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Citation: [Applied Physics Letters](#) **67**, 3529 (1995); doi: 10.1063/1.114911

View online: <http://dx.doi.org/10.1063/1.114911>

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# Comparison of one-photon and two-photon effects in the photosensitivity of germanium-doped silica optical fibers exposed to intense ArF excimer laser pulses

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(Received 30 August 1995; accepted for publication 2 October 1995)

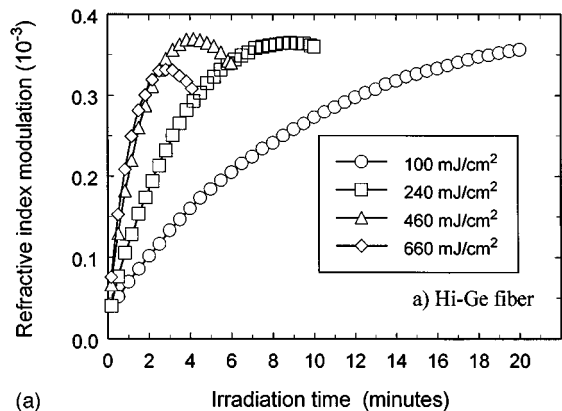
The growth rate of fiber Bragg gratings written using 193 nm light from an ArF excimer laser is linearly proportional to the laser pulse energy density for fibers with high germanium doping but proportional to the square of the pulse energy density for standard telecommunications fibers with low germanium concentration. The two-photon process in standard fibers yields refractive index increases that saturate around  $10^{-3}$ , an order of magnitude improvement over previous results in this type of fiber without sensitization treatment. The two types of photoinduced refractive index gratings have comparable thermal stability and preserve about 50% of their initial magnitude after 30 min at 600 °C. © 1995 American Institute of Physics.

A permanent increase in the refractive index of germanium-doped optical fibers is observed following irradiation with 5 eV photons (wavelengths near 242 nm), allowing the fabrication of in-fiber optical devices such as Bragg gratings.<sup>1</sup> This photosensitivity is generally associated with an ultraviolet absorption band near 5 eV due to germanium oxygen-deficient centers or GODCs.<sup>2</sup> Recently, photosensitivity has also been observed in such optical fibers and waveguides exposed to shorter wavelength light at 193 nm from an ArF excimer laser.<sup>3</sup> This form of photosensitivity arises from another absorption band of the GODC near 185 nm.<sup>2</sup> In all cases where commercially available fibers are used, the maximum photoinduced index change lies between  $1 \times 10^{-4}$  and  $4 \times 10^{-4}$ , too small for many important Bragg grating applications. When larger index changes are required, special fibers<sup>4</sup> with increased germanium concentration and/or codopants may be utilized but it is often desirable to fabricate photoinduced devices in standard optical fibers for compatibility with existing optical fiber systems. In order to write high reflectivity gratings in these fibers, sensitization techniques have been developed to increase the photoinduced index modulation to values of the order of  $10^{-3}$  and higher: flame brushing<sup>5</sup> or low temperature hydrogen loading.<sup>6</sup> More recently, it has been discovered that by using high intensity ArF laser light at 193 nm, another photosensitive regime is reached in which refractive index amplitude modulations larger than  $10^{-3}$  have been obtained *without sensitization* in SMF-28 fibers.<sup>7</sup> It is the purpose of the present letter to describe the physical mechanisms underlying this new photosensitive regime. In order to do this, the growth rate of fiber Bragg gratings written in two standard optical fibers with different germanium dopings are compared as a function of ArF laser pulse energy density. One photon (OP) and two-photon (TP) effects are observed depending on germanium concentration, and a model of the physical origin of the two types of behavior is proposed on the basis of the ultraviolet absorption spectra of such fibers. Furthermore, the ruggedness of the photoinduced index

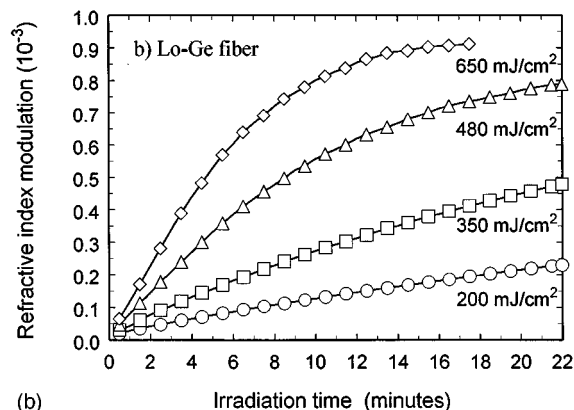
changes obtained by OP and TP processes at 193 nm is compared to that obtained using 248 nm light from a KrF excimer laser by isochronal annealing experiments.

For the growth rate measurements, we used an ArF excimer laser operating at 50 pulses/s with a fluence per pulse of 60 mJ/cm<sup>2</sup>. A focusing system is used to vary the fluence incident on the fiber. 1 mm long Bragg gratings were imprinted by the phase mask technique<sup>1</sup> in highly doped fiber (Hi-Ge fiber): Alcatel's bend-insensitive fiber with 8 mol % of germanium in the core, and in lightly doped fiber (Lo-Ge fiber): Corning's SMF-28 fiber with 3 mol % of germanium. The reflectivity of the gratings was monitored in real time during the exposure and the experiment was repeated for four different writing fluences in each of the two fibers. The refractive index modulation is determined from the reflectivity of the gratings by the standard coupled mode approximate formula. The annealing experiments were carried out in an air atmosphere by placing the fibers in which Bragg gratings had been written in a box furnace for 30 min intervals at each temperature. After each annealing step, the fibers were cooled slowly to room temperature and remeasured.

The growth of the index modulation in the two fibers as a function of the cumulative incident laser fluence is shown in Fig. 1 for different laser pulse intensities. The growth rate for the Hi-Ge fiber [Fig. 1(a)] is very fast and the index modulation saturates at a moderately high value of  $3.6 \times 10^{-4}$  in good agreement with previously published results.<sup>3</sup> On the other hand, a much slower growth rate is observed for the Lo-Ge fiber [Fig. 1(b)] but the index modulation saturates at an unexpectedly high value of  $0.91 \times 10^{-3}$  for high fluences (more than  $10^{-3}$  has been reached in another experiment<sup>7</sup>). Direct observation under a microscope and evaluation of the coupling to cladding modes in the reflection spectra of the Bragg gratings show that the index modulation obtained in both fibers is uniform across the fiber core and not linked to a damage mechanism at the core cladding interface such as those obtained under single pulse, high energy density 193 nm light.<sup>8</sup>



(a)



(b)

FIG. 1. (a) Growth of refractive index modulation amplitude in Hi-Ge fiber (Alcatel bend-insensitive) resulting from irradiation through a phase mask with ArF laser at 50 pulses/s with pulses of different energy density. (b) Same as (a) in Lo-Ge fiber (Corning SMF-28).

The large photosensitive effect in the Lo-Ge fiber from 193 nm irradiation is attributed to a different absorptive process based on the following findings. Figure 2 shows the initial growth rate plotted as a function of the writing pulse energy density for both fiber types. If we assume that  $\Delta n$  is proportional to  $I^b t$ , where  $\Delta n$  is the index modulation,  $I$  is the UV light energy density, and  $t$  the exposure time, then the slope of a log-log plot of the growth rate  $d(\Delta n)/dt$  vs  $I$

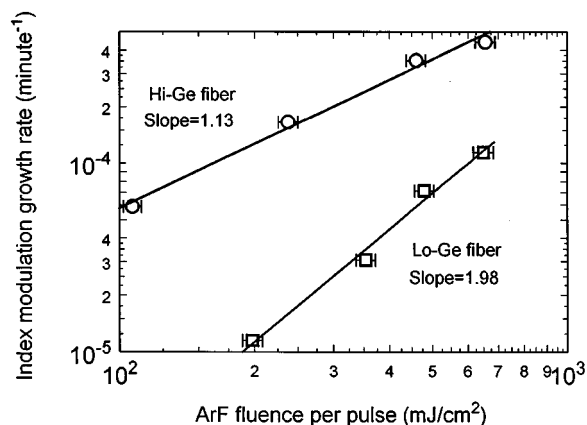


FIG. 2. Initial growth rates ( $d[\Delta n]/dt$ ) as a function of ArF laser pulse energy density for Hi-Ge fiber (open circles) and Lo-Ge fiber (open squares). The lines are least-square fits to the data.

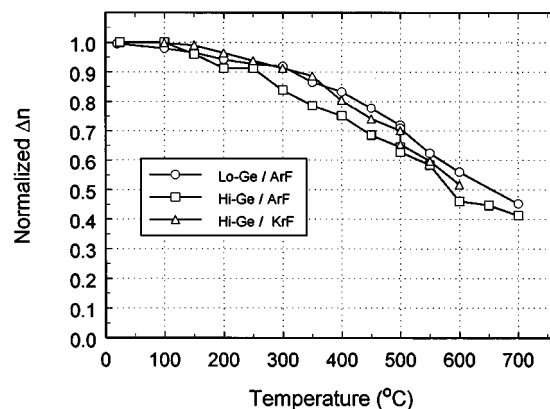


FIG. 3. Isochronal (30 min) thermal erasure of the normalized refractive index modulation amplitude for fiber Bragg gratings written in the following conditions: (a) Hi-Ge (Alcatel bend-insensitive), ArF laser, 50 pulses/s, 660 mJ/cm<sup>2</sup> per pulse, initial  $\Delta n = 0.28 \times 10^{-3}$  (open circles); (b) Lo-Ge (Corning SMF-28), ArF laser, 50 pulses/s, 650 mJ/cm<sup>2</sup> per pulse, initial  $\Delta n = 1.02 \times 10^{-3}$  (open squares); (c) Hi-Ge, KrF laser, 50 pulses/s, 300 mJ/cm<sup>2</sup> per pulse, initial  $\Delta n = 0.09 \times 10^{-3}$  (open triangles).

yields a value for the exponent  $b$ . As expected from previous experiments,<sup>9</sup> the Hi-Ge fiber shows a growth rate that varies linearly with the fluence (slope  $b = 1.13$ ). This characteristic is typical of OP, or linear absorption by GODC in the tail of either the 242 or 185 nm band. In the case of the Lo-Ge fiber, the growth rate shows a completely different behavior. The growth rate varies as the square of the energy density (slope  $b = 1.98$ ), suggesting that the index increase is governed by a TP absorption process.

It is clear from Fig. 2 that for a given light pulse energy density, the growth rate for the OP process is always significantly larger than for the TP case. Therefore, the probability of occurrence of the OP-induced photochemical reaction in which an absorbed photon modifies the refractive index is larger than the probability of the reaction induced by the TP absorption, as is usually the case.<sup>10</sup> On the other hand, the maximum index change achieved in the latter case is almost three times higher. This difference in the photosensitivity obtained with the two processes may be explained in one of two ways: (1) similar numbers of reaction products (color centers) are created by the two processes but their polarizability is different, leading to a higher index change in the TP case; (2) the same kind of color centers are created by the two processes but the TP effects creates more of them. In an attempt to discriminate between these two hypotheses and in order to verify the ruggedness of devices based on the TP process, a comparative isochronal annealing experiment was carried out on fiber Bragg gratings fabricated using three typical sets of irradiation conditions. The results for the normalized index modulation amplitude of fiber Bragg gratings fabricated using OP and TP processes at 193 nm, as well as conventional photosensitivity (linear absorption of 248 nm photons by the GODC band in SMF-28 fiber) are presented in Fig. 3. The fabrication conditions and initial index modulations of each grating are given in the caption. No significant difference in the thermal erasure of the index modulation is seen between the three cases and all preserve about

50% of the initial index modulation after 30 min at 600 °C.

Based on these results, it appears that similar color centers are formed in the three cases and that differences in the maximum index change or in the index growth rate result from the different efficiency of 5 eV, 6.4 eV, and (2×6.4) 12.8 eV photons at driving the photochemical reactions in which the color centers are produced. The surprising result that the fiber with the lowest germanium concentration has the highest index change is probably linked to the effect of the germanium dopant concentration on the ultraviolet absorption spectrum: Atkins *et al.* have obtained ultraviolet spectra for fibers containing 3 mol %<sup>11</sup> and 8 mol %<sup>12</sup> of germanium, similar to the fibers used here. Their results show that the Lo-Ge fiber has an initial absorption of less than 0.02 dB/μm at 193 nm, while the Hi-Ge fiber has an absorption of about 0.35 dB/μm at the same wavelength. It is the larger linear absorption of the incident laser photons occurring in the Hi-Ge fiber that is believed to prevent the increase of the index modulation to levels comparable to those observed in the Lo-Ge fiber: there are less photons available for the TP process to occur and this process is less probable (per available photon). Furthermore, the number of available reaction sites, or precursors, is different in the two cases: OP processes with photon energy below ~10 eV occur because a limited number of glass defects (GODCs in this case) have induced absorption bands below the band gap of the silica. The index increase stops when the defect population becomes depleted. In the TP case, however, the 12.8 eV quantum of energy absorbed is larger than the band gap of pure SiO<sub>2</sub> (around 10–12 eV). Therefore, the TP absorption can free an electron from the valence band into the conduction band at all SiO<sub>2</sub> molecules. This electron may recombine at the same site but may also be trapped elsewhere, thereby changing the polarizability of the glass and its refractive index. Since the photoinduced index changes observed from TP absorption of 193 nm light in pure silica glasses yields index changes smaller than  $5 \times 10^{-5}$ ,<sup>13</sup> the trapping sites for the free electrons in the results reported here must be associated with the presence of the germanium dopant. In

fact, the similarity of the index changes obtained here in Lo-Ge fibers with those obtained by low-temperature hydrogen loading in the same fiber indicates that a bond breaking photoreaction occurs at almost all germanium atoms.<sup>6</sup>

We have presented strong evidence for a different photosensitive process based on two-photon absorption of 193 nm light in germanium-doped glasses with a small linear absorption coefficient at that wavelength. The number of active reaction sites (precursors) for this process is much larger than for conventional photosensitivity arising from absorption in pre-existing GODC absorption bands near 242 or 185 nm, since the absorbed two-photon energy is above the band gap of pure silica. In contrast with common practice, increasing the initial GODC concentration prevents the two-photon process from taking place and limits the saturated index change to values lower than half of the maximum achievable. The thermal stability of fiber gratings written in this two-photon regime is similar to that obtained in the linear regime.

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