Quantum Electronics **33** (11) 953–957 (2003)

INTERACTION OF LASER RADIATION WITH MATTER. LASER PLASMA

PACS numbers: 42.55.Rz; 42.65.Ky; 42.70.Gi; 42.70.Nq
DOI: 10.1070/QE2003v033n11ABEH002530

Action of the 216-nm fifth harmonic of a Nd : YAP laser on photosensitive germanosilicate glass films

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***Abstract*. The absorption spectrum, refractive index, and relief of the surface of a germanosilicate glass film are studied upon the non-destructive action of the 216-nm (5.75-eV) fifth harmonic of a repetitively pulsed Nd : YAP laser. It is shown that laser irradiation of films induces a strong photorefractive effect despite the relatively low absorption coefficient. For the 100-mJ cm^{-2} energy density and above, two-photon process make a noticeable contribution to the absorption of laser radiation at 216 nm. The diffraction efficiency of photo-induced phase gratings achieved $\sim 7\times 10^{-3}$ for the exposure dose ~ 6 kJ cm^{-2}, which corresponds to the induced refractive index 1.5×10^{-3}. At higher exposure doses, a relief appears on a film surface and the diffraction efficiency of a phase grating is reduced.**

Keywords: *photosensitive films, germanosilicate glass, photorefractive effect.*

1. Introduction

Germanosilicate (GS) glass doped with boron is a photosensitive material. It is used as the core in hydrogen-unloaded optical fibres for the production of photoinduced gratings of the refractive index [1]. In addition, photo-induced planar waveguides for integrated optics are fabricated from these photosensitive glasses.

It is well known that excimer ArF and KrF lasers are widely employed to produce photoinduced variations in the refractive index both in GS fibres and planar waveguides [2]. The radiation of these lasers at 193 and 248 nm, respectively, is strongly absorbed in the GS glass (Fig. 1). Absorption at 248 nm is mainly related to the 242-nm (5.1-eV) resonance absorption band of germanium oxygen-deficient centres (GODCs), whose concentration is a technologically dependent parameter. Absorption at 193 nm is determined by the superposition of the 165-nm (7.5-eV) absorption band of GODCs and the intrinsic absorption of the GS glass [3, 4]. The latter is caused by electronic transitions between the tail states of allowed bands (the Urbach absorption). The energy of such transitions is close to the edge of the fundamental absorption in the glass, which has the energy 7.2 eV for the $90SiO_2-10GeO_2$ ($90\,\%SiO_2+10\,\%GeO_2$) glass composition [5].

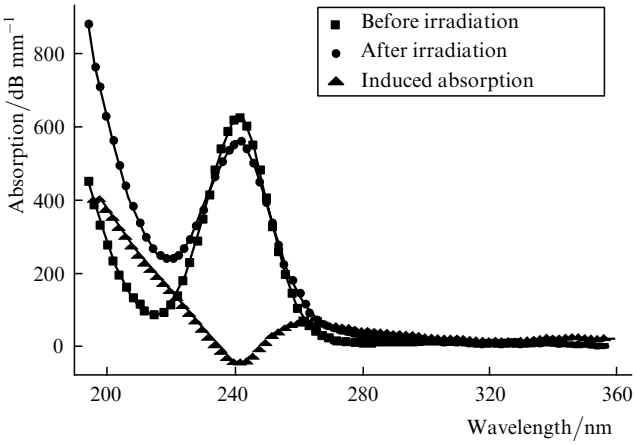

Figure 1. Absorption spectra of the $75SiO_2-20GeO_2-5B_2O_3$ glass before and after UV irradiation, and the induced absorption spectrum equal to the difference between the absorption coefficients before and after irradiation. The laser fluence is 600 mJ cm^{-2} and exposure dose is 8 kJ cm^{-2}.

A distinct feature of the Urbach absorption in the GS glass is its exponential dependence on the photon energy with the exponent equal to ~ 0.27 eV (at room temperature) and the pre-exponential factor proportional to the germanium concentration [6]. However, it is important to note that both these parameters also depend on the degree of order of the atomic structure (see, for example, Ref. [7]). The Urbach absorption is usually taken into account in the analysis of optical losses in optical fibres made of extra pure oxide glasses, in which it makes an appreciable contribution at wavelengths below 800 nm [8, 9]. A correct separation of the Urbach component against the background of strong bands related to the electronic transitions between the states of point defects is not a simple task. The problem is that the absorption coefficient α should be measured in a broad spectral range, where it changes by several orders of magnitude.

The absorption coefficient at the 193-nm and 248-nm wavelengths of the excimer lasers amounts to 1 dB μm^{-1} in photosensitive glasses with high concentrations of germanium and GODCs. A high absorption coefficient leads, on the one hand, to a high photosensitivity and, on the other,

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Received 20 January 2003
Kvantovaya Elektronika **33** (11) 953–957 (2003)
Translated by M.N. Sapozhnikov

to a substantially inhomogeneous distribution of the absorbed power over the depth at the scale of a few micrometers. This scale is typical for the core diameter of a GS fibre and the thickness of planar waveguides. The inhomogeneous distribution of the absorbed power, which is mainly absorbed in a ~ 3-μm thick layer, produces the transverse inhomogeneity of a 'line' upon the photoinduced writing of refractive index gratings. This violates the cylindrical symmetry of the core, resulting in the appearance of photoinduced birefringence, which is, as a rule, undesirable in devices [10].

By going to the 213–216-nm wavelength region, the distribution of the absorbed power can be made, in principle, more homogeneous due to the presence of a deep minimum in the absorption spectrum of a glass with a high concentration of GODCs in this region. The absorption coefficient at 216 nm is 6–8 times lower than that at 248 and 193 nm (Fig. 1). For this reason, it was interesting and important to verify whether UV radiation at 216 nm can induce a strong photorefractive effect, comparable to that produced by ArF and KrF lasers. This work is devoted to this problem.

2. Samples and the irradiation method

We used in our experiments the same irradiation method and samples as in Ref. [11]. The samples were prepared by the SPCVD method of deposition in plasma. A great advantage of this method is that it allows one to control easily the glass stoichiometry and to obtain, in particular, glasses with a large oxygen deficiency [12]. As in our previous experiments with excimer lasers [11], we used boron co-doping to increase the photosensitivity of the GS glass. The plasma-chemical technology of film deposition is described in detail in Ref. [11]. Films of thickness 10–20 μm were deposited onto KU1 silica substrates of a high optical quality. The films had the $75SiO_2-20GeO_2-5B_2O_3$ composition and were covered outside with a ~ 10-μm thick undoped SiO_2 layer. After deposition in plasma, the films were thermally treated in air by a scanning beam from a CO_2 laser producing a temperature of $\sim 1500\,^{\circ}C$ at the laser spot centre to create a high concentration of optically active GODCs.

The films were irradiated by the 216-nm (5.75-eV) fifth harmonic of a repetitively pulsed Nd : YAP laser (the pulse duration was 5 ns). UV radiation was obtained by the cascade generation of harmonics of the fundamental frequency ($\lambda = 1.0796$ μm). The fifth harmonic (ω_5) was obtained in a KDP crystal by the summation of the fourth harmonic (ω_4) with the fundamental frequency ω_1 of the laser ($\omega_5 = \omega_1 + \omega_4$). The 216-nm radiation was separated with a silica prism. The output pulse energy at the frequency ω_5 was ~ 10 mJ at a pulse repetition rate of 10 Hz.

3. Photoinduced optical absorption

We determined the dependence of the absorption coefficient of the films on laser irradiation using different exposure doses and integrated energy flux densities (i.e., different fluences). The films were irradiated by a laser beam passing through an aperture. A part of the beam behind the aperture was deflected with a mirror to measure the energy and to control the spatial distribution of the radiation intensity. To increase the fluence, the aperture was imaged on the film surface by a silica lens with a five-fold reduction. As a result, the energy density increased up to ~ 1 J cm^{-2}. The absorption spectra of the films before and after irradiation were measured with a double-monochromator spectrometer to exclude the influence of lumi-nescence.

Figure 2 shows the absorption spectra of the films after laser irradiation for different fluences f and the exposure dose equal to 8 kJ cm^{-2}. As f increases, the 242-nm absorption band of GODCs decreases only slightly, whereas absorption in the 190–220-nm and 260–300-nm regions noticeably increases. Such a change in the absorption spectrum of the GS glass differs from the effect caused by the 248-nm radiation from a KrF laser, which leads to an almost complete disappearance of the GODC absorption band [11]. We assume that in our case, as upon irradiation by an ArF excimer laser at 193 nm, a weak decrease in the 242-nm absorption band of GODCs is explained by the fact that the 216-nm laser line is located on the short-wavelength wing of this band. At the same time, induced absorption in the 190–220-nm region is substantial and comparable with absorption observed upon irradiation by an ArF laser.

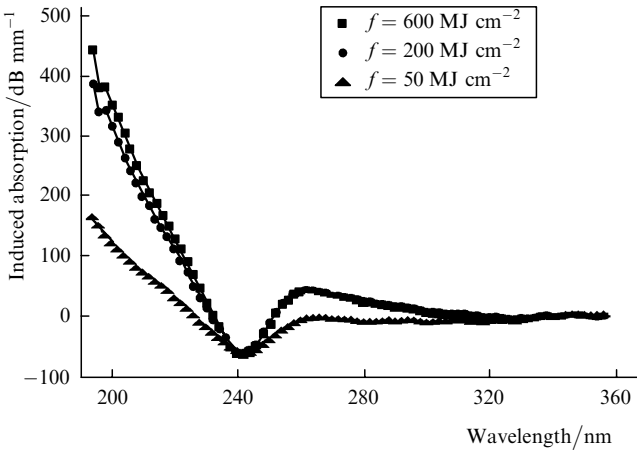

Figure 2. Induced absorption spectra of the $75SiO_2-20GeO_2-5B_2O_3$ glass obtained after irradiation at 216 nm at different laser fluences f and the exposure dose equal to 8 kJ cm^{-2}.

Another specific feature of irradiation at 216 nm is that the irradiation of the film with different fluences but the same exposure dose (8 kJ cm^{-2}) induces substantially different absorption in the short-wavelength part of the spectrum. For example, as f is increased from 50 to 600 mJ cm^{-2}, the absorption coefficient in the 190–220-nm and 260–300-nm regions substantially increases. However, the fluences $f = 200$ and 600 mJ cm^{-2} produce virtually the same effect.

This observation suggests that, for $f > 200$ mJ cm^{-2}, the induced absorption is substantially determined by two-photon absorption (TPA), which leads to interband electronic transitions accompanied at least partially by the dissociation of regular bonds. The dissociation can result in the generation of point defects in the form of dissociated or irregular chemical bonds and in the modification of a matrix due to distortions of the lengths and angles of regular chemical bonds, thereby increasing the matrix disorder. Both these processes lead to the formation of additional levels (states) in the band gap, resulting in the appearance of additional (one-photon) absorption. The increase in linear absorption reduces the effect of two-photon absorption,

which can explain, in particular, the saturation of the effect for $f = 200$ mJ cm^{-2}.

It is clear that the appearance of additional states in the band gap can be partially interpreted as the generation of different point defects. As was pointed out earlier [3], it was difficult to find for the irradiated GS glass the quantitative agreement between the concentrations of point (well-localised) defects, measured in EPR experiments, and a high level of induced absorption. For this reason, it was necessary to assume the existence of a set of diamagnetic point defects, which, however, have not been detected in optical experiments. This discrepancy can be probably eliminated by assuming that the rearrangement of the glass caused by TPA at high UV radiation fluences also involves more delocalised states, which are directly adjacent to the boundaries of the bands that do not contribute to EPR, but make, however, a noticeable, although not observed as separate bands, contribution to the induced absorption,

As mentioned above, the linear absorption coefficient at 216 nm is six times lower than that at 193 nm, the difference between the energies of corresponding photons (5.75 and 6.4 eV) being comparatively small. Therefore, when the laser fluences are the same, at the initial instant of exposure to the 216-nm radiation a greater part of absorption is caused by two-photon processes because a greater number of UV photons have time to take part in two-photon absorption events. This can explain a more efficient action of the 216-nm radiation on the Urbach tail compared to the 193-nm radiation [11]. In addition, the maximum intensity of the 216-nm radiation in our experiments exceeded that of the 193-nm radiation approximately by a factor of six.

4. Photoinduced phase grating

A change in the absorption coefficient of the GS glass in the UV region is usually accompanied by an increase in the refractive index in the visible and IR regions. We estimated the photoinduced changes in the refractive index in our experiments from the efficiency of diffraction from the induced phase grating. The grating was written in a film by the projection method described in detail in paper [11], where the method for measuring the induced refractive index from the diffraction efficiency of the phase grating was also considered.

We produced a pattern of alternating light and dark fringes on the film surface using an amplitude mask, which was imaged on the film with a five-fold compression in UV light using a silica lens. The amplitude mask was made of a metal foil of thickness 150-200 μm with rectangular holes arranged in the form of two-dimensional massive with a period of 200 μm, the holes being separated by distances equal to their diameter. A He – Ne laser was used as a probe laser. The experimental scheme is shown in Fig. 3.

The dose dependences of the diffraction efficiency (the ratio of the intensity of the first diffraction maximum to that of the zero-order diffraction maximum) of photoinduced phase gratings obtained for three different fluences are shown in Fig. 4. One can see that, for $f \approx 200$ mJ cm^{-2}, the diffraction efficiency of the phase grating increases monotonically with the exposure dose and achieves saturation ($\sim 7.1 \times 10^{-3}$; $\Delta n \sim 1.34 \times 10^{-3}$) for the dose ~ 10 kJ cm^{-2}. At higher fluences, the diffraction efficiency as a function of the exposure dose reaches the maximum and then slightly decreases. The maximum diffraction efficiency

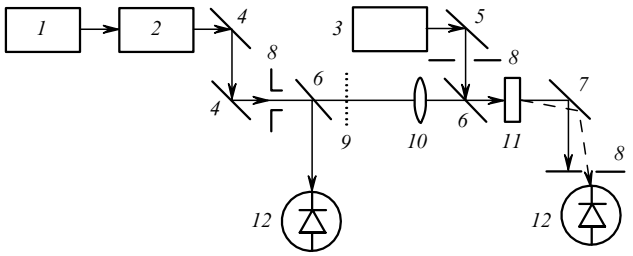

Figure 3. Scheme of the experimental setup for studying photosensitive GS glass films: (*1*) Nd : YAP laser; (*2*) harmonic generator; (*3*) He-Ne laser; (*4, 7*) dichroic mirrors at 216 and 632 nm, respectively; (*5*) deflecting mirror at 632 nm; (*6*) quartz wedge; (*8*) aperture; (*9*) amplitude mask; (*10*) quartz lens; (*11*) glass film; (*12*) photodiode.

is $\sim 7.5 \times 10^{-3}$ ($\Delta n \sim 1.37 \times 10^{-3}$) for the exposure dose ~ 6 kJ cm^{-2}. One can see from Fig. 4 that, for $f = 400$ and 600 mJ cm^{-2} and the exposure dose lower than 4 kJ cm^{-2}, the rates of the increase in the diffraction efficiency are the same, however, saturation occurs earlier at higher fluences. Note that the values of induced absorption for these two fluences at the same doses are also close to each other (Fig. 2).

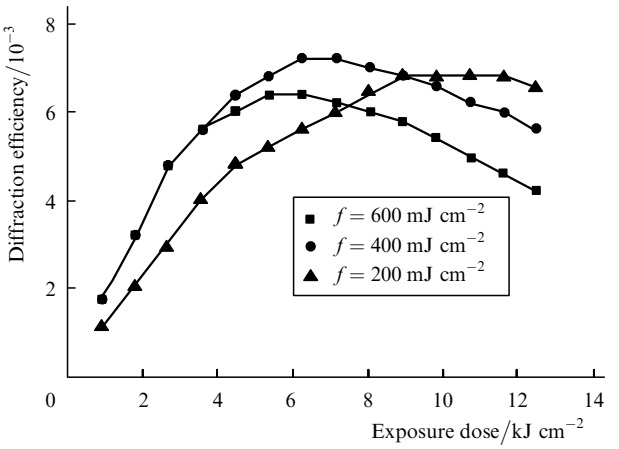

Figure 4. Dependences of the diffraction efficiency of photoinduced phase gratings on the exposure dose for different laser fluences f.

Figure 5 shows the dependence of the inverse transmission of a film on the laser fluence at 216 nm. One can see that nonlinear absorption becomes comparable with linear absorption (one-photon) for $f \sim 100$ mJ cm^{-2}, which corresponds to the laser power density ~ 10 MW cm^{-2}. The estimate of the two-photon absorption coefficient from the data in Fig. 5 gives for our films the value ~ 8 cm MW^{-1}. An increase in the laser fluence, when TPA dominates, leads to an increase in the number of absorbed UV photons because of interband excitation (photoionisation) of electrons, which stimulates photochemical reactions producing the rearrangement of the glass matrix discussed above. This rearrangement causes in turn an increase in the linear absorption coefficient, thereby reducing the TPA contribution and resulting in the saturation of photorefractive effects. Further exposure reduces somewhat the contrast of the phase grating, which is caused by the formation of a relief on the film surface.

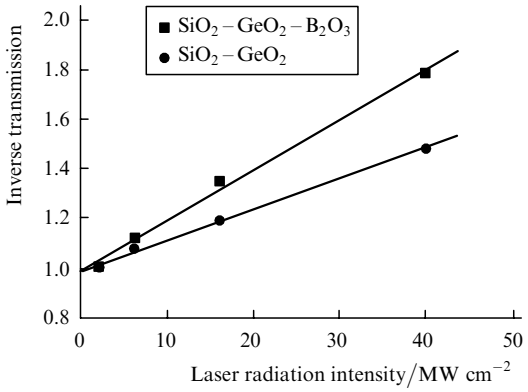

Figure 5. Dependences of the inverse transmission of GS glass films of two different compositions on the incident laser radiation intensity.

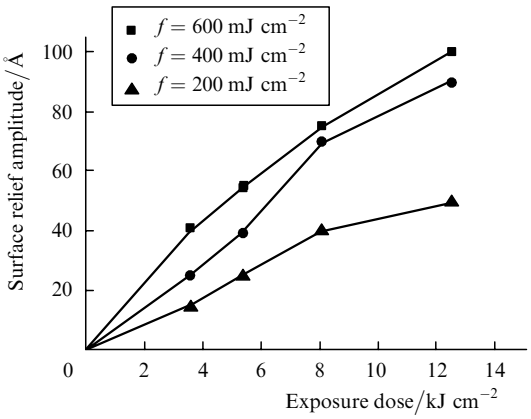

Figure 6. Dependences of the amplitude of the film surface relief on the exposure dose for different laser fluences f.

Note that the TPA coefficient of our films at 216 nm exceeds by four-five orders of magnitude the TPA coefficients for silica and GS glasses obtained at 264 and 248 nm in papers [13, 14]. Such a great difference demonstrates obviously a strong spectral dependence of the TPA coefficient and its dependence on the glass composition (in our case, on the relatively high concentration of germanium in films).

5. Formation of a relief on the film surface

We found that exposing films to UV excimer laser radiation caused their deformation (transverse compression). The compression of the film exposed to UV light through the amplitude mask leads in turn to the formation of a corrugated surface. Because a decrease in the film thickness in irradiated spots is equivalent to a decrease in the effective refractive index, the compression of the film caused a reduction in the diffraction efficiency [11].

A similar effect was also observed in our experiments upon irradiation of the films at a wavelength of 216 nm. For the fluence $f = 400$ mJ cm^{-2} and exposure doses above 6 kJ cm^{-2}, the diffraction efficiency of the written phase gratings decreased. When the fluence f was increased up to 600 mJ cm^{-2}, the diffraction efficiency began to fall at lower exposure doses. Figure 6 shows the dependences of the modulation depth of the film surface on the exposure dose for different laser fluences. The relief was measured with a ZYGO interferometer in the spots where phase gratings have been recorded. One can see that, for the exposure dose ~ 6 kJ cm^{-2} and $f \approx 600$ mJ cm^{-2}, the modulation depth of the film surface relief was ~ 50 Å, which is approximately three times lower that for $f = 200$ mJ cm^{-2} and the same exposure at 193 nm [11]. One can also see that the rate of the relief formation increases with increasing f up to 400 mJ cm^{-2}. Then, this dependence saturates, so that relief for $f = 600$ and 400 mJ cm^{-2} is formed approximately at the same rate. Note the absence of saturation in the dependence of the modulation amplitude on the exposure dose.

6. Conclusions

By exposing germanoborosilicate glass with the molar content of GeO_2 ~ 20 % to laser radiation at 216 nm, we obtained the modulation depth of the refractive index $\sim 1.3 \times 10^{-3}$, without a significant densification of the glass (the amplitude of the photoinduced surface relief was smaller that 50 Å). A comparatively weak densification of the glass along with the large induced refractive index opens up good possibilities for writing planar waveguides.

The linear absorption coefficient α at the irradiation wavelength increases from the initial value ~ 150 cm^{-1} up to ~ 600 cm^{-1} after irradiation of the film with the dose 8 kJ cm^{-2}. Photoinduced absorption observed at equal doses depends on the fluence, which indicates to the two-photon process. The TPA coefficient is ~ 8 cm MW^{-1}.

As α increases, the effective depth (α^{-1}) of light penetration decreases from 60 down to ~ 15 μm. Due to a decrease in the light intensity, the depth at which TPA is substantial also decreases. This results in some saturation of photoinduced effects in the film volume with increasing exposure dose. In particular, the rate of phase grating production is almost the same for $f = 400$ and 600 mJ cm^{-2}. On the contrary, the relief depth does not exhibit saturation with increasing exposure dose, however, the rate of its formation depends on the fluence and saturates at $f = 400 - 600$ mJ cm^{-2}. It seems that, as in the case of two-photon processes in other low-melting silicate glasses [15], photoinduced densification is related to the dissipation of the energy of a glass matrix absorbed by electrons due to the electron-phonon interaction. The relaxation of the matrix upon such excitation is similar to a local laser melting, and, other conditions being the same, increases with decreasing the softening point of the glass.

This work was supported by the Russian Foundation for Basic Research (Grant Nos 01-02-17812 and 00-15-96650).

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