Improved silica fiber with enhanced ultraviolet transmission

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Received August 21, 2006

When a silica optical fiber is used for transmitting ultraviolet (UV) light, the problems associated with the damage and transmission deterioration of silica fiber in the UV region need to be solved in the fabrication process. In this paper, an improved silica fiber fabrication process was presented to enhance UV transmission, which combined the UV pre-irradiation on high-OH concentration preform with heat treatment while drawing fiber. The impact of the structural defects and color centers was diminished greatly by the new method of fabrication. The experimental results accorded with the theoretical analysis, and transmission was improved about 0.4—0.7 dB/m for wavelength from 350 to 400 nm.

OCIS codes: 060.2800, 060.0060, 060.2280, 060.2330.

Extensive applications of excimer lasers and other strong ultraviolet (UV) sources have promoted many investigations of how to solve the deterioration of silica fiber transmission properties in the UV region, particularly for high-power and short-wavelength UV transmission. Up to now, a number of silica fibers have been widely expanded to the applications of UV transmission in the field of curable resin, microfabrication, medical treatment, excimer laser lithography, and even some military affairs[1−3].

Many previous literatures reported that only high-OH concentration fibers were suitable for UV-laser application, since low-OH silica material would suffer from strong UV-absorbing due to color centers[4]. In addition, UV irradiation can result in the structural defects in the silica glass, which decreases the fiber transmission[5]. The transmission loss of silica glass becomes more remarkable, as UV wavelength becomes shorter and its light power becomes higher. Even these silica materials show unwanted solarization[6] leading to transmission decrease during irradiation. The reason for the solarization is the creation of color centers.

In order to reduce transmission loss of silica glass due to UV irradiation, or to improve resistance of silica glass to UV ray, some approaches have been introduced. A basic approach[7] is to optimize the high-OH core silica material properties. They developed an improved all silica preform for the production of silica fiber with drastically improved resistance to UV-light. However, the transmission improvement of silica fiber is restricted by saturation of OH doping concentration. Hydrogen doping[8] is another well-known approach to improve the UV performance of silica fibers. High hydrogen doping concentration in the order of 10^{19} cm^{-3} is needed to improve UV transmission. To load the silica fibers with such high hydrogen doping concentration they need to be stored for several weeks in a high pressure cylinder containing the gas. The approach of loading hydrogen in the fibers is not only expensive but also time-consuming. The method of combining pre-irradiation upon the silica fiber using an ArF excimer laser with annealing treatment[9] can improve the UV transmission effectively. But the pre-irradiation process was for the silica fiber directly and the annealing treatment needed an additional process compared to the technique presented in this paper.

We presented a new method of manufacturing an improved UV silica fiber with heat treatment following UV irradiation, so that the transmission loss of high-OH silica fibers could be greatly reduced. The structural defects and color centers were purposefully caused in silica glass by irradiating silica glass preform with UV ray and then could be removed by heat treatment while drawing fibers. In the following, the mechanism of fabricating such improved silica fiber is described firstly. Then, the measurement result of the transmission loss spectrum of the improved silica fiber will be presented. Finally, the comparison of the fiber with and without UV irradiation will be discussed.

When a silica glass fiber is irradiated by UV ray, especially shorter wavelength such as ArF (193 nm) excimer laser beam, various structural defects and color centers are generated. Most color centers are the E' centers which consist of an unpaired electron on a silicon bonded to three oxygens ($\equiv$ Si·), and nonbridging oxygen hole centers (NBOHCs) which have a hole trapped on a nonbridging oxygen ($\equiv \mathrm{Si-O}\cdot$)[10,11]. The symbol ($\equiv$ Si) represents a silicon atom bonded to three oxygens in the glass network and the dot denotes an unpaired spin. Such color centers can cause the transmission deterioration for UV wavelength range.

In order to reduce the influence of the structural defects and color centers, we proposed an improved fabrication method for UV transmission. The whole fabrication procedure is shown in Fig. 1.

First, we purposefully irradiated the preform by UV ray, so that some color centers and structural defects were formed, then the heat treatment was applied during drawing fiber process. When silica glass preform was irradiated by UV ray, the UV photons would have

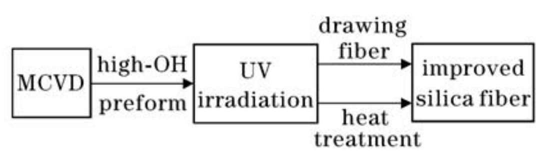

Fig. 1. Fabrication process of the improved silica fiber.

1671-7694/2006/120687-03 http://www.col.org.cn

sufficient energy to cut strained Si-O bonds resulting in E' centers and NBOHCs[7]

$$\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si} \cdot + \cdot \mathrm{O} - \mathrm{Si} \equiv . \quad (1)$$

Radiolysis of a Si − H bond was also proposed to form E' center as expressed by[12]

$$\equiv \mathrm{Si} - \mathrm{H} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si} \cdot + \mathrm{H}^0. \quad (2)$$

On the other hand, E' center was considered to be related to the trapping of a hole at oxygen-deficient center (ODC)[13] as

$$\equiv \mathrm{Si} - \mathrm{Si} \equiv \xrightarrow{h\nu} \equiv \mathrm{Si} \cdot + {}^{+}\mathrm{Si} \equiv . \quad (3)$$

Because of these color centers and structural defects caused by UV irradiation, the induced losses of silica fibers increase, which cause the transmission properties to be worse.

The heat treatment method could be used to produce a structural relaxation of the silica fiber and decrease the amount of color centers[14]. During the drawing fiber process in the high temperature furnace, heat treatment cured the silica glass material, which resulted in bond angle change of Si − O − Si network in the silica fiber and significant decrease of centers and defects. The heat treatment process can be described by

$$\equiv \mathrm{Si} \cdot + \mathrm{H}_2 \equiv \xrightarrow{\text{heat treatment}} \equiv \mathrm{Si} - \mathrm{H} \cdot + \mathrm{H}^0, \quad (4)$$

$$\equiv \mathrm{Si} - \mathrm{O} \cdot + \mathrm{H}_2 \equiv \xrightarrow{\text{heat treatment}} \equiv \mathrm{Si} - \mathrm{OH} \cdot + \mathrm{H}^0. \quad (5)$$

After the heat treatment process, the color centers and structural defects were partially removed and the structural relaxation of Si − O − Si bond angle occured in silica fiber. The average Si − O − Si bond angle depends on the heat treatment temperature of silica fiber[15]. The Si − O − Si bridging bond angle increases with heat treatment temperature increasing.

Based on the above whole fabrication procedure, a high-OH concentration silica fiber preform with 10-mm diameter and the content of OH almost 700 ppm was fabricated by modified chemical vapor deposition (MCVD) technique firstly. Then the preform was equally cut into two segments. One was drawn into the UV fiber, another was purposefully treated with radiation by UV source (model: ZWS UV lamp) with 253.7-nm wavelength. The segment was rotated during UV treatment process in order to irradiate the preform uniformly.

Some factors have to be considered in UV irradiation process. The irradiation wavelength, irradiation period, and irradiation intensity should be matched properly and keep constant during irradiation process. According to the result of our experiment, a shorter irradiation time was required for shorter wavelength and higher intensity source whereas a longer irradiation time was required for long wavelength and low intensity source. In the fabrication process, we found that about 20-hour irradiation was the best choice for the ZWS UV lamp source.

During the high-temperature process, the argon gas flow was blasted into the fiber drawing furnace to prevent the furnace from undergoing any reaction with air.

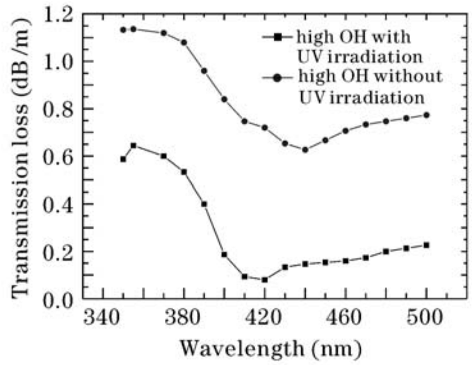

Fig. 2. Comparison of the transmission loss spectra per meter for high-OH UV fiber with and without UV irradiation.

The heat temperature should keep constant that ranged from 1850 to 2000 °C during the whole process. Immediately after the fiber drew with heat treatment, the fiber was taken out of the hot furnace and laid in the room temperature. They would cool down within several minutes. The fiber diameter was measured to be 150 μm.

The above high-OH concentration fibers with and without UV-light irradiation were tested using cut-back method. First the transmission spectrum of 10-m-length fiber was measured by optical spectrum analyzer (Model: MS9701B of Anritsu). Then the fiber of 3-m length was cut away and the transmission spectrum of 7-m-length fiber was measured also. Finally the difference of two results was recorded in optical spectrum analyzer, which represented the transmission loss spectrum for 3-m-length fiber. The transmission loss spectra per meter of the two different type fibers were shown in Fig. 2.

From Fig. 2, it can be seen that there is distinct difference between fibers with and without UV irradiation. The most dramatic difference is about 0.4—0.7 dB from 350 to 400 nm, which proves the better transmission properties for high-OH concentration silica fibers treated by our technique. The method is also suitable for low-OH silica fibers, and the enhanced effect of UV transmission is about same. The high-OH silica fibers have lower UV transmission loss than low-OH ones because UV transmission of silica fibers with high-OH concentration is intrinsically better.

In conclusion, a new method was investigated for improving silica fiber transmission in the UV range. UV irradiation and heat treatment were combined for high-OH concentration core silica fiber to decrease the amount of color centers and structural defects. As shown in the experimental result, after the preform exposure to UV irradiation, many color centers and structural defects were purposefully generated in the silica materials. Then during the succeeding heat treatment process, the color centers and structural defects were removed partially and the SiO_2 molecular structure was also relaxed. The improvement of transmission loss was obtained about 0.4—0.7 dB/m in wavelength range from 350 to 400 nm. Because of the good compatibility with the traditional MCVD process, this simple and cheap technique can hopefully be applied to commercial production.

This work was supported by the National Natural Science Foundation of China (No. 60577043 and 60477032) and the Shanghai Leading Academic Discipline Project (No. T0102). T. Wang's e-mail address is tywang@mail.shu.edu.cn.

References

1. G. Lu, G. F. Schötz, J. Vygra, and D. Fabricant, Proc. SPIE **3355,** 884 (1998).
2. G. Zhang, X. Li, S. Xu, J. Dong, and Y. Wei, Acta Opt. Sin. (in Chinese) **14,** 1068 (1994).
3. P. Karlistchek, G. Hillrichs, and K.-F. Klein, Opt. Commun. **116,** 219 (1995).
4. K. Kajihara, Y. Ikuta, M. Oto, M. Hirano, L. Skuja, and H. Hosono, Nuclear Instruments and Methods in Physics Research B **218,** 323 (2004).
5. B. Skutnik, W. Neuberger, J. Castro, V. P. Pashinin, L. M. Blinov, V. I. Konov, and V. G. Artjushenko, Proc. SPIE **1649,** 55 (1992).
6. B. J. Skutnik, Spectroscopy **16,** 78 (2001).
7. J. Vydra and G. F. Schötz, Proc. SPIE **3596,** 165 (1999).
8. P. Karlistchek, G. Hillrichs, and K.-F. Klein, Opt. Commun. **155,** 376 (1998).
9. K. Saito, A. J. Ikushima, T. Kotani, and T. Miura, Opt. Lett. **24,** 1678 (1999).
10. H. Imai and H. Hirashima, J. Non-Cryst. Solids **179,** 202 (1994).
11. Q. Zhou, L. Liu, L. Xu, W. Wang, J. Qiu, C. Zhu, and F. Gan, Chin. J. Lasers (in Chinese) **32,** 119 (2005).
12. H. Imai, K. Arai, J. Isoya, H. Hosono, Y. Abe, and H. Imgawa, Phys. Rev. B **48,** 3116 (1993).
13. H. Nishikawa, R. Tohmon, and Y. Ohki, J. Appl. Phys. **65,** 4672 (1989).
14. B. Malo, J. Albert, D. C. Johnson, F. Bilodeau, and K. O. Hill, Electron. Lett. **28,** 1598 (1992).
15. E. Wendler, U. Herrmann, W. Wesch, and H. H. Dunken, Nuclear Instruments and Methods in Physics Research B **116,** 332 (1996).