

Mechanism of E' center induced by γ ray radiation in silica optical fiber material (Postprint)

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Abstract

The characteristics of the best known defect centers E' in silica optical fiber material irradiated with γ ray were investigated by ESR at room temperature. A mechanism model of production of the E' center defect was established. The production of E' center includes two processes creation and activation. The strained bonds (or oxygen replacement) in silica networks lead to the creation of new defects whose concentration increases linearly with the dose. The pre-existing defects produce the activation, which tends to saturation. According to this model, the relation of E' center concentration changing with irradiation dose was obtained theoretically. The results are in good agreement with the experimental results.

Full Text

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Mechanism of E' center induced by γ ray radiation in silica optical fiber material
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Abstract The characteristics of the best known defect centers E' in silica optical fiber material irradiated with γ ray were investigated by ESR at room temperature. A mechanism model of production of the E' center defect was established. The production of E' center includes two processes creation and activation. The strained bonds (or oxygen replacement) in silica networks lead to the creation

of new defects whose concentration increases linearly with the dose. The pre-existing defects produce the activation, which tends to saturation. According to this model, the relation

of E' center concentration changing with irradiation dose was obtained theoretically. The results are in good agreement with the experimental results. Key words E' centers, γ ray radiation, Silica optical fiber material, ESR, Mechanism model

However, the mechanism of defect formation is not very clear until now. Therefore, it is essential to study defect center characteristics deeply, which is also in radiation environments, the characteristics of silica helpful for improving the performance of material in optical fibers are affected seriously because the radiation environment. F. R. Galeener et al.[18] have radiation can induce defect centers in silica material, suggested a creation plus activation model to fit the such as E' centers, non-bridging-oxygen hole centers, experiment results of ESR signals in vitreous silica by per-oxy radicals, and self-trapped holes. As the best X-rays from Cu-target tube. In our previous paper[16], known defect, E' center plays a major role in the we proposed a kinetic model for the radiation-induced radiation-induced transmission loss for silica optical production of the intrinsic point E' defect center. The fibers. Since R. A. Weeks[1] first reported the ESR relation of E' center concentration changing with dose spectrum of E' center in 1956, many works have been obtained theoretically. tried to understand the basic mechanisms of radiation- In this paper, the characteristics of E' centers in induced defect formation in silica glasses[1-11]. silica optical fiber material irradiated with γ rays at Recently, D. L. Griscom[2] gave a review about half a room temperature are investigated and measured by century of research on radiation-induced point defects using ESR. We obtain the relationship between the E' in pure and doped glassy silica. Our previous center concentration changing and irradiation doses works[12-17] discussed the influences of thermal accumulation by the experiments, which is in good annealing temperatures on irradiation induced E' agreement with the theoretical result. The mechanism centers in silica glass, and influences of irradiation on of the radiation-induced E' center in optical fiber network microstructure, formation and conversion of material has also been explained by these results. defect centers of low water peak optical fiber. —————Supported by National Program on Key Basic Research Project (973 Program, No.2012CB723405), Natural Science Foundation of China (No.60937003, 61077068, 61275090, 61275051, and 61027015) and Shanghai Natural Science Foundation (No.12ZR1411200) * Corresponding author. E-mail address: tywang@mail.shu.edu.cn Received date: 2013-02-28

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2 Experimental 3 Results and discussion All samples in our experiments were made of high- The E' centers generated by γ ray irradiation come purity silica, which produced by Shanghai Xinhua from pre-existing extrinsic defects and weakly Glass, Inc., but sample of Group 1 and Group 2 were bonding states of

normal Si-O-Si bonds in silica from two different batches. For ESR measurement, the glasses[11]. The pre-existing extrinsic E' center was an samples are made into rods with a 2-mm diameter and oxygen vacancy, which is related to the trapping of a a 2-cm length. The ESR spectra were obtained at room hole at a neutral oxygen deficient center as expressed temperature on Varian E112 spectrometer (Shanghai by Eq.(1). The other process of the E' center creation Institute of Applied Physics, Chinese Academy of is the cleavage of a strained Si-O bond in silica glasses. Sciences), operating at 9.53 GHz (X band), and The pair generation of E' centers and NBOHC' s from employing a modulation field of 100-kHz frequency. intrinsic Si-O bonds occurs commonly in all the All spectra of the same group samples were recorded samples irradiated by rays. This mechanism model is on the same chart by changing only the amplifier gain. expressed by Eq.(2). In addition, the strained Si-O For Group 1, center magnetic field strength was 3412 bonds can become to pre-existing E' center by oxygen Gauss, sweep range was 100 Gauss, response time replacement, as expressed by Eq.(3). constant was 0.25 s, and microwave power was 50 Si-Si +hν→ Si • +Si+ +e-(1)

mW. In Fig.1(a), the amplifier gain was 1.25e3 for 50 Si-O-Si +hν→ Si • + • O-Si (2) kGy sample; and 5e4, for initial sample. For Group 2, Si-O-Si +hν→ Si-Si + O (3) center magnetic field strength was 3405 Gauss, sweep The production of E' center includes two processes : [16]

range is 50 Gauss, response time constant was 0.128 s, the creation of new defects, NC(D), and the activation and microwave power was 50 mW. In Fig.1(b) the of pre-existing defects, NA(D). The strained bonds (or amplifier gain was 3.2e3. The intensities of the oxygen replacement) in silica networks lead to the observed signals were normalized by the standard creation of new defects, and the pre-existing defects pitch signal. Samples were irradiated with rays from produce the activation. Therefore, the total defect a 60Co source at Shanghai Hexin Irradiation Factory. concentration can be written as Eq.(4)[16]. The irradiation doses are from 1 kGy to 50 kGy with a dose rate 2 kGy/h. The initial sample is not irradiated.

$$k_c k_p N C k_c^2 N C k_c k_p N p (0) k_p^2 N p (0) 1 e (k_p k_e) D N (D) N C (D) N A (D) D (4) k_c k_p (k_c k_p)(k_p k_e)$$

where k_c , k_p and k_e represent creation rate, activation rate and the rate of recombination of new defects, $N(D) = k_c k_p N C k_c k_p D k_c^2 N C (k_c k_p)(k_p k_e) (k k) D 1 e p e (6)$ respectively. N_c and $N_p(0)$ are concentrations of the strained bonds and pre-existing defects. In Eq.(4), the first term on the right side is the process of defect We measured ESR spectra of the initial sample creation, the concentration increases linearly with the and irradiated samples at the room temperature. Fig.1 dose. The second term shows the process of defect shows the ESR spectra of E' centers of Group 1 and activation, which leads to defect concentration to tend Group 2 samples before and after 50 kGy irradiation. to saturation. If $k_c=0$, that is, without considering the It can be seen that the ESR spectra have the same g creation

of new defects, and value as the E' center characterized by $g = 2.0006$. $N(D) = k_p N_p(0) + (k_p - k_e) D$ (5) Therefore, the observable ESR signal is attributed to E' color centers. The expression in Eq.(5) is the same as the Ref.[18]. The initial sample of Group 1 has a weak Without considering the preexisting defects, $N_p(0) = 0$, signal of E' center before irradiation (Fig.1(a)), but the we can get from Eq.(4). initial sample of Group 2 has not any ESR signals

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(Fig.1(b)), indicating that the structure of samples of Group 1 and Group 2. The E' center concentrations Group 2 is more stable than Group 1. increase with irradiated doses obviously, and the simulated and experimental results have a good agreement for either Group 1 or Group 2. Moreover, this increase shows nearly linear trend for Group 1 (Fig.2(a)), and nonlinear trend for Group 2 (Fig.2(b)) in the dose range from 0 to 60 kGy.

Fig.1 ESR spectra of E' centers irradiated with 50 kGy and the initial one. (a) Group 1, (b) Group 2.

According to a double integration of the derivative spectra, the E' concentrations with different irradiated doses are calculated (Fig.2). Based on these experimental results, the parameters k_c , k_p , k_e and N_c , N_p used in Eq.(4) of the above theoretical model are determined, which are shown in Table 1. Fig.2 shows Fig.2 Simulated and experimental results of E' center that the E' center concentrations change with doses for concentrations changing with doses. (a) Group 1, (b) Group 2.

Table 1 Parameters used in simulation

$N_p(0)/\text{cm}^{-3}$ N_c/cm^{-3} $k_c/\text{cm}^2 \cdot \text{kGy}^{-1}$ $k_p/\text{cm}^2 \cdot \text{kGy}^{-1}$ $k_e/\text{cm}^2 \cdot \text{kGy}^{-1}$ Group
 1 1.84×10^{15} 3.20×10^{17} 2.58×10^{-33} 8×10^{-38} 0×10^{-3} Group
 2 2.84×10^{14} 2.72×10^{17} 2.58×10^{-33} 8×10^{-38} 42.0×10^{-10}
 The simulated curve can be analyzed by Eq.(4). curves at higher doses ($D > 20$ kGy) for Group 2. Fig.3(a) shows that the number of creative E' center $NC(D)$ increases faster than the activated E' center $NA(D)$, and the combined E' center concentration $N(D)$ increases linearly with radiation doses, indicating that the creation of new defects is the main process for Group 1 in this dose range. In Fig.3(b), the number of activated E' center $NA(D)$ increases rapidly at low doses ($D < 20$ kGy), then tends to saturation; the number of creative E' center $NC(D)$ keeps linear increasing in the whole dose range. It indicates that all pre-existing defects in the first process were activated, thus accounting for the initial nonlinear region of combined $N(D)$ curves; in the second process, the strained bonds were ruptured to generate new E' center defects while activated E' center became saturation, Fig.3 Simulated curve by theoretical model. (a) Group 1, (b) thereby accounting for the linear portion of $N(D)$ Group 2.

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The above theoretical model is called as concentration increases linearly with the radiation activation plus creation model[18], whose mathematical doses. For

Group 2, activation dominates at low doses; expression is very simple as Eq.(4). The important and creation, at high doses, so E' center concentration parameters were determined as follows: N_c , the increases nonlinearly at first, then linearly with concentration of the strained bonds, $N_p(0)$, the radiation doses. The simulated results are in good concentration of pre-existing defects, k_c , k_p and k_e , the agreement with the experimental ones. This theoretical rate to create new defects, the rate to activate pre- analysis is simple, and can fit experimental results by existing defects and the rate of recombination of new adjusting simulation parameters for each kind of defects. All determined parameters used in simulation samples. The structure information of samples can be are listed in Table 1. It can be found that in the inferred from the determined parameters. The creation samples of Group 1, there are more pre-existing plus activation model can separate the two processes. defects and more strained Si-O bonds than Group 2. References So the samples' structure of Group 2 is more stable than Group 1, which also can be seen from ESR 1 Weeks R A. J Appl Phys, 1956, 27: 1376-1381.

signals of the initial samples in Fig.1. The rate of 2 Griscom D L. J Non-Cryst Solids, 2011, 357: 1945-1962.

activation of pre-existing defects is greater in the 3 Griscom D L, Levy P. In proc. radiation effects of optical

samples of Group 1, while the rate of recombination of materials, The Society of Photo-optical Instrumentation

new defects is smaller than Group 2. Although the rate Engineers Confer, Bellingham, WA, 1985, 541, 38-59.

of creation of new E' centers is the same in two groups, 4 Griscom D L, Galeener F L, Weber M J. In Proc. Defects

the number of strained bonds in Group 1 is more than in Glasses Symp, Pittsburgh, PA, 1986, 213-221.

in Group 2. For Group 1, creation is the main process; 5 Zatsepin A F. J Non-Cryst Solid, 2011, 357: 1856-1859.

for Group 2, activation dominates at low doses, and 6 Skuja L. J Non-Cryst Solid, 1998, 239: 16-48.

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Although the samples of Group 1 and Group 2 4886-4890.

are made of high-purity silica, and produced by the 8 Devine R A B, Arndt J. Phys Rev B, 1989, 39:

same company, there is still very small difference in 5132-5138.

the microstructure for different batches. The above 9 Agnello S, Nuccio L. Phys Rev B, 2006, 73: 115203.

theoretical analysis shows that the samples of Group 2 10 Friebele E J, Griscom D L, Marrone M J. J Non-Cryst

have more stable microstructure than Group 1 since Solid, 1985, 71: 133-144.

they have fewer pre-existing defects and strained 11 Imai H, Arai K, Isoya J, et al. Phys Rev B, 1993, 48:

bonds. So the radiation hardness of Group 2 is better 3116-3123.

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Note: Figure translations are in progress. See original paper for figures.

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