Photosensitivity and photoluminescence of Sn/Yb codoped silica optical fiber preform

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Sn/Yb codoped silica optical fiber preform is prepared by the modified chemical vapor deposition (MCVD) followed by the solution-doping method. Ultraviolet (UV) optical absorption, photoluminescence (PL) spectra under 978-nm laser diode (LD) pumping, and refractive index change after exposure to 266-nm laser pulses are obtained. There is only a little change in the PL spectra while a positive refractive index change up to 2×10^{-4} is observed after 30-min exposure to 266-nm laser pulses. The results show that both of the peculiar photosensitivity of Sn-doped silica and the gain property of Yb-doped silica fiber are preserved in the Sn/Yb codoped silica optical fiber preform. The experimental data suggest that the photosensitivity of the fiber preform under high energy density laser irradiation should be mainly due to the bond-breaking of oxygen deficient defects, while under relatively low energy density laser irradiation, the refractive index change probably originates from the photoconversion of optically active defects.

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Optical fiber gratings written in rare-earth-doped fibers have potential applications in optical telecommunication and sensor systems[1−4], because they combine signal amplification and signal processing functions in the same device. There is currently considerable interest in the investigation of a fiber with two main features, i.e., high permanent photosensitivity and good gain property, in certain wavelength windows[5]. Chiodini *et al.* reported the Er_2O_3-SnO_2-SiO_2 monolithic glasses prepared by sol-gel route[5]. Their results show that a photosensitivity comparable with that of only-tin-doped silica can be obtained together with luminescence from the $^4I_{13/2}$ level of the Er^{3+} ion similar to that observed in erbium-activated sol-gel silica. The ultraviolet (UV) induced refractive index change of the samples follows nearly the same kinetics observed in Er-free samples, which indicates that the erbium activation does not influence the structure responsible for the photorefractive process.

It has been recently found that tin-doped silica has the same order of refractive index change with Ge-doped silica while the tin concentration is two orders of magnitude lower than Ge concentration. At the same time, the induced refractive index change has better thermal stability in tin-doped silica than that of Ge-doped silica[6,7]. But the photosensitivity mechanism of tin-doped silica has not been well understood yet.

In this letter, we present the results of our investigation on the photosensitivity of Sn/Yb codoped silica optical fiber preform produced by modified chemical vapor deposition (MCVD) followed by the solution-doping method. The peculiar photosensitivity of Sn-doped silica and the gain property of Yb-doped silica are both preserved in this fiber preform. The results indicate that UV irradiation has nearly no influence on its gain property when a positive UV-induced refractive index change of 2×10^{-4} is observed. The changes in UV absorption spectra suggest that the process of photon-induced refractive index change in the fiber should depend on the energy density of UV laser pulses.

In our study, the Sn/Yb codoped silica optical fiber preform was prepared by the MCVD followed by the solution-doping method. Three layers of SiO_2 soot were deposited at about 1400 °C after the deposition of one layer of fused SiO_2. The sample was then soaked in the solution containing about 30 wt.-% $SnCl_4$ and 1 wt.-% $YbCl_3$ at room temperature for about two hours. Then the soaked soot layer was sintered into clear glass at about 1900 °C. The preform was subsequently collapsed into a solid rod with a diameter of about 10 mm in the conventional way. Slices about 1.0 mm thick with a core diameter of about 1.5 mm were cut from the preform and optically polished for absorption and Raman spectra measurement. Both end surfaces of the 150-mm-long preform were optically polished for photoluminescence (PL) measurement.

The 266-nm laser from the fourth harmonic of a Q-switched Nd:YAG laser was used to irradiate the preform. The laser pulse width was 10 ns and the repetition rate was 10 Hz. Absorption spectra of the slices before and after exposure to 266-nm laser pulses were measured using a UV-3101PC spectrophotometer (Shimadzu Corp.). A pure silica substrate was used in the reference arm to correct the Fresnel reflection. Both absorption changes were obtained by subtracting the absorption spectrum before irradiation from the absorption spectra after irradiation, respectively.

Figure 1 shows the UV absorption spectrum of the preform and its three spectral components, Peak 1 at

191 nm, Peak 2 at 225 nm, and Peak 3 at 252 nm indicated by the broken curves, which are obtained by Gaussian fitting. The inset shows the absorption spectrum of the fiber preform from 950 to 1100 nm, and the absorption peak is at 976 nm.

The absorption spectra of the preform before and after exposure to 266-nm laser pulses with low energy density (about 10 mJ/cm^2) are shown in Fig. 2. It can be seen that the absorbance below 213 nm and over 286 nm is increased after exposure and the largest negative absorption change appears at 262 nm (inset of Fig. 2). Figure 3 shows the absorption spectra before and after exposure with high energy density (about 50 mJ/cm^2). In contrast to the above observation, the absorbance within the investigated wavelength range is decreased obviously as irradiation time increases. It can be found from the inset of Fig. 3 that there is no positive change in the whole absorption band and a valley of negative absorption change appears at 256 nm after 20-min exposure. It is necessary to point out that no difference in the absorption band of Yb (around 980 nm) has been found after exposure to 266-nm laser pulses with both low energy density and high energy density.

The preform was pumped by a 978-nm laser diode (LD) with full width-at half-maximum (FMHM) of 2.4 nm. The PL from the other end of the preform was collected with an optical spectrum analyzer (AQ6317B, Ando). The PL spectra of the preform before and after irradiation are shown in Fig. 4. It can be found that the PL peaks shift toward shorter wavelength a little after irradiation, while the shapes of the spectra are similar except for a small difference below 1040 nm. The PL spectrum of Sn-free Yb-doped sample is given in the inset of Fig. 4 for comparison.

The refractive index profiles of the preform before and after exposure were measured using a preform analyzer (P104 NETTEST). In our experiment, we found the refractive index change in the core of the preform after being irradiated by 266-nm laser pulses with both low energy density (about 10 mJ/cm^2) and high energy density (about 50 mJ/cm^2). Figure 5 shows the profiles of refractive index of the preform before and after exposure to 266-nm laser pulses with 50 mJ/cm^2 for 30 min. It is observed that the maximum change of refractive index in the core of the preform is about 2×10^{-4}.

Raman spectra of the preform slices pumped with a 632.8-nm He-Ne laser were recorded by a Raman spectrometer (Labram-1B, Dilor) The Raman spectra in the core of the preform before and after irradiation (with density of 50 mJ/cm^2) comprise the typical structures of the silica Raman spectrum[8], and the cladding (pure silica) Raman spectrum is also recorded for comparison, as shown in Fig. 6. From the Raman spectra of the doping area, we could see that no any other feature peaks appeared after irradiation, but the relative intensities of two peaks D_1 and D_2 decrease obviously while the whole

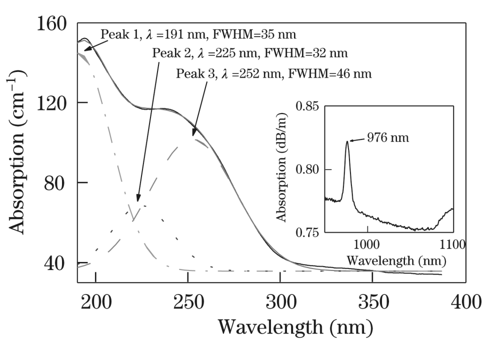

Fig. 1. UV absorption spectrum of the Sn/Yb codoped silica optical fiber preform and its three spectral components, Peak 1 at 191 nm (related to Si-ODC), Peak 2 at 225 nm (related to E' center), and Peak 3 at 252 nm (related to Sn-ODCs) indicated by the broken curves.

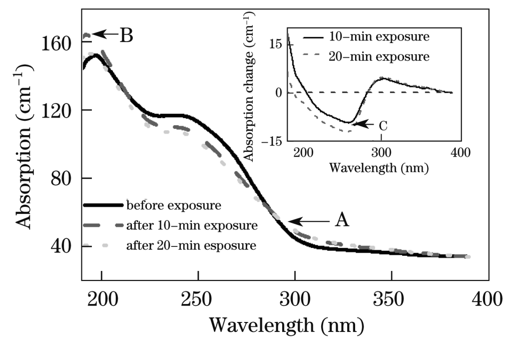

Fig. 2. Absorption spectra of the Sn/Yb codoped silica optical fiber preform before and after exposure to 266-nm laser pulses with low energy density (about 10 mJ/cm^2). The inset shows the absorption change after irradiation. Two absorption bands (A and B) appear and another band (C) is bleached.

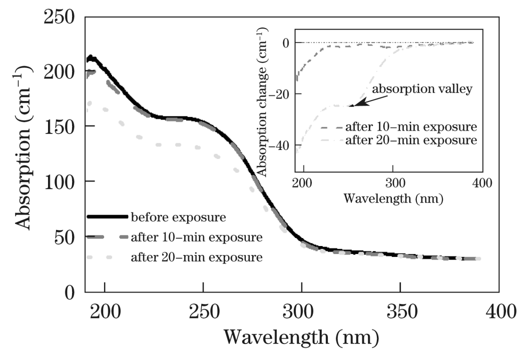

Fig. 3. Absorption spectra of the Sn/Yb codoped silica optical fiber preform before and after exposure to 266-nm laser pulses with high energy density (about 50 mJ/cm^2). The inset shows the absorption change after irradiation. An absorption valley at 256 nm appears.

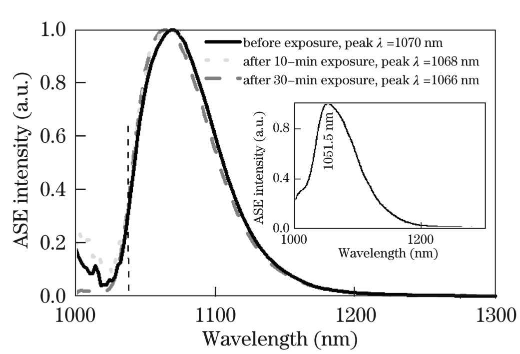

Fig. 4. PL spectra of the Sn/Yb codoped silica optical fiber preform before and after UV laser irradiation. The inset shows the PL spectra of Sn-free Yb-doped silica optical fiber.

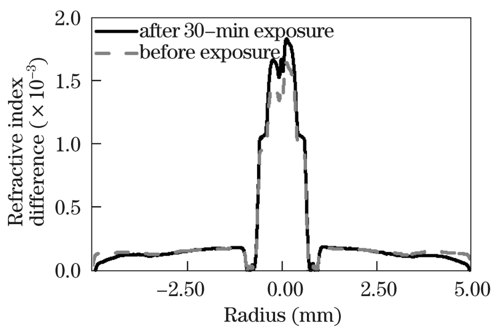

Fig. 5. Refractive index profiles of the Sn/Yb codoped silica optical fiber preform before and after exposure to 266-nm laser pulses with 50 mJ/cm^2 for 30 min.

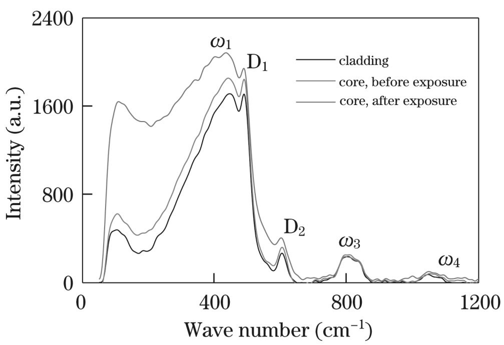

Fig. 6. Raman spectra excited at 632.8 nm in the core and cladding of the Sn/Yb codoped silica optical fiber preform before and after UV laser irradiation. D_1 and D_2 are the peaks representative of four-fold and three-fold ring tetrahedra, and ω_1, ω_3, ω_4 are the broad bands of vitreous silica.

spectrum becomes much stronger.

From Gaussian fitting (Fig. 1), it is found that the absorption spectrum consists of two kinds of components (absorption peaks at 191, 225, and 252 nm). The peak at 252 nm is related to Sn oxygen deficient centers (ODCs)[9] and the other two peaks are probably related to Si-ODC and E' center respectively. At the same time, it is observed that the investigated fiber preform has a strong absorption peak at 976 nm, which is corresponding to that of Yb-doped silica optical fibers. On the other hand, the Raman spectra (Fig. 6) confirm the lack of interaction between Yb and Sn in the preform and the absence of spurious phases, and assess the glassy state of the fiber.

The maximum refractive index change of about 2×10^{-4} has been achieved after exposure with 50 mJ/cm^2 for 30 min, as shown in Fig. 5. This means the photosensitivity of Sn-doped silica is preserved in the fiber although the maximum index change is less than that previously reported[6,7]due to the lower concentration of SnO_2 in our sample (only about 0.1 mol%). The shape of PL spectrum of the preform is similar to that of Sn-free Yb-doped sample (Fig. 4) while the peak shifts to 1070 nm. The PL peak shifts toward shorter wavelength a little after irradiation, while the shape keeps the same except for the PL spectrum below 1040 nm. The difference in the PL spectrum below 1040 nm is due to measuring error.

The above results show that the peculiar photosensitivity of Sn-doped silica and the gain property of Yb-doped silica are both preserved in the Sn/Yb codoped silica optical fiber preform. This makes the investigated preform a promising candidate with double functionality for some applications, such as optical fiber lasers and optical fiber sensors working within the wavelength from 1040 to 1100 nm.

The previous works have indicated that the photosensitivity in SnO_2:SiO_2 fibers may be related to the fiber itself (fabrication, geometry, stress, etc.)[6], and the photosensitivity of Sn-doped silica cannot be simply attributed to photo-conversion of optically active defects[9]. Our experimental results indicate that the UV-induced absorption changes in as-prepared preform are relevant to the energy density of UV laser pulses[10].

When exposed to the UV irradiation with relatively low energy density, the preform shows a new pattern of absorption change. Two absorption bands (one at 286 nm and the other below 213 nm) appear while the 256-nm band related to Sn-ODCs[11] is bleached by UV irradiation (Fig. 2). This means that the photo-conversion of optically active defects take place during UV irradiation. At present, we are not able to determine the defects corresponding to the rising bands and the detailed converting process of these optically active defects. However, the results suggest that the photosensitivity of the fiber preform should be mainly due to the photo-conversion of optically active defects and explained by Kramers-Krönig relationship[12].

UV irradiation with relatively high energy density results in a negative absorption change within the range investigated and a clear absorption valley at 256 nm. These features of the UV-induced absorption change imply that the photosensitivity of the fiber preform cannot be simply interpreted by Kramers-Krönig relationship. Moreover, after irradiation, the decrease in relative intensity of the peaks D_1 and D_2 of the Raman spectrum means the statistics of four-fold and three-fold tetrahedra rings become lower. At the same time, the whole spectrum becomes much stronger in intensity because of the existence of a strong luminescence background. This also indicates that the breaking of network bonds exists in the core due to Sn-doping[8]. Based on the above facts, it may be considered that the refractive index change in the fiber preform is mainly due to the microscopic structural modifications, which start from bond-breaking related to ODCs when irradiated by UV laser pulses with high energy density.

In summary, the peculiar photosensitivity of Sn-doped silica and the gain property of Yb-doped silica are both preserved in the Sn/Yb codoped silica optical fiber preform, which is prepared by MCVD followed by the solution-doping method. The recorded PL spectra show that UV irradiation almost has no influence on its gain property when a positive UV-induced refractive index change of 2×10^{-4} is observed. The measurement data indicate that the photosensitivity of the fiber depends on the energy density of UV laser pulses. Under high energy density irradiation, photosensitivity should mainly originate from the microscopic structural modifications starting from bond-breaking of ODCs. On the contrary, under low energy density irradiation, photo-conversion of optically active defects should play an important role in the generation of photosensitivity. Further work is needed to determinate the detailed process of photoconversion in the fiber preform .

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