Photoinduced optical absorption and 400-nm luminescence in low-germanium-content optical fiber preforms irradiated with ArF and KrF excimer-laser light

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The optical absorption spectrum and the 400-nm photoluminescence (PL) of a 1.4-mol.% Ge photosensitive optical fiber preform subjected to high fluence of 193-nm ArF and 248-nm KrF excimer-laser irradiation are measured. The largest absorption increases occur near 200 nm in both cases, but a small net bleaching of absorption is obtained near the laser wavelength for KrF irradiations. The blue PL decreases during ArF exposure but increases with the KrF laser. In similarly excited 9-mol.% Ge fiber preforms the blue PL always decreases. A study of the PL intensity as a function of irradiating laser light intensity shows no evidence of multiple photon absorption effects.

One- and two-photon absorption effects were recently observed in the photosensitive behavior of 8- and 3-mol.% Ge optical fibers, respectively,[1] when the fibers were exposed to 193-nm (6.4-eV) ArF excimer laser light. In the fiber with the higher doping, the refractive-index growth is well explained by one-photon absorption into a 200-nm absorption band associated with Ge oxygen-deficient centers (GODC's),[2] a situation strictly similar to that of conventional photosensitivity with irradiation wavelengths near 242 nm to bleach another GODC band.[3] These GODC's are known to be related to photoluminescence (PL) bands at 3.1 eV (400 nm) and 4.3 eV (290 nm).[4,5] The former, hereafter referred to as the blue band, has been the subject of numerous papers, the purpose of most of which was to shed light on the various proposed physical models for the GODC's and by extension on the photosensitivity of Ge-doped silica.[6–10] In fibers with only 3-mol.% Ge, however, it was shown that, whereas in-band bleaching at 248 nm leads to relatively small photoinduced index changes, irradiating the fiber at 193 nm increases the index changes by at least an order of magnitude in spite of the fact that the glass is more transparent at that wavelength.[1,2] In Ref. 1 it was demonstrated that this phenomenon is due to two-photon absorption into the band gap of silica (9 eV) followed by trapping of excited species by defects associated with the presence of Ge.

Here we investigate whether such Ge-concentration-dependent behavior could be observed in the VUV–UV absorption and PL spectra of optical fiber preforms irradiated with ArF (193-nm) and KrF (248-nm) excimer lasers.

Two types of sample were studied: the low-Ge-content samples all came from the same 12-mm-diameter preform with a 2.4-mm-diameter core doped with 1.4 mol.% Ge. The high-Ge-content samples were also disks obtained from a 12-mm-diameter fiber preform with a 400-μm-diameter core doped with 9-mol.% Ge. We exposed the preforms during the PL experiments by illuminating through a lens a 250-μm-diameter pinhole with 193-nm (ArF) or 248-nm (KrF) excimer-laser light and then imaging this pinhole onto the preform disk core. By varying the distance between the lens and the pinhole, we obtained laser fluences ranging from 10 to 700 (mJ/cm^2)/pulse. The exposures carried out between absorption measurements were done in a similar way. The PL signal was collected in parallel, the laser repetition rate was kept constant at 20 pulses/s, and all experiments were carried out at room temperature.

Figure 1(a) shows the absorption coefficient spectrum of the low-Ge-content fiber preform at various stages of exposure to the ArF laser, which reveals a continuous increase in absorption as the exposure progresses. The end result is depicted in the inset of Fig. 1(a), which shows the induced absorption coefficient that was obtained by subtraction of the unirradiated material spectrum from the one measured after the final exposure. Immediately apparent is the

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induced band near 200 nm. This band has been related to Ge E′ centers,[11] and it was recently observed that such centers can be produced in SiO_2:GeO_2 glasses from the conversion of precursors induced by two-photon absorption of ArF, KrF, and XeCl excimer light.[12] Given the high laser fluences needed for the absorption changes measured here, we can conjecture that we are observing a similar phenomenon.

Figure 1(b) is the equivalent of Fig. 1(a) but for exposure with the KrF laser. Here we also observe an overall increase in absorption as the exposure progresses, and again the inset shows an induced absorption band near 200 nm. What is noteworthy here is that the two spectra are quite similar, the only difference being that the absorption change is negative near the laser wavelength in the KrF case (where GODC's are reported to have an absorption band, as discussed above). Although the same measurements could not be carried out in the high-Ge preform because of the smallness of the core, previous research with similar material with high-GODC initial concentrations yielded results qualitatively similar to those observed here: The overall absorption increases throughout the UV, with a 242-nm spectral notch (under ArF irradiation) or net bleaching (with KrF).[2]

Figure 2 shows the behavior of the blue PL band during prolonged exposure to ArF UV photons for both the high-Ge-content and the low-Ge-content preforms [Figs. 2(a) and 2(b), respectively]. We observe that in both cases the integrated intensity of the blue band diminishes (in spite of the fact that the UV absorption increases at the irradiation wavelength for this delivered energy interval). Because the refractive indices of such materials increase with UV radiation, the decrease in PL agrees with that in models in which the photodestruction of blue-emitting GODC's from UV irradiation leads to a rise in refractive index.[6–10] On closer examination of Fig. 1(a), we can associate the decrease in blue PL with the decrease of an individual 242-nm GODC band against a rising background of VUV–UV absorption. Unfortunately this model breaks down when a similar experiment is carried out with KrF laser light: Figure 3 shows that the blue PL band decreases in the high-Ge-content preform but increases in the low-Ge preform when Fig. 1(b) shows that the absorption decreases at the irradiation wavelength. This result provides further evidence that the blue PL is not uniquely related to the 242-nm GODC absorption band: It could arise from other precursors, there could be a recombination channel competing with the one supplying the electrons to the high-energy level of the 400-nm PL transition, or both situations could exist. This channel could become more or less prevalent, depending on the energy and density of the incident photons and on the Ge doping level. However, the similarity in the evolution of the absorption spectra during irradiation, as seen in the insets of Fig. 1, does not help in elucidating the difference between the ArF- and the KrF-excited PL, and more spectroscopy may be required.

In an attempt to elucidate further the phenomena involved, we investigated the dependence of the blue PL band of the low-Ge-content sample on the inten-

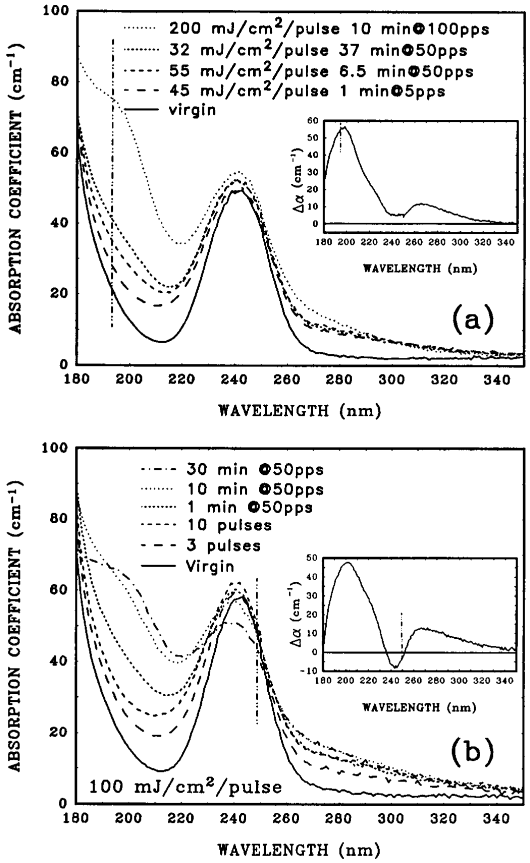

Fig. 1. Absorption coefficient spectrum versus wavelength for the low-Ge-content (1.4-mol. %) fiber preforms at various stages of excimer UV light exposure for (a) ArF (193 nm, 6.4 eV) photons and (b) KrF (248 nm, 5.0 eV) photons. In both cases the laser energy is represented by a vertical dotted–dashed line and the inset depicts the induced absorption coefficient, i.e., it is obtained by subtracting the virgin material spectrum (bottommost at 200 nm) from the spectrum taken after the ultimate exposure (topmost at 200 nm). The exposure duration, laser repetition rate, and laser fluence are indicated. pps, Pulses per second.

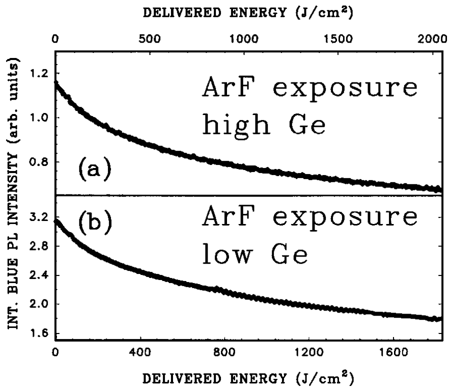

Fig. 2. Integrated PL intensity of the blue band (400 nm) versus the accumulated energy delivered to the preform core by ArF photons for (a) the high-Ge-content preform (9 mol. %) where each data point was accumulated over 1.6 s at a 92-(mJ/cm^2)/pulse and (b) the low-Ge-content (1.4 mol. %) one where each data point was accumulated over 1 s at a-76 (mJ/cm^2)/pulse fluence.

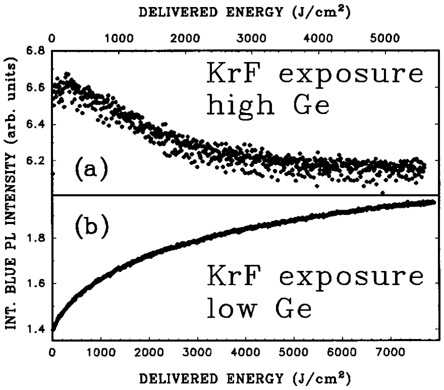

Fig. 3. Integrated PL intensity of the blue band (400 nm) versus the accumulated energy delivered to the preform core by KrF photons for (a) the high-Ge-content preform where each data point was accumulated over 3 s at a 133-(mJ/cm^2)/pulse fluence and (b) the low-Ge-content one where each data point was accumulated over 4 s at a 141-(mJ/cm^2)/pulse fluence.

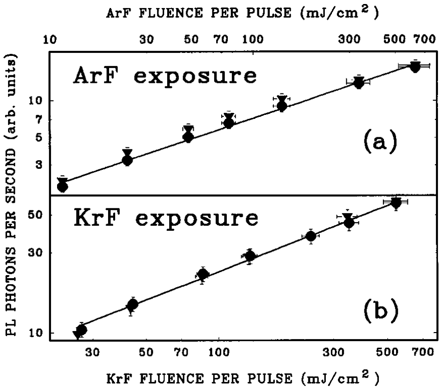

Fig. 4. Temporal yield of PL photons stemming from the low-Ge preform versus the excimer-laser fluence for ArF and KrF photons. In both cases two data sets appear. We obtained the case represented by the circles and the solid lines by successively increasing the laser fluence, and the other, represented by the triangles, by successively decreasing the laser fluence. Each data point is the result of accumulating the PL generated by the laser operating at 20 pulses/s for a few seconds and then normalizing to time. The slopes of the fitted regressions are all ~0.6.

sity of the irradiating light. The goal was to determine whether multiphoton effects were involved and related to Ge content, as was observed in the refractive-index growth rate in fibers.[1] The result is shown in Fig. 4. Each data point on this graph is the result of a short exposure (1–4 s), and consequently the cumulative UV exposure is low. Hence one would expect the data sets taken with increasing light intensity to overlap those taken with decreasing intensity, and within the error bars that is what we observed. A linear regression on all data points yielded an expression of the form $I_{\mathrm{PL}} = C(I_{\mathrm{excimer}})^{0.6}$ for the rate of PL light generation as a function of laser pulse energy density. Although it is not shown here, the same result was obtained for the high-Ge-content preform. These numbers differ from the values obtained from index growth measurements under ArF excitation[1] where a clear two-photon signature was observed for a 3-mol. % Ge fiber exposed under similar conditions. Furthermore, the similarity of the PL dependence on laser intensity for ArF and KrF irradiations is difficult to reconcile with the results of Figs. 2(b) and 3(b). However, we can say quite clearly that the PL is not due to a two-photon absorption effect and suggest that we are dealing with PL generated by single-photon absorption impaired in some way, perhaps by a dependence on the excitation density or by concentration quenching, as was observed previously.[13,14]

In conclusion, we have found that modifying the absorption spectra of low-Ge-content preforms requires high fluences of excimer-laser light and that the only difference between the KrF- and ArF-induced optical absorption spectra is a net resonant bleaching at the KrF laser wavelength. Also, we found no obviously simple relationship in the laser intensity dependence and rates of change between the blue PL and the two other most commonly used measurands of photosensitive behavior: refractive-index change and optical absorption. The model in which photodestruction of blue emitting centers is uniquely associated with index increases is also put in doubt by some of the results shown here. Finally, no evidence of a two-photon absorption effect was observed in the blue PL intensity, by contrast with refractive-index growth rates in 3-mol. % Ge fibers.

References

1. J. Albert, B. Malo, K. O. Hill, F. Bilodeau, D. C. Johnson, and S. Thériault, Appl. Phys. Lett. **67,** 3529 (1995).
2. J. Albert, B. Malo, F. Bilodeau, D. C. Johnson, K. O. Hill, Y. Hibino, and M. Kawachi, Opt. Lett. **19,** 387 (1994).
3. G. Meltz, W. W. Morey, and W. H. Glenn, Opt. Lett. **14,** 823 (1989).
4. L. N. Skuja, A. N. Trukhin, and A. E. Plaudis, Phys. Status Solidi **84,** K153 (1984).
5. M. Kohketsu, K. Awazu, H. Kawazoe, and M. Yamane, Jpn. J. Appl. Phys. **28,** 622 (1989).
6. M. Gallagher and U. Osterberg, J. Appl. Phys. **74,** 2771 (1993).
7. Y. Duval, R. Kashyap, S. Fleming, and F. Ouellette, Appl. Phys. Lett. **61,** 2955 (1992).
8. V. Mizrahi and R. M. Atkins, Electron. Lett. **28,** 2210 (1992).
9. H. Patrick, S. L. Gilbert, and A. Lidgard, Opt. Mater. **3,** 209 (1994).
10. E. M. Dianov and D. S. Starodubov, Opt. Lett. **21,** 635 (1996).
11. V. B. Neustruev, J. Phys. **6,** 6901 (1994).
12. H. Hosono, H. Kawazoe, and J. Nishii, Phys. Rev. B **53,** R11921 (1996).
13. D. Y. Stepanov, F. Ouellette, and G. R. Atkins, Electron. Lett. **29,** 1975 (1993).
14. V. N. Bragratashvili, S. I. Tsypina, P. V. Chernov, A. O. Rybaltovskii, Y. S. Zavorotny, S. S. Alimpiev, Y. O. Simanovskii, L. Dong, and P. St. J. Russell, Appl. Phys. Let. **68,** 1616 (1996).