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Photosensitivity in phosphorus-doped silica glass and optical waveguides

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Irradiation of hydrogen loaded or flame brushed phosphorus doped, germanium free silica glass with a 193-nm ArF excimer laser changes the optical absorption at ultraviolet wavelengths by 40–140 dB/mm and the refractive index by more than 2×10^{-4}. Bragg gratings with 90%–95% reflectivity are photoinduced in channel optical waveguides made from this glass. The thermal stability of the photosensitivity is measured by annealing up to 700 °C.

The discovery of photosensitivity in germanium-doped silica glass (GeO_2:SiO_2), whereby permanent refractive index modifications result from exposure to light,[1] has led to several practical applications: fiber sensor,[2] lasers,[3,4] and narrowband filters.[5,6] The phenomenon has been associated with the presence of an absorption band near 242 nm caused by oxygen deficient defects of the germanium oxide.[2,7,8] In fact, recent experiments have confirmed that the occurrence of refractive index changes is linked to the bleaching of this absorption by in-band laser light, as explained through the Kramers–Kronig relations.[9] On the other hand, several examples of photosensitivity in germanium-free silica have been published,[10,11] and we have recently shown in experiments using 193 nm light that in-band bleaching of absorption near 242 nm in GeO_2:SiO_2 is not essential to induce refractive index changes.[12]

In addition to germanium, phosphorus is often used as a dopant in the fabrication of high silica optical waveguides and fibers. In particular, low loss P_2O_5 doped silica planar optical waveguides have been developed,[13] as well as optical waveguide amplifiers obtained by co-doping with erbium.[14] In this letter we present results on photosensitivity in P_2O_5:SiO_2 glass. The glass does not contain germanium and has an ultraviolet absorption edge below 200 nm. Experiments have been carried out on as-deposited and photosensitized P-doped thin films and waveguides using both KrF and ArF excimer lasers emitting at 248 and 193 nm, respectively.

For the optical absorption measurements, a 30 μm thick layer of P_2O_5:SiO_2 was deposited on a synthetic fused silica substrate by the flame hydrolysis technique.[15] The molar ratio of P_2O_5 to SiO_2 is approximately 10%, yielding a refractive index difference of +1.2% with the substrate. No other dopants are used in the fabrication of the thin films. The optical absorption spectra were measured with a CARY 3 double beam spectrophotometer spanning the wavelength range from 190 to 900 nm, with 1 nm resolution and 0.05 dB accuracy. Under these conditions, the absorption of the as-deposited silica films is too small to detect, except for a small absorption increase of about 3 dB/mm observed between 190 and 195 nm [see Fig. 1(a)].

To evaluate the photosensitivity of this material, we irradiated the thin film using ultraviolet (UV) light from an excimer laser operating at 50 pulses/s with either KrF or ArF gas mixtures. The KrF laser emits pulses with an intensity of 400 mJ/cm^2 at a wavelength of 248 nm, whereas the ArF laser emits 40 mJ/cm^2 pulses at 193 nm. After exposing the thin film for 5 min to 248 nm light (6.0 kJ/cm^2 total UV dose), no change could be detected in the absorption spectrum. In contrast, irradiation for 30 min with 193 nm light (UV dose of 3.6 kJ/cm^2) creates a wide absorption band peaking near 260 nm [see Fig. 1(b)]. However, the magnitude of the induced absorption is quite small in comparison to that obtained in typical photosensitive materials,[12,16] and we do not expect the photoinduced index changes to be larger than $\sim10^{-5}$.[16] In view of these results, we applied the two photosensitization techniques—flame brushing[17] and hydrogen loading,[18] which have been used to enhance the photosensitivity in Ge-doped silica.

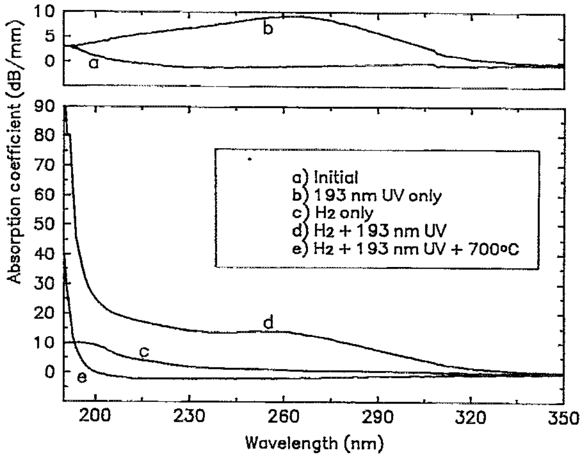

FIG. 1. Optical absorption spectra of phosphorus-doped silica thin films exposed to 193 nm UV light, showing the absorption changes that occur with and without hydrogen loading, and also the effect of annealing.

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[a] On leave from NTT Opto-Electronics Laboratories.

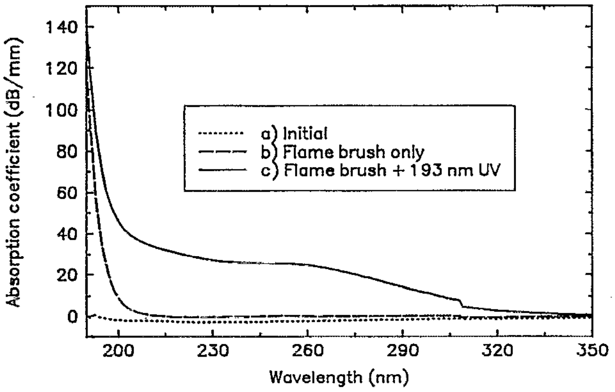

FIG. 2. Optical absorption spectra of phosphorus-doped silica thin films following flame brush photosensitization and exposure to 193 nm UV light.

In the case of hydrogen loading, the P_2O_5:SiO_2 thin film is placed in a pressure vessel with 75 atm of hydrogen gas at room temperature. Assuming that the diffusivity of molecular hydrogen is close to that of pure silica (i.e., ~10 $\mu m^2/h$) and using a solubility of 1.2 mol % H_2/100 atm, the average concentration of molecular hydrogen dissolved in the 30 μm doped layer is about 0.7 mol % after 11 days in the vessel.[18] When the silica film is taken out of the hydrogen, the absorption spectrum shows an increase of ~10 dB/mm at wavelengths below 220 nm [Fig. 1(c)]. The sample is then irradiated with the same incident ArF laser dose as above (3.6 kJ/cm^2), and the spectrum of optical absorption remeasured [Fig. 1(d)]. A broad absorption band is induced at wavelengths shorter than 350 nm; the peak of the induced absorption is in the vacuum UV and exceeds 100 dB/mm. Absorption changes of this magnitude indicate that significant refractive index changes should be observed at longer wavelengths.[16]

In the case of flame brushing, the P_2O_5:SiO_2 film is kept in the flame of an oxygen-hydrogen burner for several minutes at a maximum temperature below 1600 °C. Following the flame brush treatment, the absorption at short UV wavelengths increases sharply, as shown in Fig. 2(b). The increase is attributed to a reduced form of P_2O_5, created by the reaction of hydrogen in the flame with weakly bonded oxygen atoms in the glass. This hypothesis based on two previous results: (1) the absorption band induced by the flame brush in Ge-doped silica coincides with the 242 nm oxygen defect (or reduced GeO_2) band, and result in strong photosensitivity under 248 nm irradiation,[17] (2) the similitude of the induced spectrum with that of P-doped silica heated in a reducing hydrogen atmosphere, where a band peaking at 176 nm has been observed.[19] In Fig. 2(b), we see that there is still negligible absorption near 248 nm but more than 60% of the incident light at 193 nm will be absorbed in the 30 μm thick doped layer. Therefore, we exposed the flame brushed P-doped silica to 3.6 kJ/cm^2 of ArF laser light at 50 pps, using the same exposure conditions as in the two cases above. The final absorption spectrum shown in Fig. 2(c) has features similar to that obtained in the hydrogen loading case, but the magnitude of the absorption is higher by a factor of about 2. The difference is likely due to a higher reacted hydrogen concentration in the glass from flame brushing than from our hydrogen loading conditions. Note that it is possible to dissolve several mol % of hydrogen with higher pressures and longer loading periods than was used in our experiments.[18] In order to measure the amount of hydrogen introduced in the glass, we carried out a composition analysis of the films at various stages of the processes described above using Elastic Recoil Detection over the topmost 1000 nm of the films.[20] The results indicate a concentration of 0.6±0.2 mol % of atomic hydrogen (relative to SiO_2) in hydrogen loaded films after UV exposure, and also after annealing to 700 °C, indicating that this dose of UV light induced a permanent reaction to fix about one half of the dissolved hydrogen atoms into the glass. In the flame brushed sample however, the hydrogen concentration attained is 7.0±0.4 mol %, confirming the efficiency of this method to diffuse and fix hydrogen in the silica in a matter of minutes.

As far as using the KrF laser to photoinduce index changes, we note that no absorption is generated at 248 nm by either of the two sensitization methods. This lack of absorption does not preclude a photosensitivity enhancement since hydrogen loaded Ge-doped silica reacts strongly to 248 nm light without apparent initial absorption at that wavelength.[12] Consequently, we exposed hydrogen loaded P-doped silica with over 130 kJ/cm^2 of 248 nm light from the KrF laser. The absorption changes resulting from such exposure were less than 3 dB/mm. There is only one case where KrF laser irradiation changes the absorption properties of a P-doped silica film: it is when the film has been preirradiated at 193 nm to photoinduced an absorption at 248 nm. In this case, KrF laser light partially bleaches the absorption at wavelengths surrounding 248 nm. In fact, the broad absorption band extending from 200 to 300 nm can be generated and erased by successive irradiations with light at 193 and 248 nm, respectively.

The photosensitive behavior at 193 nm was verified by writing Bragg reflection gratings in single mode P-doped silica channel waveguides fabricated using flame hydrolysis and reactive ion etching.[15] The channels have a 7×7 μm core with an index difference of 0.3% with the silica cladding. The waveguides were either flame brushed or hydrogen loaded and then exposed to 193 nm radiation through a zero-order nulled phase mask with a grating period of 1.06 μm.[21] Figure 3 shows the transmission spectrum of a 6-mm long grating written in a waveguide which had been hydrogen loaded for 5 days at 110 atm and irradiated for 5 min at 50 pulses/s with pulses of 160 mJ/cm^2. A Bragg reflection of 95% with a bandwidth of 0.27 nm is observed at a wavelength of 1534 nm, which is in good agreement with theoretical calculations of a Bragg reflector with a refractive index modulation of 2×10^{-4}. The broader peak at shorter wavelengths is attributed to mode coupling from the core to the cladding caused by the grating. This peak is absent in the reflection spectrum. Similar results of photoimprinted Bragg gratings were achieved using flame brushing photosensitization.

The thermal stability of the photoinduced changes was examined by measuring the decrease in reflectivity and in-

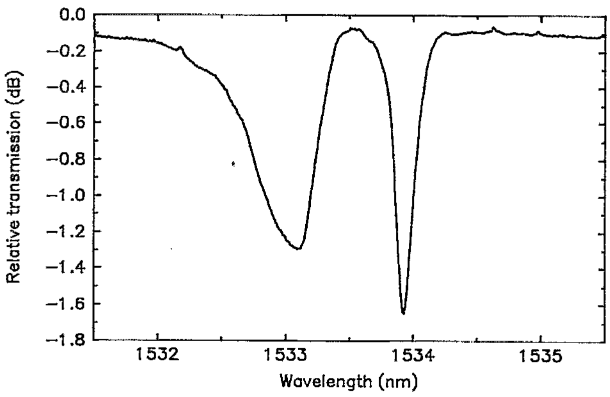

FIG. 3. Transmission spectrum of a Bragg grating photoinduced by ArF laser light in a hydrogen loaded phosphorus-doped channel waveguide.

duced absorption during annealing of a Bragg grating for 30 min time intervals at increasing temperatures from 100 to 700 °C, simultaneously with the thin-film sample whose spectrum is shown in Fig. 1(d). No decrease in the photoinduced index change is observed at 100 °C, but gradual erasure of both index change and absorption occurs at higher temperatures [Figs. 1(e) and (4)]. The origin of this gradual erasure of the refractive index grating is not known but we observe that the tail of the vacuum UV absorption band, measured at 193 nm, decreases at the same rate as the index change. This result indicates that index change and vacuum UV absorption are linked through at Kramers–Kronig relationship. We also note that the ERD results show that the hydrogen content of the glass does not decrease after annealing. However, attempts to recreate the absorption bands with 193 nm light irradiation of the annealed samples were unsuccessful.

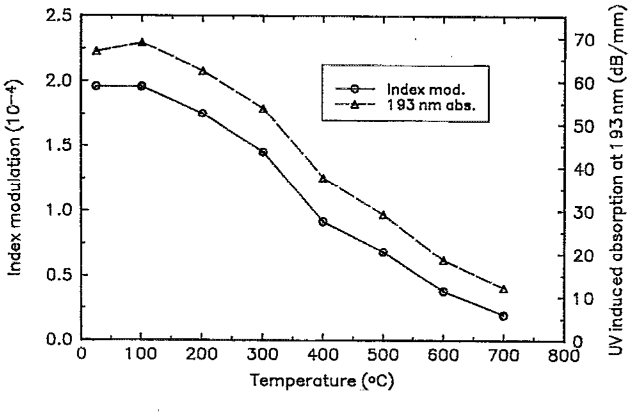

FIG. 4. Thermal erasure of the photoinduced refractive index change in a channel waveguide Bragg grating, and of the induced absorption measured at 193 nm in a planar thin-film sample. Annealing is performed for 30 min at each temperature.

In conclusion, we have demonstrated photosensitivity in phosphorus-doped (germanium free) silica using 193 nm light from an ArF excimer laser, but only after treating the glass with an oxygen-hydrogen flame or exposing the glass for a prolonged time to hydrogen gas at high pressure and ambient temperature. Furthermore, narrow band Bragg gratings with more than 90% reflectivity have been written in P-doped silica channel waveguides. These advances have led to the first demonstration of a single mode planar glass waveguide laser with photoinduced Bragg reflectors, fabricated from erbium co-doped, phosphorus-doped silica.[22] In contrast, we have seen little evidence of photosensitivity in treated or untreated P-doped silica glass with 248 nm light irradiation.

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