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Influences of irradiation on network microstructure of low water peak optical fiber material

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ABSTRACT

A study of the influences of irradiation on network microstructure in optical fiber material by Raman and infrared spectroscopy is presented. A local doping hybrid three- and four-membered ring (3MRs–4MRs) microstructure model is proposed for the binary silica optical fiber material. Density functional theory (DFT) calculations for doping hybrid rings show that the germanium atom is easily doped among mixed rings and network interstices to form steady doping hybrid rings of network microstructure. Ge-doped 4MRs microstructure is found to be energetically more stable than 3MRs while the Ge–O bond is easier to rupture and generates color centers by the external energy effect. The theoretical calculations are validated with Raman and infrared spectra measurement of fiber material microstructure by gamma-ray irradiation. The number of the 3MRs and 4MRs, especially 3MRs, are obviously reduced with increasing irradiation doses.

1. Introduction

It is generally believed that defect centers play a major role in the radiation-induced transmission loss of various optical fibers. Those defect centers, such as E′ color center and Ge E′ color center, have an unpaired electron localized in a dangling sp^3 hybrid orbital of a Si or Ge atom. Many studies [1–7] revealed that small-ring populations have higher concentration in amorphous silicon dioxide [8–10]. Previous works have reported the influences of irradiation on various types of fibers [11,12] and calculation models of silicon dioxide microstructure [9,12–15]. However, the influence of irradiation on optical fiber material network microstructure is not yet clear, and there are no detailed theoretical studies of the micro-structural transformation [16]. In order to understand the mechanism of the irradiation effect on Ge-doped optical fiber material, we report infrared (IR) spectrum and Raman spectroscopy analysis of low water peak single-mode optical fibers irradiated by cumulative doses of about 1 kGy and 5 kGy. The irradiation-induced effects on vibration bond and ring microstructure can be clearly described by our experiments.

For optical fiber material, germanium atoms are doped into irregular vitreous silica and form a stable network structure. Many papers have reported that the $(1-x)$ SiO_2-x GeO_2 glasses binary system is composed of SiO_4 and GeO_4 tetrahedral units. The Si–O and Ge–O bond distribution is confirmed by the large number of bridging oxygen with T–O–T (T Si or Ge) bond linkage. Some analysis results [7–21], such as Raman and IR spectroscopy can be assigned to identify Si–O–Si or Ge–O–Ge vibrations, and Ge–O–Si symmetric stretching. So the Ge-doped silicon dioxide binary system is homogenous with Si–O–Si, Si–O–Ge and Ge–O–Ge bonds and forms hybrid network structure rather than phase segregation. Then a large number of bridging oxygen with T–O–T (T Si or Ge) bond linkages finally result in the formation of network structure [22,23]. In this paper, we propose a new structure model based on hybrid three- and four-membered ring (3MR–4MR) structure; this has tetrahedral-like configurations containing edge-sharing 2MR. The restricted and unrestricted Becke-type three parameter Lee–Yang–Parr (B3LYP) function with a 6-31G (d) and 6-31G + (d) basis set [24,25] is used and the changes of vibration band and ring microstructure with charge are analyzed. The increase of irradiation-induced attenuation is due to the demolition of network microstructure and the transformation of the ring structure in optical fiber material. These may provide theoretical evidence of pre-irradiation [26], photobleaching and heat treatment to enhance radiation hardness properties of optical fiber material [27,28] from molecular microstructure level.

2. Experimental section

Optical fiber samples are treated by gamma ray irradiation with a cumulative dose of about 1 kGy and 5 kGy from Cobalt-60 source at room temperature (Irradiation Center at Medical College of Soochow University), respectively. Spectral optical losses, both before and after irradiation, for the low water peak optical single-mode fiber (ITU-T G.652D, 500 m in length, Jiangsu Fasten Photonics Co., Ltd.) are measured by the cutback technique using a broadband optical spectrum

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analyser (YOKOGAWAAQ6315A) in the 900–1600 nm wavelength region with a spectral resolution of 0.2 nm. The germanium concentration in the fiber core of standard single-mode fiber is less than 10 mol%. The GeO_2-doped core diameter is about 8 μm.

Fourier transform-infrared spectra of the optical fiber samples are recorded with a spectrometer (AVATAR 370 FT-IR). A conventional KBr disc technique is employed to measure the infrared (IR) spectra in the frequency range from 400 cm^{-1} to 2000 cm^{-1} with a spectral resolution of 4 cm^{-1}. Each sample is prepared in the same form as a polished naked fiber with the same weight of about 5.0 mg. The samples are crushed together with standard KBr by 'manau' mortar under a dry atmosphere, and then pressed into discs with 1 mm thickness.

The Raman spectra of the optical fiber samples are measured by a 'Renishaw in Via' plus laser Raman spectrometer in the range from 200 cm^{-1} to 1000 cm^{-1} at 0.5 cm^{-1} spectral resolution. Each sample in the form of polished naked fiber was severed by an optical fiber cleaver, and the optical fiber cross section was excited with an argon ion laser light source. The Raman cross-section spectra are obtained from the surface with a spot size of about 100 μm.

3. Results

The loss spectra of the pre-irradiated and irradiated low water peak single-mode (SM) optical fiber (ITU-T G.652D) are shown in Fig. 1. The irradiation-induced attenuation increases with increasing irradiation doses, due to influences of irradiation on the network microstructure of the optical fiber material and structure demolition.

Fig. 2 shows IR spectra of the pre-irradiated and irradiated optical fiber samples; these exhibit three main absorption bands at 1100, 800 and 480 cm^{-1}, which are assigned to asymmetric stretching, symmetric stretching and bending oscillations of the Si–O–Si bonds, respectively [8,29]. It should be noted that the IR spectra of optical fiber samples are irradiated with cumulative doses about 1 kGy and 5 kGy, respectively. The differences that can be seen are that the bending motion absorption peak at 480 cm^{-1} band is somewhat weakened, and the Si–O–Si symmetric stretching oscillation absorption peak at 800 cm^{-1} band is distinctly weakened as compared with the corresponding un-irradiated optical fiber sample. Although the Si–O–Si asymmetric stretching band becomes narrow, especially on the higher-frequency side of the band with increase of irradiation dose, the intensity of the Si–O–Si band asymmetric stretching oscillation at 1100 cm^{-1} is basically unchanged. In fact, all IR spectral features of the optical fiber samples irradiated with different doses gamma rays change only a little.

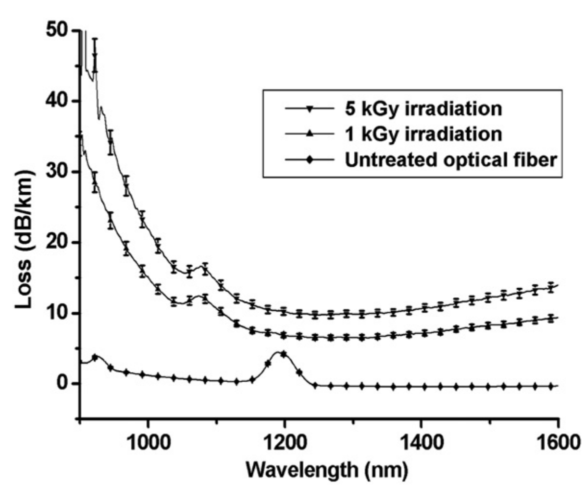

Fig. 1. The spectral loss of the treated and untreated low water peak single-mode optical fiber.

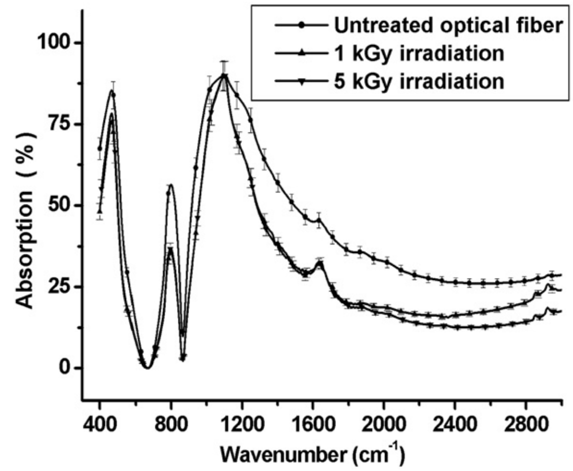

Fig. 2. Infrared absorption spectra of optical fiber material before and after irradiation.

For fiber-optic communications, amorphous silica is an important material in low water peak single-mode optical fibers. The Si–O and Ge–O distribution functions have revealed that the binary system is composed of SiO_4 and GeO_4 tetrahedral units, which are not randomly scattered, but homogeneously distributed in the matrix. The network structure also consists of a large number of SiO_4 tetrahedron unites, which contain irregular rings of order $n = 2, 3, 4\ldots$, where n is the number of Si atoms in a ring, and at the same time determines the size of ring structure [30]. This description of network structure is only to visualize the structure model, and some form of network interstices will be found within the network structure. Then the doping germanium atoms are embedded into them. That is, germanium atoms are doped into the inner network structure, or they replace the site of the original silicon atom, and then they jointly form a binary system. For amorphous silica optical fiber material, there are mainly a large number of hybrid 3MR and 4MR units. The geometry and the statistics of these rings can be precisely determined by some testing methods [29]. For example, Raman spectroscopy is routinely used for investigating molecular structure vibration properties of various materials [8,31,32], and now is used to ascertain the micro-structural change of the optical fiber material. Raman spectra of the low water peak optical fiber samples, irradiated and un-irradiated, are shown in Fig. 3. It is found that the four sharp peaks marked $\omega_1 = 440\ cm^{-1}$, $\omega_2 = 800–820\ cm^{-1}$, $D_1 = 495\ cm^{-1}$ and $D_2 = 606\ cm^{-1}$ can be observed with Raman spectroscopy [10,33,34]. The peaks D_1 and D_2 arise from the symmetric stretch vibration of regular 4MRs and planar

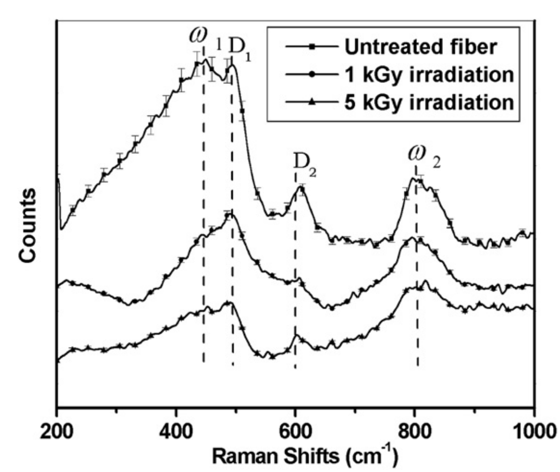

Fig. 3. Raman cross-section spectra of optical fiber materials under varying irradiation conditions.