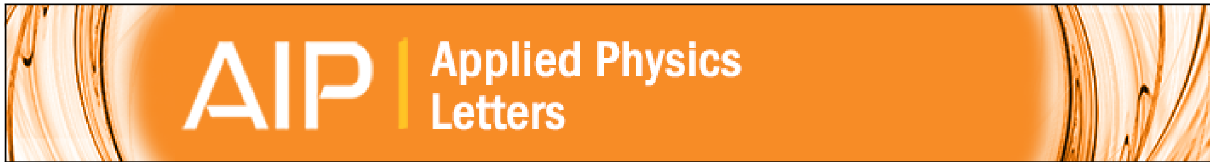

Ion implantation-induced strong photosensitivity in high-purity fused silica: Correlation of index changes with VUV color centers

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Ion implantation-induced strong photosensitivity in high-purity fused silica: Correlation of index changes with VUV color centers

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We have studied optical changes induced by ArF (6.4 eV/193 nm) excimer laser light illumination of high purity SiO_2 implanted with Si^{2+} (5 MeV) at a fluence of 10^{15} ions/cm^2. Optical absorption was measured from 3 eV (400 nm) to 8 eV (155 nm) and showed evidence of several well-defined absorption bands. A correlation in the bleaching behavior appears to exist between the so-called D band (located at 7.15 eV) and the well-known $B_2\alpha$ band which is attributed to oxygen vacancies. Changes in the refractive index as a function of ArF illumination were measured and found to be in good quantitative agreement with a Kramers–Kronig analysis of the optical absorption data.
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In the early works on photosensitivity, germanium doping was through to be essential. Later experiments showed that a few other dopants could be used and that photosensitivity could be enhanced. The techniques of flame brushing,[1] hydrogen loading,[2] and ion implantation[3] all lead to enhanced photosensitivity of silica glass. Thus far, ion implantation appears to be the only technique able to produce planar photosensitive waveguides in undoped pure silica.[4] Here, ion bombardment induces compaction and creates defects in the near-surface region. The resulting positive index change is of the order of 10^{-2} for a typical dose of 10^{15} Si^{2+}/cm^2. By illuminating the photosensitive waveguides with UV light the optical absorption bands related to the color centers are bleached and a negative index change[4] is induced which is of the order of 10^{-3} for a typical ArF laser illumination of 2 J/cm^2 (20 pulses of 100 mJ/cm^2). For such a low laser fluence, this value of the index change compares with the best results obtained in strongly photosensitive doped glasses.

A large number of radiation-induced optical absorption bands have been reported for silica.[5] Among these, the B_2 (5.02 eV), E_1' (5.85 eV), and E (7.6 eV) bands were shown to be inducible by high energy (5 MeV) silicon and germanium irradiation of high purity synthetic fused silica.[4] Tohmon *et al.*[6] reported that in as-prepared silica the B_2 band might have two contributions peaking at 5.06 and 5.17 eV, respectively, called the $B_2\alpha$ (FWHM: 0.35 eV) and $B_2\beta$ (FWHM: 0.48 eV) bands. Three other bands are reported in irradiated high purity silica: the A_2 (2.0 eV), D_0 (4.8 eV)[7] and D (7.15 eV)[8] bands.

The high-purity synthetic fused silica samples were 0.5 mm thick Suprasil-2 substrates (Heraeus Amersil Inc.). The concentration of OH groups in the silica matrix is 900–1200 wt ppm. Silicon ions (Si^{2+}) were accelerated at 5 MeV using the Université de Montréal 6 MV Tandem accelerator. The expected projected range (R_P) of silicon ions is 3.3 μm with a longitudinal straggling (ΔR_P) of 0.25 μm.[9] The samples were implanted at room temperature in a vacuum of 10^{-7} Torr; the implanted dose was 10^{15} ions/cm^2 for all of the substrates (corresponding to an average concentration of 10^{18} implanted ions per cm^3 or 100 ppm). The ion beam had a diameter of 3 mm, its current was 200 nA, and it was scanned over an area of 1 cm^2 on the silica samples. The implanted region was limited to a 3 mm$\times$5 mm surface by a steel contact mask placed on the samples.

Four implanted samples were subsequently exposed to 20 ns pulses of 6.4 eV light with 100 mJ/cm^2 per pulse generated by a Lumonics EX 500 excimer laser operating on an ArF gas mixture. The laser repetition rate was 2 Hz and the samples were exposed to cumulative energy densities ranging from 0.4 to 10 J/cm^2 (4–100 pulses of 100 mJ/cm^2). In order to minimize the background vacuum ultraviolet optical absorption from the relatively thick substrate, all the samples were thinned by chemical etching after implantation and bleaching. High concentration HF (48.8% HF; 51.2% H_2O) etching yielded samples having 20–40 μm in thickness. Optical absorption in the visible-UV region (3.1–6.5 eV) was measured by a CARY-5 (VARIAN) double-beam spectrophotometer. In the UV–VUV range (5.0–8.0 eV), optical absorption measurements were carried out in a vacuum of 10^{-6} Torr using a VM-502 (Acton Research Corp.) spectrophotometer. We measured absorbance spectra in the implanted region and in the nonimplanted region of the thinned samples. By subtracting the virgin material spectrum from the implanted one and dividing by the thickness of the implanted region ($R_P+\Delta R_P=3.6$ 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.[9] The index of refraction at 589 nm was determined before and after laser irradiation with an Abbe refractometer (relative accuracy: 2.5×10^{-4}).

Figure 1 shows the difference spectra obtained by subtracting the partly bleached sample's absorption spectrum

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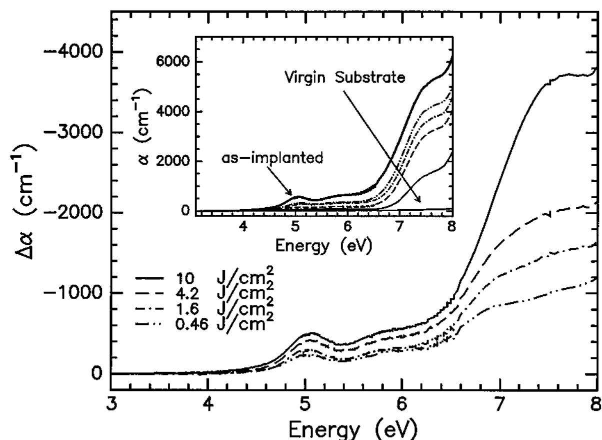

FIG. 1. Difference absorption spectra between the as-implanted and bleached samples at different stages of ArF excimer laser light illumination (2 Hz repetition rate; 100 mJ/cm²/pulse). The energies appearing in the legend are the cumulative energies delivered to the samples. The inset shows the absorption spectra of high-purity synthetic fused silica implanted to a dose of 10^{15} Si/cm².

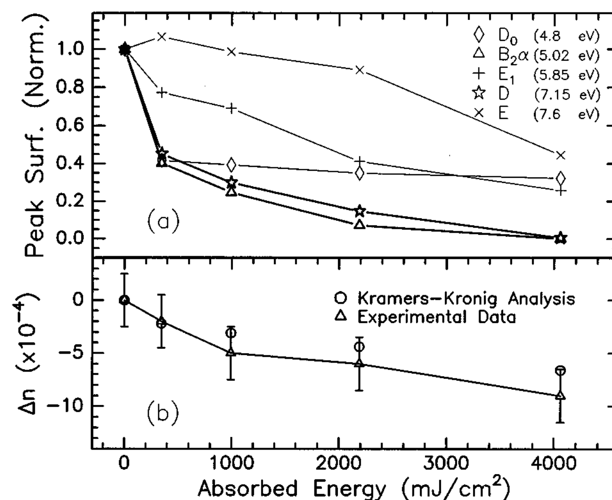

FIG. 2. (a) Normalized surface of the peaks obtained after fitting the absorption spectra as a function of the cumulative ArF excimer laser energy absorbed by the samples. The name and position of each fitted band appears in the legend. (b) UV-induced refractive index change measured at 589 nm as a function of the cumulative ArF excimer laser energy absorbed by the samples. The triangles are experimental data measured with the Abbe refractometer and the circles are the data obtained from a Kramers–Kronig analysis. The line is a guide to the eye.

from the absorption spectrum of the as-implanted sample. This figure shows the net effect of bleaching on the absorption spectra of implanted silica samples. The existence of a peak around 7 eV is strongly suggested at the early stage of bleaching. This band appears near the spectral position of the previously reported[10] D band located at 7.15 eV and observed in 46.5 MeV Ni^{+6} implanted silica (10^{14} ions/cm²). The inset of Fig. 1 shows the evolution of the absorption spectrum as a function of the cumulative energy delivered by the excimer laser. The B_2 (5.02 eV), E_1' (5.85 eV), and E (7.6 eV) bands are clearly seen. The D_0 (4.8 eV) band is not apparent but is required in the curve-fitting procedure in order to reproduce the low energy tail of the absorption spectrum. As reported previously[4] the intensities of the B_2, E_1', and E bands decrease monotonically with bleaching up to a cumulative laser energy of 10 J/cm² (100 pulses of 100 mJ/cm²).

The evolution of the absorption spectrum with bleaching was then studied using a 5 Gaussian lineshape peak fitting procedure with fixed centers and widths. The B_2 band is reasonably well fitted with a Gaussian peak centered at 5.02 eV with a full width at half-maximum of 0.37 eV. The results obtained by Tohmon *et al.*[6] indicate that the $B_2\alpha$ band is the major contributor (if not the only one) to the B_2 band we observed. The normalized Gaussian peak surface of each band is presented in Fig. 2(a) as a function of the absorbed UV energy. The most striking feature of this figure is that both the B_2 and D bands are completely bleached by laser light. Moreover the bleaching behavior of the oxygen vacancy B_2 band is strongly correlated to that of the 7.15 eV D band. In agreement with the observations of Antonini *et al.*[10] who observed a correlation between the growth of the B_2 and D bands created by implanting heavy ions, protons, and electrons, these results indicate a common origin for both bands. Additionally, there are two separate contributions to photosensitivity in the VUV region, namely the E band and the D band. The E band is not bleached as rapidly as the B_2 band and thus these bands arise from different defects as suggested by Imai *et al.*[11]

A Kramers–Kronig analysis[12] was carried out in order to compare the changes of refractive index calculated from our absorption measurements with the changes of refractive index decreases as UV light is absorbed by the implanted layer and this change approaches 10^{-3} after 4 J/cm² of absorbed laser light. The Kramers–Kronig analysis is in good quantitative agreement with the experimental data although this analysis has a tendency to underestimate by 25% the measured refractive index variation for an absorbed UV energy greater than 1 J/cm² laser light illumination. This discrepancy might be due to different reasons. The first one could be the bleaching of absorption bands located beyond 8 eV. The second is that the compacted implanted volume has relaxed by 0.03% according to the Lorentz–Lorenz[13] equation following a UV irradiation. It is important to note that the Kramers–Kronig analysis indicates that 70% of the change in refractive index is caused by the bleaching of the E band (≈30%) and the presumed D band (≈40%). This results indicates that photosensitivity is mainly due to the E and D bands located in the VUV region of the optical spectrum.

Optical absorption was studied in Si-implanted silica illuminated by 6.4 eV ArF excimer laser light. The absorption spectra measured from 3.0 to 8.0 eV showed that major changes in absorption involved the E band located at 7.6 eV but also another band of importance around 7 eV which might be the D band located at 7.15 eV. Correlation between the oxygen vacancy B_2 band and the presumed D band was evidenced by bleaching experiments. Finally the Kramers–Kronig analysis proved that the UV absorption changes account for at least 75% of the changes in photoinduced refractive index changes.

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