Recent Research on Photosensitive Amorphous Materials for Optical Devices

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Abstract

Photosensitive amorphous materials are attractive for the formation of several optical elements by a specific laser beam irradiation. For example the optical fiber gratings prepared by UV laser irradiation are one of the key elements for the recent worldwide progress of wavelength division mutiplexing optical fiber network. This paper reviews the representative studies on the photosensitive materials and the origin of photosensitivity in amorphous oxide materials.

1. Introduction

In 1978, it was found out that the core of the optical fiber has a photosensitivity against UV light.[1] Recently permanent fiber Bragg gratings due to periodic refractive index modulation can be easily formed by irradiation with excimer laser or frequency doubled Ar laser through a phase mask.[2] Fiber gratings are considered as one of the key components for the dispersion compensation in long distance communication and wavelength division multiplexing in the subscriber loops of the fiber network. Ge-doped SiO_2 glasses are used for the conventional fiber core. It was predicted that the photochemical reaction or photon-induced structural change around Ge ions is the origin of refractive index changes. I investigated the photochemical reactions caused by irradiation with excimer laser in a Ge-doped SiO_2 glass fiber preform. In the first section, the formation reactions of several color centers related to the positive refractive index change are reviewed.

In the second section, I briefly summarized the completely opposite photon induced phenomena observed in a Ge-doped SiO_2 thin films deposited by a conventional rf-sputtering method. In spite of the similar composition with the fiber core, the irradiation with excimer laser to the films induced the large negative refractive index and positive volume changes. A surface Bragg gratings could be formed upon this film by irradiation with excimer laser through the phase mask.

2. Formation mechanism of fiber Bragg gratings

The color center models based on Kramers-Kronig relations were suggested in several papers in order to explain the positive photon-induced refractive index change.[3-6] There are two formation channels of color centers: extrinsic oxygen-deficient defect channel[5] and intrinsic non-defect channel.[6] It is well known that the oxygen deficient defects causing intense absorption bands near 5eV(the 5eV band) is often incorporated in Ge-doped SiO_2 glasses for the optical fiber preform during their preparation process. Two possible oxygen deficient defects with distinctive natures give the 5eV band: a neutral oxygen monovacancy and a neutral oxygen divacancy associated with Ge ions.[5] The former is readily changed to Ge E' center by illumination with an UV lamp emitting 5eV light, and then the intense absorption band peaking at 6.3 eV is induced, which is one of the origin of the UV-induced positive refractive index change. The concentration of GeE' estimated by electron-spin-resonance(ESR) increased linearly with the absorption intensity at 6.3eV.[7] This photochemical reaction, therefore, is explained by the following equation:

$$\equiv \text{Ge-Ge} \equiv \ \rightarrow \ \text{Ge E'} + GeO_3^+ + e.$$

The latter defect, which can be expressed as Ge^{2+}(=Ge:), emits intense luminescence peaking at 3.3 and 4.3eV, but this type of defect is insensitive at least against illumination with UV lamp(i.e. one-photon absorption process).

A different formation processes of color centers was found out by irradiation with dense UV photon flux such as excimer laser pulses.[6] The band-to-band excitation generates pairs of electron and hole. An electron is trapped by a fourfold coordinated Ge ion, giving an GEC. It suggested that the bridging oxygens are the most plausible hole traps from observation of ESR signal of self-trapped hole (STH). A quantitative study was carried out to define the formation and relaxation processes of electron and hole trapped.[8] The laser irradiation and the ESR measurement were made at 77 K to minimize thermal effect on the formation and relaxation of the defects.

Figure 1 shows the ESR spectra of glasses after irradiation

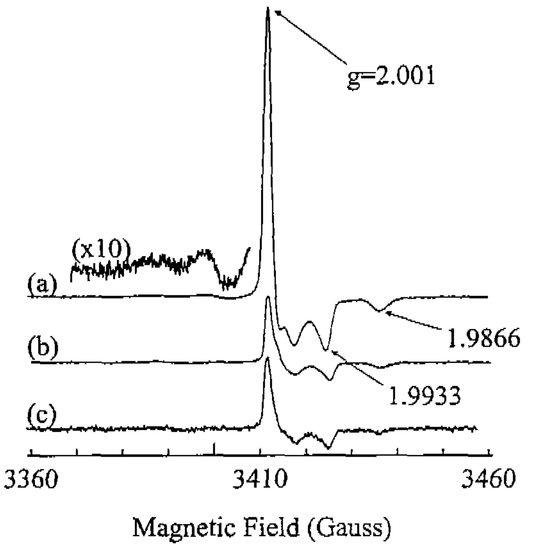

Fig.1. ESR spectra of $10GeO_2$-$90SiO_2$ glasses irradiated with 200 KrF laser shots of $2.3mJ/cm^2$: (a)irradiated at 77K, (b)irradiated at 77K followed by annealing at 298K for 5min, (c)irradiated at 298K. All of the spectra were recorded at 77K without change in spectrometer sensitivity.

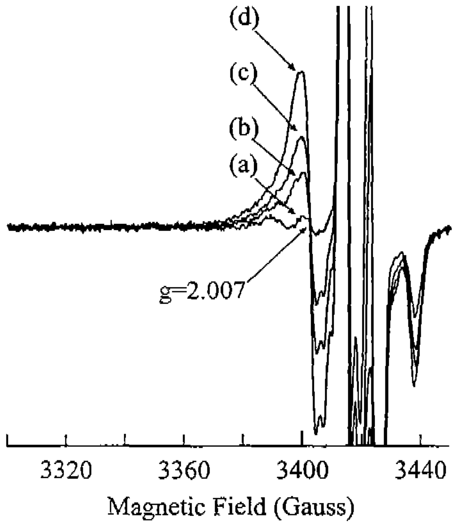

Fig.2. ESR spectra of $10GeO_2$-$90SiO_2$ glasses irradiated with KrF laser pulses at 77K. The power density(mJ/cm^2) of a pulse and the shot number were (a)5, 200, (b)17, 200, (c)17, 3000, (d)63, 3000, respectively.

with KrF laser pulses at 77K(spectrum a) and at room temperature(spectrum c). The shot number and the power density were 200 and $2.3mJ/cm^2$, respectively. Signals observed in the region $g<2$ can be assigned to electron trapped centers associated with fourfold-coordinated Ge ion.[9, 10] Two kinds of GECs, i.e., Ge(1) and Ge(2), were reported, depending on the number of the nearest neighboring Ge ions, one or two, respectively.[10] The downward peaks at g=1.9933 and 1.9866 agree with those of Ge(1) and Ge(2). The upward peak at g=2.001 also agree with those centers. The total concentration of GECs after irradiation at 77K was estimated as 5.6×10^{17} cm^{-3}. As shown by curve (b), the intensity of the signal was decreased to approximately 1/2 after annealing at room temperature for 5 min. No apparent spectral change was noted by annealing for >5 min. The spin concentration of GECs was estimated as 3.5×10^{17} cm^{-3}, which is almost same with that(3.4×10^{17} cm^{-3}) of the specimen irradiated at room temperature(see curve c). It can be recognized in curve (a), on the other hand, that the weak signals were induced in the region $g>2$, which were almost bleached after the annealing of the specimen at room temperature. These weak signals could be attributed to a hole trapped center judging from the positive g-shift. The formation of hole trapped center could be confirmed more clearly with increasing the cumulative laser dose.

Figure 2 shows the ESR spectra after irradiation with intense KrF laser pulses at 77K. The signal intensity increased gradually with increasing both of power density and shot number until the cumulative laser dose reached 2 J/cm^2. The signal centered at $g = 2.007$ is assignable to self-trapped hole(STH), because the g value and the line shape are well agree with the g_2 value of the STH_2 in SiO_2 glasses created by irradiation with X-ray or ArF excimer laser at 77 K.[11] It was suggested that the STH_1 comprises a hole localized on a normal bridging oxygen in the glass network, and the hole in STH_2 is delocalized over two *2p* orbitals of two separate bridging oxygen atoms. After annealing of the specimen at room temperature for a few minutes, the STH almost disappeared, whereas a half of GEC remained as shown by curve (b) in figure 1. Therefore, the concentration of STH observed after irradiation at room temperature was much lower than that of GEC.

Figure 3 shows the change in the ESR spectra upon annealing for 5 min at room temperature, which was obtained by subtraction of the spectrum after annealing from that of as-irradiated. The curve (a) was obtained after irradiation with 10 KrF laser pulses of $120mJ/cm^2$ followed by the annealing. The signals attributed to STH and GEC were observed. The line shape of GEC changed gradually with increasing the irradiated shot number(see curve b and c). As denoted in the figure, the typical g-values are identical with those of GeE'.[12] Similar change was recognized by irradiation at room temperature[13]. It is, therefore, evident that the relaxation of GECs to GeE' can proceed even if at 77K. The another interesting evidence is exemplified by

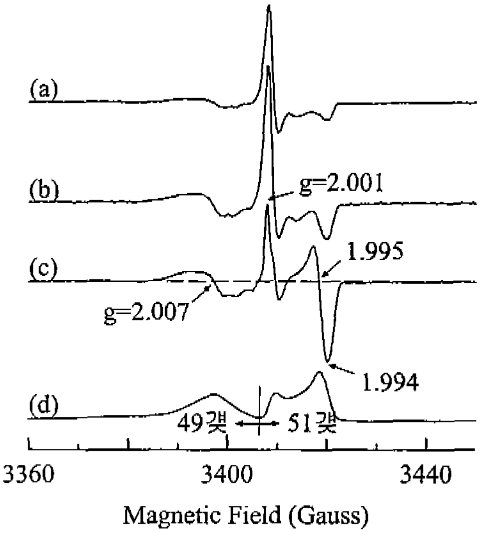

Fig.3. Difference ESR spectra of $10GeO_2$-$90SiO_2$ glasses between before and after annealing at 298K for 5mim. Numbers of KrF laser pulses(120mJ/cm²/pulse) irradiated at 77K were (a)10, (b)100 and (c)8000, respectively. Curve (d) is the integrated spectrum of curve (c).

curve (d) in figure 3, which is obtained by the integration of signal (c). The ratio of the integrated signal intensities of STH to (GEC + GeE') is almost 1 : 1. This result indicates the uv-induced electron transfer from a bridging oxygen to a fourfold-coordinated Ge ion is completely balanced. It is, therefore, reasonable to consider that a pair generation of GEC and STH occurs as the essential photochemical reaction.

Figure 4 shows the relation between the laser power density and the GEC concentration estimated from the difference ESR signals before and after annealing at room temperature. It is recognized that the concentration of GECs(N) is proportional to the energy density of a pulse(I) on log-log plots in the range of laser power density lower than 10mJ/cm². The slope of the relationship is 2. Taking the band-gap-energy of the glass(7.2eV) [6] into account, the formation of GEC is primarily controlled by the two-photon absorption process, i.e., $N = kI^2$, where k is the apparent formation efficiency(5×10^{13} spin cm/mJ²). This k value was higher than that for the GECs stable at room temperature[17], which was 4×10^{11} spin cm/mJ². When the power density exceeded 10mJ/cm², there was no change in the concentration of GECs. Similar tendency was recognized for STH observed at 77K. It is, therefore, concluded that the following photo-chemical reaction channel proceeds essentially both at 77K and room temperature: Ge^{4+}(fourfold coordinated) + O^{2-}(bridging oxygen) → GEC + STH.

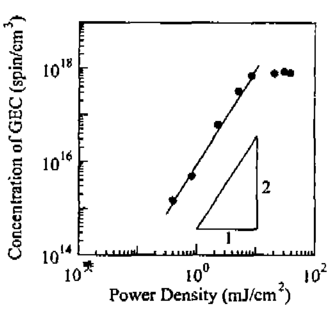

Fig.4. Concentration of GECs created by irradiation with 200 KrF laser pulses as a function of power density. The slope of the line is about 2.

The acceptor of a hole released from a STH during annealing at room temperature is still remained as an ambiguous point. Figure 5(a) shows the relation between the cumulative dose of KrF laser pulses and the integrated intensity of two emission bands of Ge^{2+} peaking at 3.2 and 4.3eV, which were measured by excitation with 5.2eV light of Xe lamp. The intensity was decreased by 60% with increasing the dose. Similar change in emission intensity has been reported by Poirier et al.[14] We reported that the change in emission intensity due to Ge^{2+} by dense irradiation with excimer laser light suggests a possible reaction path related with Ge^{2+}.[13] As shown by figure 5(b), which is the relation between the total spin density of [GEC]+ [GeE'] and the laser dose, there is a intimate relation between the changes in the emission intensity and the spin density of Ge related centers induced by laser irradiation. Thus it is concluded a photochemical

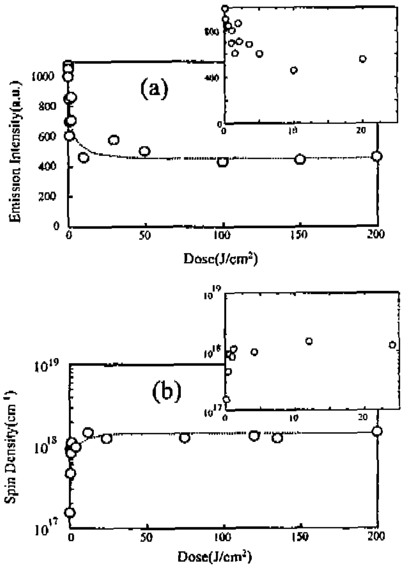

Fig.5. Changes of (a)integrated emission intensity at 3.2 and 4.3eV bands of Ge^{2+} and (b)total spin density of GEC and GeE' induced at 77K against the dose of KrF laser pulses. Emission spectra were measured at room temperature upon photoexcitation with 5.2eV light of Xe lamp. The insets are the plots in the area of low dose(<25J/cm²).

reaction related with Ge^{2+} should be important to explain the hole release from STH.

It was observed in the present study that the pair of STH and GEC(or GeE') was reproducible by the KrF laser irradiation to the identical specimen after annealing at room temperature. Consequently, the formation reaction of STH and GEC and the relaxation of GEC to GeE' are reversible. Therefore a reaction cycle shown in figure 6 is suggested. The relaxation of GECs to GeE' involves a bond scission between Ge and O, which might be one of the trigger of the structural relaxation of the glass matrix. It was reported by Albert[15] that the UV-induced refractive index change estimated by the diffraction efficiency of fiber gratings increased continuously until the dose of the laser power exceeding 1000 J/cm^2. The densification of the glass was actually observed after similar dense irradiation.[16] At least by the ESR observation, however, the formation reactions of the color centers are saturated at the dose much lower than such level. For example, the total concentration of UV-induced color centers in our specimen was saturated at $1x10^{18}$ - $4x10^{18}cm^{-3}$ when the dose of the KrF laser pulses reached $2J/cm^2$. While the participation of Ge^{2+} to our model is vague, the laser induced cyclic reaction in figure 6 should be related with the gradual relaxation of glass matrix, resulting in a positive refractive index change of the glass.

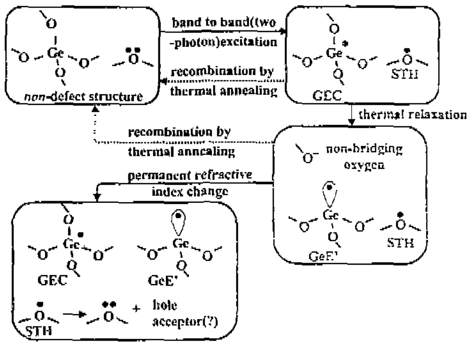

Fig.6. A photochemical reaction model induced in GeO_2-SiO_2 glasses by irradiation with KrF laser pulses.

In 1993, the sensitization of Ge-SiO_2 glasses was achieved by high pressure hydrogen molecule loading.[17] After treatment of optical fibers of 125 micron dia. for 2 weeks at room temperature, 3.3% H_2 molecule was loaded in the fiber. The refractive index change of this fiber by irradiation with KrF laser(30Hz, $300mJ/cm^2$, 10min) was $5.9x10^{-3}$, which was much higher than that of unloaded fiber. The origin of this large index change is attributed to the photochemical reaction between the glass network and H_2 molecule. After irradiation with UV light, the absorption peaks due to Si-OH(1.39 micron) and Ge-OH(1.41 microm) were induced. During the formation of OH functions, the photochemical reduction of GeO_4 to $\equiv$Ge-Ge$\equiv$ or =Ge: proceeded resulting the formation of GeE'.

Similar photosensitivity was reported for SiO_2 based optical fibers doped with SnO_2[18,19] or TiO_2[20]. Especially the high photosensitivity of SnO_2 doped fiber enable the direct UV writing of Bragg gratings through UV transparent resin coating without H_2 loading, which is advantageous to inhibit the reduction of mechanical strength of the fiber.[18]

3. Photon induced phenomenon in sputter deposited Ge-doped SiO_2 thin film

A completely new photo-sensitive phenomena in Ge-doped SiO_2 thin film prepared by the sputtering deposition method.[21-23] Ge-doped SiO_2 thin glass films were deposited upon substrates of Si wafer or SiO_2 by a conventional rf-sputtering method. Sputtering target was prepared by sintering of the mixture of SiO_2 and GeO_2 powders. The nominal content of GeO_2 was 0 - 80 mol%. Sputtering deposition was carried out under 1.33 Pa pressure of an O_2-Ar mixture gas at a growth rate of 15 nm/min. The films had a tendency to become yellow under the deposition in a 100% Ar atmosphere. The origin of coloration is tentatively attributed to the formation of large amount of Ge^{2+} having an intense absorption band peaking at 5eV. Introduction of 1% O_2 was effective to suppress such coloration, but excess introduction decreased the photo-sensitivity of the film. The amorphous nature of resulting thin films were confirmed by x-ray diffraction. The composition of the film was determined from the intensities of Si 2*p* and Ge 3*p* peaks of x-ray photoelectron spectroscopy(XPS). ArF excimer laser pulses with a repetition of 10 Hz were irradiated to the film at room temperature. The power density of a pulse was 40 mJ/cm^2. The changes in refractive index and thickness of the film were measured by an ellipsometer at a wavelength of 633nm. Chemical etching of the film was carried out using a 0.01% HF solution at 25±0.5℃ after irradiation.

Figure 7 shows the relationships between the power density of a pulse and the changes in refractive index and thickness for the film with the $46GeO_2$-$54SiO_2$. The number of irradiated pulses were 200 for each point. These changes became evident gradually with increasing the power density of a pulse. The highest index change of -10% and volume change of +30% were attained without ablation when the irradiated power density of a pulse was 43mJ/cm^2. Figure 8 shows the relationship between the GeO$_2$ content and the changes in refractive index and thickness of the film after irradiation with 1200 ArF laser pulses. The thickness of the film was about 150nm. The negative index and positive volume changes were confirmed distinctly in the region of GeO$_2$ content higher than 30 mol%, but the ablation of the film was caused in the region of GeO$_2$>63mol%.

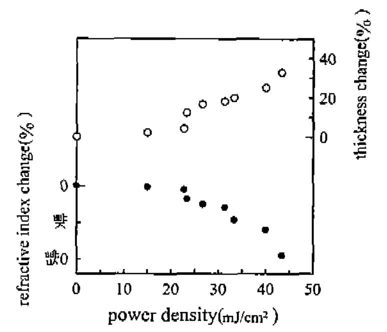

Fig.7 Relationships between the power density of a laser pulse and the changes in refractive index and thickness for the film with the 46GeO$_2$-54SiO$_2$.

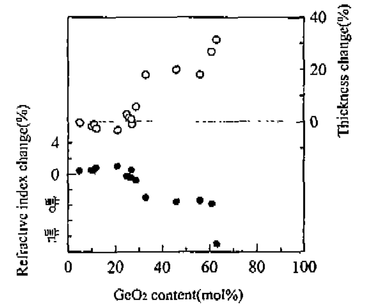

Fig.8 Relationship between GeO$_2$ content and the changes in refractive index and thickness of the film after irradiation with 1200 ArF laser pulses(40mJ/cm^2). The thickness of the film is 150nm.

The durability of the irradiated area against 0.01%HF solution became much lower than that of the unirradiated area. Figure 9 shows the relationships between the etching time and the changes of refractive index and thickness in the irradiated and unirradiated areas. The thickness in the unirradiated area decreased gradually at the rate of 0.37nm/sec, while the refractive index in the same area did not change by the etching. The thin film in the irradiated area, on the other hand, was etched very quickly compared with that in the unirradiated area, which was estimated as 11.3nm/sec. After the etching for 20sec, the etching rate in both area became in the same level, and a step profile of 92nm in depth was remained. The refractive index of the irradiated area apparently increased to the original level after the etching for 20sec. Therefore,

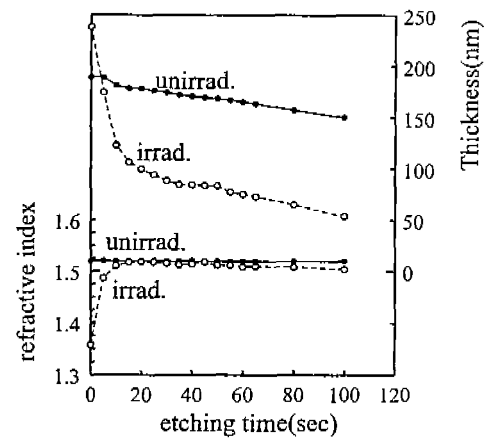

Fig.9 Changes in refractive index and thickness of the laser irradiated area(200-shots ArF laser pulses of 40mJ/cm^2) and unirradiated area of 46GeO$_2$-54SiO$_2$ thin glass film against the etching time.

the laser induced refractive index and thickness changes should be caused around 100nm in depth from the original surface.

A Bragg grating was printed upon the 46GeO$_2$-54SiO$_2$ thin glass film(200nm thick) by irradiation with 200-shots of ArF laser pulses(40mJ/cm^2). Figure 10 shows an example of the AFM image of the grating. Diffraction characteristics of the gratings were investigated using an He-Ne laser(0.9mW) as a light source.

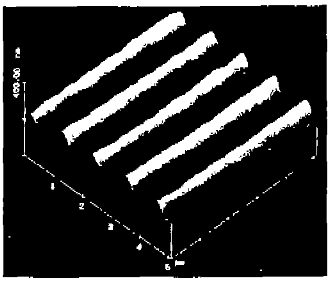

Fig.10 AFM image of the grating printed upon Ge-SiO2 thin film.

Figure 11 shows the relationships between the etching time and the first- and zero-order diffracted powers, which were observed at angles of -42.0 and -7.8degree, respectively, when the incident angle of probe beam was +7.8degree. The power ratio of first-order diffracted beam to zero-order one was as high as 3.6% for the as printed grating. Such diffraction was caused by the positive pattern printed upon the thin glass film. After the etching for 9sec, the ratio was decreased to the level of 0.1%. The area of the positive volume expansion by the laser irradiation was quickly etched compared with the unchanged area, and a quasi-flat surface should be formed in the early stages of etching. The first- and zero-order diffracted power ratio gradually increased up to 91.7% after the etching longer than 80sec. These optically and chemically printed gratings withstood heat treatment above several hundred degree, which is useful for several optical applications.

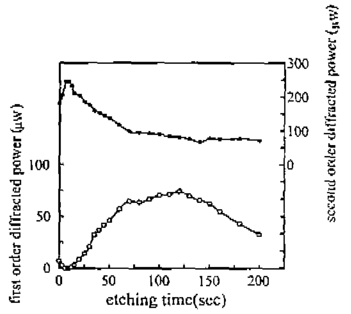

Fig.11 Relationship between the etching time and the diffracted power of He-Ne laser beam(633nm) from the $46GeO_2$-$54SiO_2$ thin film grating. The grating was formed by irradiation with 200-shots ArF laser pulses of 40mJ/cm² through the phase mask (1067nm pitch).

4. Summary

Recent studies on photosensitivity and application of oxide amorphous materials were reviewed. Formation processes of paramagnetic centers in the Ge-doped SiO_2 glass fiber preform was investigated by irradiation with eximer laser. It was concluded that the essential photo-chemical reaction is the pair-generation of GEC and STH, and their precursor is not extrinsic oxygen deficient defects but intrinsic non-defect type species. Considering the intimate relation between the generation of Ge related paramagnetic centers and the quick decay of emission intensity due to Ge^{2+}, it is not possible to ignore the reaction related with Ge^{2+}. A most plausible reaction might be the hole transfer from STH to Ge^{2+} and its simultaneous relaxation.

Sputter deposited Ge-doped SiO_2 thin glass films exhibited the high sensitive changes of refractive index and volume by irradiation with ArF excimer laser pulses. The etching rate of the irradiated area by the HF solution was much faster than that of the unirrdiated area. Using these characteristics, it is possible to prepare the Bragg gratings both with positive and negative patterns upon the film. This film is expected to be applicable to optical devices and optical memory.

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