption bands at around 4.5 and 5.6 eV and that GeE′ defects have one at 6.4 eV [4], we have fitted the absorption spectra by considering those absorption bands which are difficult to detect before deconvolution. Five Gaussian shape bands have been used to fit the spectra. 4.5 and 5.6 eV for the GEC's, the 5.14 eV band known as the GLPC (Germanium Lone Pair Center) defect, the 6.4 eV band for the GeE′ and another band around 7.1 eV which is close to the band edge and that we believe could be a form of germanium oxygen deficient center GODC (see Fig. 4). All the absorption bands are gradually bleached after the exposure to the UV light, but the differences are seen in the amount of integrated delivered energy by one or the other lasers required to bleach the absorption bands. The ArF laser seems to have a resonant effect on the GeE′ absorption band which is bleached more rapidly compared to the KrF laser case. After a fluence of 530 J/cm^2 of ArF laser, the 6.4 eV band completely disappears but is still present after the same dose of KrF. This phenomenon can be partly explained by the fact that there exist two processes in competition when the implanted sample is irradiated with KrF laser. First, one component of the 5 eV band is transformed to GEC centers which in turn are transformed to GeE′ [5] when irradiated with UV light and second, the GeE′ centers produced by ion implantation are bleached at the same time by the laser. No such transformation is seen in the case of ArF irradiation where all the bands are gradually decreased, and this can explain the efficiency of the ArF laser to bleach the

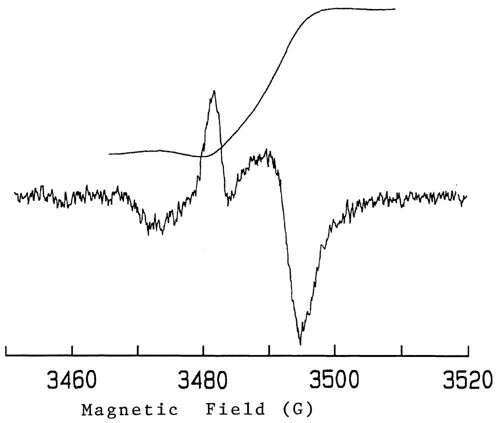

Fig. 3. GEC + GeE′ signals measured on the as-implanted Ge-doped silica sample.

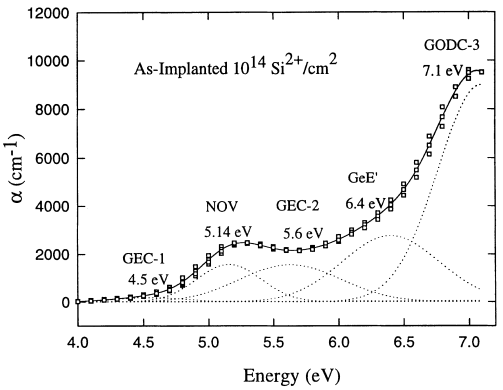

Fig. 4. Five Gaussian shape absorption bands to fit the as-implanted absorption spectrum. Open squares are experimental data and solid line is the fit result.

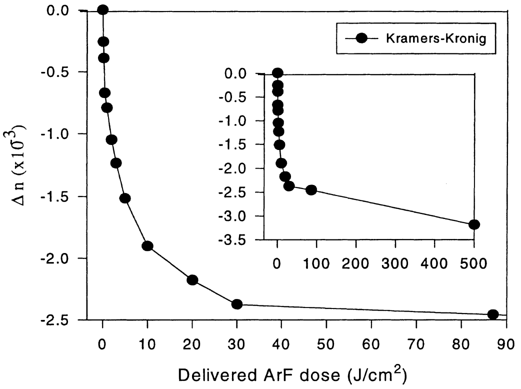

Fig. 5. Kramers–Kronig analysis of the refractive index change following ArF irradiation of implanted sample.

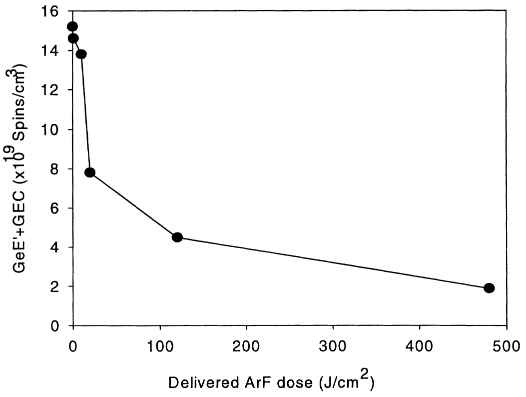

Fig. 6. Evolution of the concentration of GEC and GeE′ centers with the delivered ArF laser dose.

bands compared to the KrF. Fig. 5 shows the negative evolution of the refractive index change larger than 10^{-3} in relation with the decrease of the absorption bands by Kramers–Kronig analysis. Most of the change is done up to 30 J/cm^2 and seems to saturate for longer irradiation with the ArF laser. Fig. 6 confirms the decrease of the concentration of the GEC and GeE′ defects in relation with the bleaching of the 5.6 and 6.4 eV bands with the ArF laser. The concentration of these paramagnetic defects is estimated to 1.5×10^{20} spins/cm^3 for a dose of 10^{14} ions/cm^2 and this is about ten times higher compared to the population of paramagnetic centers produced by high fluence of ArF irradiation of the Ge-doped preform rod [4].

4. Conclusion

Ion implantation of Ge-doped silica induces strong absorption bands which lead to an important refractive index change when bleached by UV light. Photobleaching of the absorption bands measured on the implanted samples by both ArF (6.4 eV) and KrF (5.0 eV) excimer lasers, leads to negative refractive index change of the order of 10^{-3}. The details of the process are different for each laser. We have estimated this change as a function of delivered laser dose by using the Kramers–Kronig relation after deconvoluting the different absorption spectra. ESR measurements show the presence of GEC and GeE′ centers in the implanted samples and this helps in the deconvolution of the absorption spectra into individual defect bands.

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