Correlation between oxygen-deficient center concentration and KrF excimer laser induced defects in thermally annealed Ge-doped optical fiber preforms

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Abstract

The amplitude of the 5 eV optical absorption band of oxygen-deficient germanium-doped silica samples ($3GeO_2$:$97SiO_2$) was varied by annealing in oxygen at 1000°C for different periods of time. Each sample was irradiated with the same dose of 5 eV light from a KrF excimer laser to study the effect of the absorption band amplitude on the photo-induced changes. ESR (Electron spin resonance) and optical absorption measurements were carried out after each annealing and each laser irradiation cycle. We find that samples with an initially higher 5 eV absorption band amplitude exhibit a larger increase in the absorption bands related to the photo-induced paramagnetic Ge E′ and GEC (Germanium Electron Center) when irradiated with the same laser dose. Deconvolution of the measured spectra shows that the concentrations of the photo-induced paramagnetic Ge E′ and GEC defects are well correlated with the concentration of GLPC (germanium lone pair center) defects associated with a 5.14 eV absorption band. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The presence of an intense absorption band around 5 eV in as-prepared GeO_2 glasses was first reported by Garino-Canina [1] and Cohen and Smith [2] in 1958. Since then, the properties and behaviour of this band, which is known to be due to oxygen-deficient centers, have been examined by several groups [3–7]. The elucidation of the nature of these oxygen-deficient centers (ODC) in germanosilicate glass has aroused considerable interest because of the currently expanding uses of the non-linear properties of these materials in optical fibre devices and instruments. Tsai et al. [8] found a close correlation between the conversion efficiency of second harmonic generation and the laser induced Ge E′ center concentration. Simmons et al. [9] demonstrated a similar correlation response for the generation of Ge E′ centers and the formation of the photosensitive grating effect in germanium-doped silica glass fibres. Dong et al. [10] found that an index change up to 10^{-4} in the

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infrared can be explained mostly by the bleaching of the band at 5 eV and the growth of the strong band at 6.35 eV related to Ge E′ centers concentration. Since it has been found that the absorption band centered at 5 eV in as-prepared SiO_2:GeO_2 glasses is due to GODC (germanium oxygen deficient centers) and is composed of two different components [3], no further work to our knowledge, has been done to elucidate the exact transformation process of each of the two components following UV irradiation with relation to the starting amplitude of the 5 eV band. It has been reported that the first component has a peak at 5.06 eV and a FWHM (full width at half-maximum) of 0.38 eV, and is known to result from a NOMV (neutral oxygen mono-vacancy) [3]. This defect is bleachable by illumination with UV light which in turn generates Ge E′ centers. A second component peaking at 5.16 eV with a FWHM of 0.48 eV is reported by Hosono et al. [3] to be due to two-coordinated Ge. Recently Tsai et al. [11] demonstrated that the 5.16 eV band is not related to two-coordinated Ge defects but that it is a divacancy oxygen deficiency center associated with Ge, also designated as a GLPC. In the past, this last band was not found to be bleached when irradiated with 5 eV light but it emits luminescence bands at 3.2 (intense) and 4.3 eV (weak) [3]. Recently, however, Crivelli et al. [12] demonstrated that both components of the 5 eV absorption band are partially bleached following UV irradiation.

In summary the photo-induced changes in the ultraviolet absorption bands of SiO_2:GeO_2 glasses are one among the sources of photosensitivity of this material [10], and the bleaching of the 5 eV band is associated with the growth of several other bands [3,6,12–15] and can lead to positive refractive index changes [10]. More specifically the photo-bleaching of the 5.06 and 5.14 eV absorption bands is accompanied by the appearance of absorption bands at 4.6 eV (270 nm), 5.8 eV (213 nm) and 6.4 eV (190 nm) [15,16]. In the literature, the 4.6 and 5.8 eV bands are linked to the creation of electron trapped centers associated with fourfold co-ordinated Ge ions (GEC) [17,18] while the 6.4 eV band is attributed to the creation of germanium paramagnetic E′-centers Ge E′ (Three oxygen bonded to germanium having an unpaired electron) [15]. It has been reported that the GECs are induced in Ge-doped silica by UV photons from ArF, KrF, or XeCl excimer lasers through a two-photon process [13,15,19]. The GEC are then converted to the Ge E′ centers through prolonged UV irradiation [14,20].

In this study we vary the initial intensity of the 5 eV band by annealing in O_2 atmosphere and correlate the contribution of the different components of this band to the creation of other centers associated with photosensitivity of the Ge-doped silica when exposed to UV light. The samples were annealed at 1000°C in an oxygen atmosphere for different periods of time. All the samples were then irradiated with the same dose of KrF laser light in order to establish a relationship between their photosensitive response and different starting intensities of the 5 eV band. The behaviour of the 5.14 eV absorption band under UV illumination is reported. We find a relation between the initial intensity of the GLPC (5.14 eV) band and the concentration of UV-induced optical absorption defects created at higher and lower photon energies. We also propose an explanation of the photo-conversion process of the defects associated to the 5.14 eV band to other different absorption bands sensitive to ESR spectroscopy in relation to the starting 5 eV band amplitude.

2. Experimental

The samples used were optically polished glass plates 0.5 mm thick, cut from a germania-silicate glass rod prepared by the vapour phase axial deposition method. Their nominal chemical composition is 97SiO_2:3GeO_2 in mol%. Annealing was performed in a controlled atmosphere furnace at a temperature of 1000°C under a continuous flow of oxygen at atmospheric pressure at 1 cm^3 per min. The optical absorption measurements in the 190–400 nm wavelength range were carried out using a UV-visible spectrophotometer. Irradiation of the samples was conducted with an excimer laser producing 20 ns pulses at 20 Hz with pulse energies at 248 nm (KrF) of 150 mJ/cm^2. ESR studies were conducted to evaluate the presence and development of paramagnetic structural defects in the

material. Spin concentrations were determined by double numerical integration of the first derivative spectra, and by comparison with the signal from a standard strong pitch composed of 0.11% pitch in KCl provided by the Bruker Company [21].

3. Results

5 samples cut from the same rod, were annealed for 4, 8, 42 h, 7 and 11 days, respectively. Fig. 1 shows the difference absorption spectra obtained after subtraction of the unannealed spectrum from each spectrum of the different annealed samples which are shown in the inset of the figure. The negative intensities represent an amount of absorption removed by the annealing treatment. A shift to higher energies of the position of the bands removed by annealing in oxygen can be observed, indicating that the absorption band around 5 eV is composed of two different components for which the annealing rate is different. The inset of Fig. 1
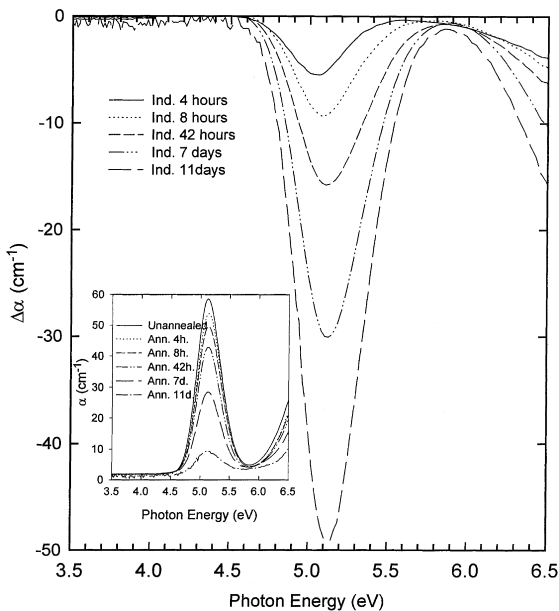
shows the gradual decrease of the 5 eV absorption band and a decrease of the tail of an absorption band around 6.5 eV, as the annealing time is increased. The 5 eV band is almost completely bleached after an annealing time of 11 days. The induced absorption spectrum was fitted with two Gaussians. The fitted result obtained after an annealing time of 42 h, shown in Fig. 2 confirms the presence of absorption bands at 5.06 eV and the 5.14 eV as listed in the literature [3,4]. The NOMV (5.06 eV) band is bleached first since after 4 h, the difference spectrum can be fitted by a single Gaussian centered at 5.06 eV (see the inset of Fig. 2). As the annealing time increases, a new Gaussian at 5.14 eV is needed to fit the difference spectra. The intensity of the removed 5.06 eV component ($\sim$5.5 cm^{-1}) is the same as that removed after 4 h, suggesting that the whole band is

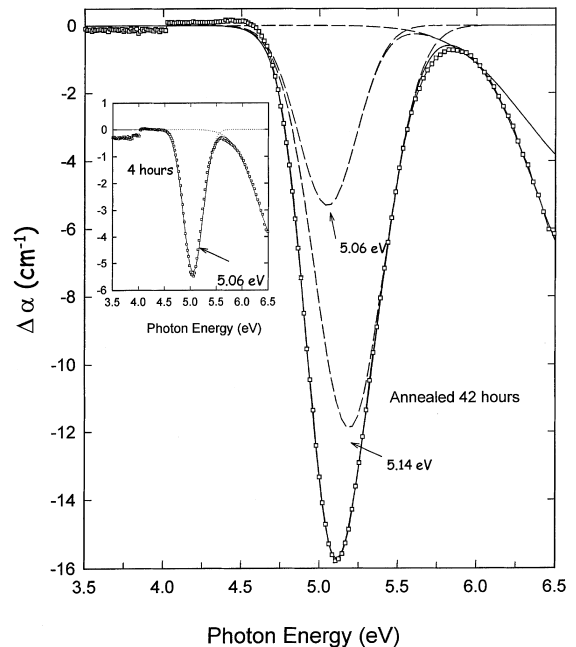Fig. 1. Induced absorption spectra of $3GeO_2$:$97SiO_2$ glasses after annealing at 1000°C under a continuous flow of oxygen for 4, 8, 42 h, 7 and 11 days. The absorption spectrum of the unannealed sample is subtracted from those of the annealed samples which are shown in the inset.

Fig. 2. Deconvolution of the induced absorption spectrum following annealing of the $3GeO_2$:$97SiO_2$ glasses for 42 h. Two absorption bands at 5.06 and 5.14 eV are necessary to fit the spectrum. The inset shows the fitted result of the induced absorption spectrum after 4 h of thermal annealing. Only the 5.06 eV band is needed to fit the spectrum in this case. Open squares denotes the experimental data, solid lines are the fitted result and the dashed lines denote the separate Gaussian components.

removed in the first few hours of the treatment. This value of the 5.06 eV absorption coefficient stays unchanged in the deconvolution of the other spectra obtained for annealing times of 7 and 11 days since it has completely disappeared during the first hours of annealing.

Each sample was then irradiated with the same dose of 2 kJ/cm^2 from a 5 eV KrF laser light. We show in Fig. 3 the spectra of absorption changes induced by the UV irradiation of each sample. The spectra are obtained by subtracting the absorption measured after annealing from the absorption measured after irradiation. We can clearly observe a difference in the intensities of the UV-induced absorption bands between the samples annealed for different durations. Deconvolution of these spectra gives four spectral components of Gaussian shape: Three around 4.6, 5.8 and 6.4 eV are positive and another one at 5.14 eV is negative (see Fig. 4). The FWHM of each band has been fixed according to their values given in the literature [3,15]. The relative error is estimated from the program used to fit the difference spectra. The values of the centers and widths of the different absorption bands stay unchanged for all the deconvoluted spectra from different annealed and laser irradiated samples. Therefore we assume that the peak amplitudes are a good measure of the evolution of defects.
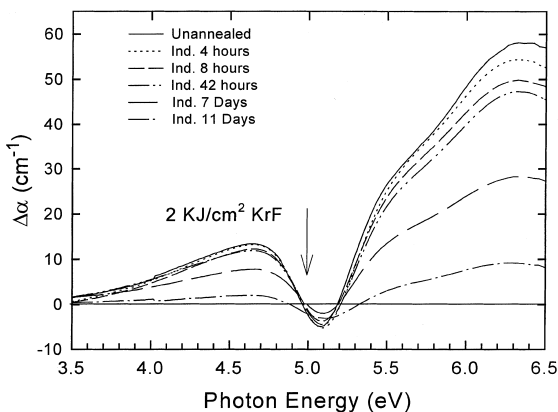

Fig. 4. Deconvolution of the induced absorption spectrum measured after 42 h of annealing and irradiation with 2 kJ/cm^2 KrF laser light. Open squares denote the experimental data, solid lines are the fitted result and the dashed lines denote the separate Gaussian components.

Fig. 5 shows a linear relationship between the ESR measured concentration of the Ge E′ centers and the intensity of the 6.4 eV band induced by the KrF irradiation after different annealing periods indicating a good correlation between them. A starting value of ~18 cm^{-1} which correspond to a zero concentration of Ge E′ is due partly to the lack of sensitivity of the ESR spectrometer to the detection of the weak

Fig. 3. Induced absorption coefficient spectra following 2 KJ/cm^2 of KrF irradiated unannealed and annealed 3GeO$_2$:97SiO$_2$ glasses for different periods of time. Each spectrum results from the difference of that obtained after irradiation to that before irradiation.
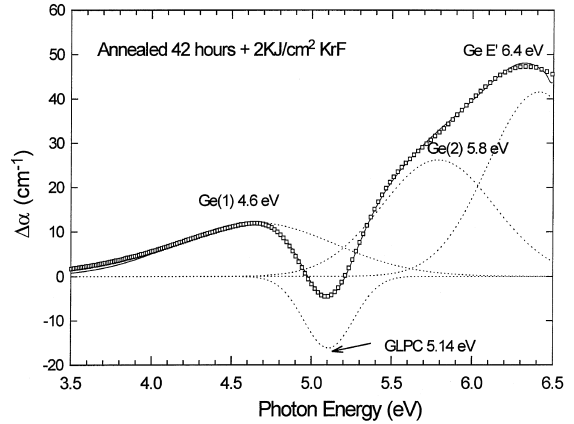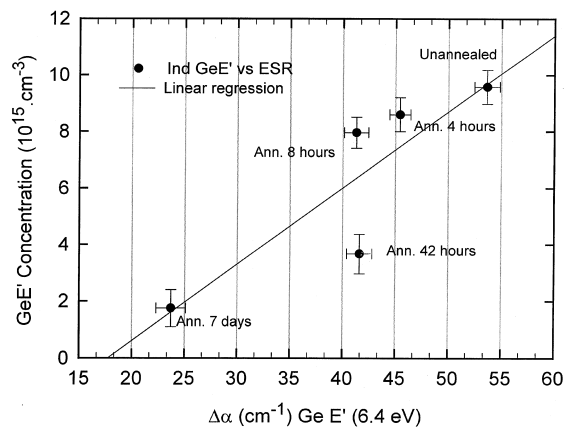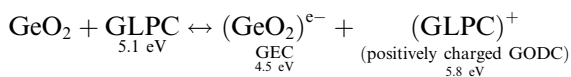

Fig. 5. Correlation between the concentration of Ge E′ centers measured by ESR spectroscopy and the change of the absorption coefficient at 6.4 eV under KrF laser illumination of different annealed samples.

concentration of Ge E′ paramagnetic centers present in the samples before irradiation and partly to the presence of a small absorption shoulder (20 cm^{-1}) around 6.4 eV in the unannealed and annealed samples before UV irradiation (see the inset of Fig. 1). The relative error of the ESR signal intensity is specified in the Bruker ESP 300 E machine manual and is within ±10% for an optimum used microwave power of 50 μW. Nishii et al. [22] found that as the concentration of Ge E′ increases resulting in an increase in absorption around 6.4 eV, another contribution to the growth of the absorption band at 6.4 eV also exists but it does not have an ESR signature. In the following, we consider the deconvoluted 6.4 eV optical absorption to be representative of the concentration of Ge E′ centers.

4. Discussion

The assignment of the absorption bands at 4.6 and 5.8 eV has been discussed in several papers [17–19]. In Refs. [17,18], the two absorption bands are found to have a similar defect origin in the form of an electron trapping center associated with fourfold co-ordinated Ge ions (GEC). The two bands would reflect two types of GECs, (Ge(1) and Ge(2) respectively, (differentiated by the number of Ge atoms in the next nearest-neighbor positions). Recently, Nishii et al. proposed that UV-induced GECs can originate from bridging oxygens by two photon absorption [20], a process which would also yield a self-trapped hole. On the other hand, Fujimaki et al. [19] found that a clear proportionality exists between the generation of paramagnetic centers [(Ge(1) and Ge(2)], the decrease of the 5.1 eV absorption, and the increase of the 4.5 eV and 5.8 eV absorption bands. They speculate that Ge(1) and Ge(2) are assigned to a single form of GEC and to a positively charged GODC (GLPC)$^+$, respectively. The mechanism of the absorption change is expressed in Ref. [19] as follows:

$$\text{GeO}_2 + \underset{\substack{\text{5.1 eV}}}{\text{GLPC}} \leftrightarrow \underset{\substack{\text{GEC} \\ \text{4.5 eV}}}{(\text{GeO}_2)^{e-}} + \underset{\substack{\text{(positively charged GODC)} \\ \text{5.8 eV}}}{(\text{GLPC})^+}$$

We must add that in Ref. [13], the precursor for the UV-induced GEC is identified as a GODC absorbing at 5.1 eV, without definite assignement of the band to either NOMV or GLPC.

Our results, shown in Fig. 6, indicate that both GEC bands and the Ge E′ band increase linearly in proportion to the amount of bleaching of the GLPC optical band. This occurs in samples for which there is no longer a contribution to the optical absorption from NOMV centers which have been annealed out in the first 4 h of treatment. This allows us to isolate the two-photon regime proposed by Nishii in Ref. [20] by eliminating the contribution of NOMV to defect generation in our samples. Therefore it appears that any model of the KrF excimer laser-induced generation of GECs must include the GLPC as a precursor and the simultaneous generation of Ge E′ centers.

In similar experiments, but with hydrogen-loaded samples, Awazu et al. [7] proposed that the GLPC transforms into the Ge E′ center under UV illumination and that the photochemical change from the GLPC to the Ge E′ center is related to the presence of hydrogen molecules dissolved in the glass. They found a one-to-one correlation in the concentrations of GLPC and Ge E′ centers generated. Since that the concentration of hydrogen molecules trapped in our as-received preforms is
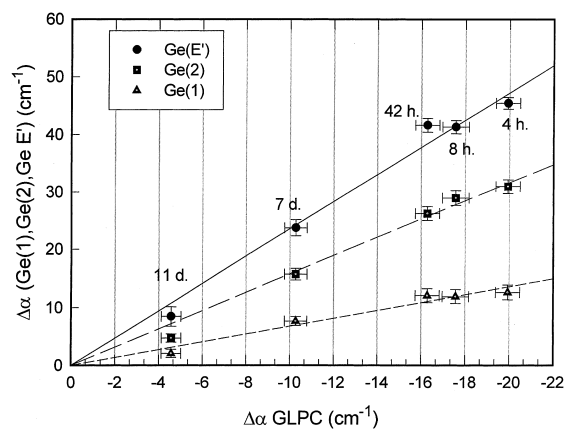

Fig. 6. Correlation between the bleaching of the GLPC (5.14 eV) and the growth of the Ge(1)(4.6 eV), Ge(2)(5.8 eV) and Ge E′ (6.4 eV) absorption bands at the same dose of laser irradiation of samples annealed for different periods of time.

very low compared to the H_2 loaded one (2% of H_2 molecules in [7]), we suggest that a transformation of the GLPC to Ge E′ through a reaction involving hydrogen cannot be invoked to explain our results.

The linear relationship observed on Fig. 6 between the decrease of GLPC (5.14 eV) and the increase of both GEC bands (4.6 and 5.8 eV) and of the Ge E′ absorption band requires the interpretation of the GLPC as the precursor to all these defects. This is difficult to imagine without resorting to an intermediate stage in which the GLPC first transforms into a NOMV, and then into a Ge E′ free electron pair, the free electron being captured at fourfold coordinated germanium sites to form a GEC. Since this requires the breaking of network bonds, a two-photon process must be involved. The whole transformation process is shown schematically in Fig. 7. We must point out that in our experimental conditions we could not find evidence for the transformation of GECs into Ge E′-non-bridging oxygen pairs observed in Ref. [20] upon prolonged irradiation with excimer laser light.

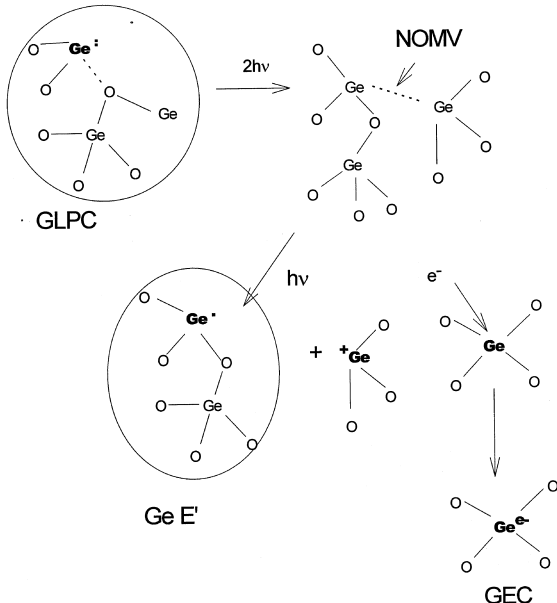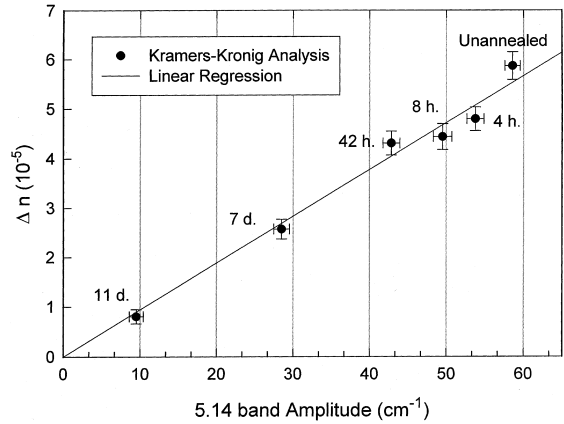Finally, the large positive induced UV absorption observed in our results is expected to corres-

Fig. 8. Estimated UV-induced refractive index change calculated from a Kramer–Kronig analysis of the deconvoluted data from different annealed samples irradiated with the same dose of KrF laser.

pond to a large induced Δn according to Kramer–Kronig relationship. Fig. 8 shows the expected increase of the induced refractive index as a function of the starting 5 eV band amplitude when irradiated with 2 kJ/cm² of KrF laser light. The data are obtained by performing the Kramer–Kronig analysis using the deconvolution results. We have measured the absorption in the vaccum UV region in a few cases of the different annealing steps covering the range from 3.5 to 7.5 eV. The result after subtracting the different annealing spectra from the unannealed one shows no absorption change above 6.5 eV. Also the Gaussian centered at 6.4 eV has a major part of its surface in the region of the vaccum UV. We therefore assume that the absorption changes presented in this paper are representative of the calculated induced refractive index change through the Kramer–Kronig analysis since there is no contribution from absorption at higher energies. The index increase obtained with this dose of laser light varies from 1 to 6×10^{-5} depending on the GLPC band amplitude as determined by the annealing time.

5. Summary

The generation mechanism of Ge E′ centers following KrF irradiation in samples with different starting concentration of GLPC defects

Fig. 7. Proposed model explaining the possible transformation of the GLPC to Ge E′ and GEC.

has been investigated through absorption and ESR measurements. A direct relationship between the starting GLPC concentration and that of the induced Ge E′ and GEC centers suggests that they are likely the only precursors responsible for the generation of these centers at this relatively low dose of KrF irradiation. The creation of Ge E′ centers following 5 eV energy laser illumination is proposed here to result from a transformation of the GLPC through the intermediary of NOMV and to occur simultaneously with the transformation of GEC defects to Ge E′. The intensities of the induced GEC and Ge E′ absorption bands are demonstrated to be closely related to the initial intensity of the 5.14 eV band. This finding confirms that the highest photosensitive index changes can be achieved with KrF light by increasing the intensity of 5 eV absorption band originating from a higher concentration of GODC defects induced during fabrication.

Acknowledgements

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