Resistivity for deep-UV laser irradiation in fluorine doped silica glass fiber

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ABSTRACT

Optical fibers for propagating deep ultraviolet light were developed using fluorine doped silica glasses called modified fused silica. Optimizing the fiber drawing conditions improved the transmission of the fiber in the deep UV region. The transmittance of the fiber at 193 nm reached more than 65% per 1 m long without reflection loss. Significant absorption bands from defects were not observed throughout the wavelengths of the deep UV-visible-infrared region. Hydrogen-impregnation into the fibers suppressed the degradation of the transmission induced by irradiating with an ArF excimer laser and 4th harmonic generation of Nd:YAG laser . Transmission in the DUV region and resistance to laser irradiation were drastically improved compared to high OH silica fibers.

Keywords: Optical fiber, deep UV, silica glass, modified fused silica

1. INTRODUCTION

Industrial applications using deep UV light stimulate the need for optical fibers to transmit deep UV light energy. The flexibility of optical fibers, in term of supplying light power, provides compact and adaptable irradiation systems for applications such as excimer laser lithography for semiconductors and material processing by laser ablation. However, optical fibers that possess both a high transparency and a high resistivity to deep UV light have yet to be achieved. Commercially obtained UV fibers that use high-OH-silica glass sustain immediate damage during the UV light propagation. Thus, applications of these fibers are restricted to a small field [1].

In our previous work, we fabricated optical fibers using fluorine doped silica glass called “modified fused silica”, which was developed for vacuum ultraviolet (VUV) lithography of optical materials [2,3]. The modified fused silica glass, characterized by being F-doped and OH-free, exhibits a high optical transmittance in VUV region and an excellent resistance to color center formation by irradiating with DUV light [4,5]. Fluorine doping is effective for removing strained Si-O-Si bonds, which govern optical transparency in the VUV region and radiation sensitivity [4,5]. In the present work, we investigated the detailed properties of the fiber to improve the transmission and UV-resistance. Also, these fibers were experimentally compared to the high OH silica fibers.

2. EXPERIMENTAL

Core glass rods were fabricated by a vapor phase axial deposition (VAD) method. Then, the core rod was shaped to approximately ~25mm in diameter and ~40cm in length and covered with a clad glass tube by a rod-in-tube technique. The core glass contained ~200-ppm fluorine and ~5-ppm OH. The clad glass contained 10,000-ppm to 20,000-ppm fluorine and less than 1-ppm OH (see Fig. 1). An electron probe microanalyzer (EPMA) and infrared absorption spectroscopy measured the fluorine and OH contents in the glass, respectively. The refractive index difference, measured at a He-Ne laser wavelength, was 0.005 to 0.01. Thus, the calculated numerical aperture was 0.12 to 0.22.

The perform rods were drawn to form step index type multimode fibers with clad diameters of 200 μm to 1100μm and 180 μm to 1000μm core diameters. The drawing temperatures ranged between 1800°C - 2000°C and the drawing speed from 0.5 to 50 m/min. To impregnate H_2 after drawing, the fibers were immersed in a 10~100 MPa hydrogen atmosphere at room temperature for 5 to10 days.

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The transmission spectra of the fibers were measured by a cutback method [6] using a Seya-Namioka type VUV spectrophotometer (Bunko-Keiki Co., Ltd.), and a conventional Czerny-Turner-type monochromater system (JASCO) measured the visible-infrared region. The cutback length of each fiber was 1 m from the total length of ~2 m. We used a deuterium lamp and a halogen lamp for light source of UV and VIS-IR region, respectively. The intensity of the incident light to the fiber was ~0.1 mW. Concentration of hydrogen in the fibers were measured by Raman backscatter methods using second harmonic generation of Nd-YAG laser.

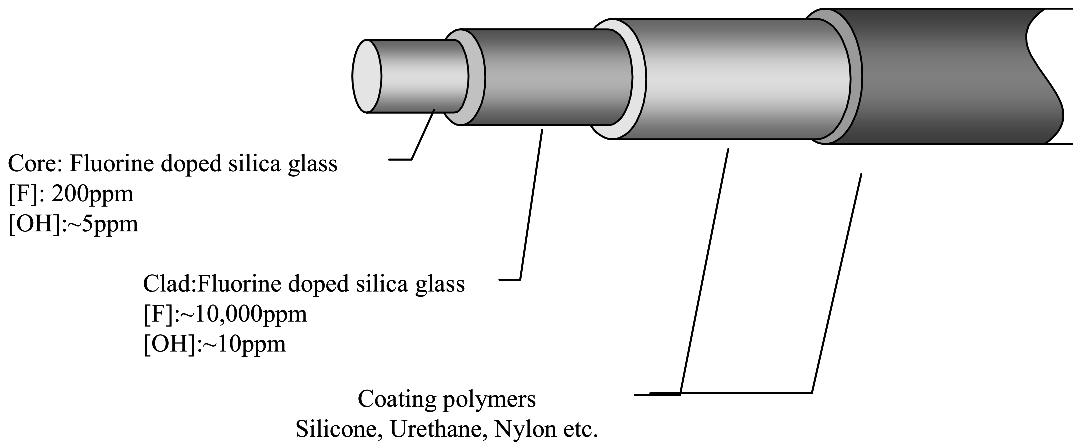


Fig. 1 Structure of the fluorine doped silica glass fiber.

3. RESULTS AND DISCUSSION

3.1. Transmission of fluorine doped silica fibers

Figure 2 shows a typical optical loss spectrum of a fabricated fiber in comparison with conventional high-OH silica fiber. The fiber absorption abruptly increased around 200 nm and a peak, which was assigned to higher order harmonics of OH stretching vibrations, appeared in the infrared region (1380 nm) [7].

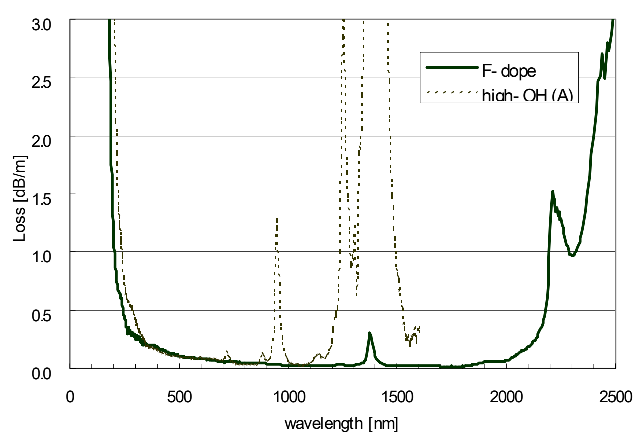


Fig. 2. Typical optical loss spectra of a fluorine doped silica fiber (solid line) and conventional high-OH silica fiber (dashed line).

The fluorine doped silica glass fibers were strongly dependent on the fiber drawing conditions. Figure 3 shows the transmission spectra of the fibers drawn under various conditions. Strong absorption bands were observed with a drawing temperature and speed of 2000 °C and 50 m/min, respectively (dotted line in Fig. 3), around 220 nm and 250 nm. A wide slope of the transmission was also observed around 260 nm to 350 nm. Similar features were noted when the drawing conditions were 1850°C and 2 m/min (dashed line in Fig. 3). The absorption bands around 220 nm, 250 nm, and 260 nm are *E'* center, ODC (II), and NBOHC, respectively [8]. Table 1 represents the concentrations of the defects calculated by Smakula's equation and the reported values of oscillator strength [8].

In contrast with the two aforementioned conditions, an excellent transmission was obtained for the fiber fabricated when the drawing temperature was 1800°C and the drawing speed was 0.5 m/min (solid line in Fig.3). Except for a small absorption at 250 nm, presumably due to ODC (II), a high transmission was exhibited in the DUV region. The estimated concentration of ODC (II) was 6×10^{12} cm^{-3}, which is one order magnitude smaller than that of other two conditions. *E'* center and NBOHC were not observed (see Table 1). The transmittance at 193 nm (the wavelength of ArF excimer laser) was over 65 %/m.

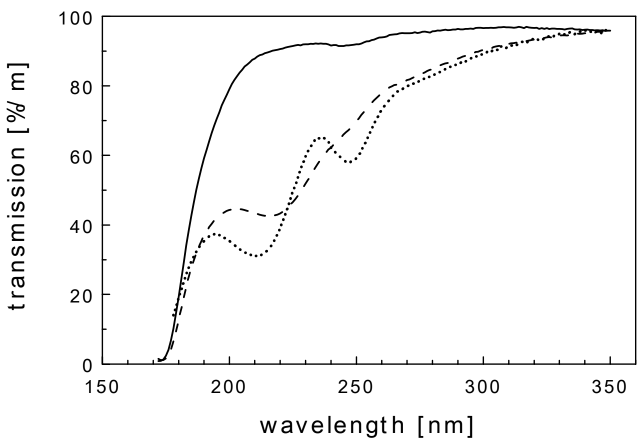


Fig.3. Transmission spectra of a fiber drawn under different conditions. (solid line: 1800°C and 0.5 m/min, dashed line: 1850°C and 2 m/min, dotted line: 2000°C and 50 m/min) [3].

Table 1. Concentrations of defects in the fibers drawn under the conditions in Fig. 3.

Defects [cm^{-3}]	ODC (II)	*E'* center	NBOHC
50 m/min, 2000°C	9×10^{13}	2.1×10^{14}	1.1×10^{14}
2 m/min, 1850°C	6×10^{13}	1.5×10^{14}	1.0×10^{14}
0.5 m/min, 1800°C	6×10^{12}	-[a]	-[a]

a) Not detectable

Fibers with high transmissions were fabricated using fluorine doped silica glass and with lower drawing temperatures and drawing speeds. It is believed that higher temperatures stimulate the dissociation of Si-F bonds, which induce ODC(II)s and F_2 molecules [9]. Higher drawing speeds enhance the formation of "drawing induced defects", which correspond to a pair formation of *E'* center and NBOHC via bond-breaking of Si-O-Si [10,11].

A piece of 10 mm-length fiber with both sides polished was prepared and its transmission in the VUV region was measured to determine the limitations of the fiber's optical transmission in the VUV region. Inset of figure 4 shows the transmission spectra of the fiber piece (dashed line). The transmittance measurements included a loss of the surface reflection since the fibers are too short to be measured by a cutback method. The spectrum of the fiber piece exhibited strong absorption bands at 163 nm (7.6eV), which are assigned as an oxygen-deficient center [ODC (I)] [12] and weak absorption bands from a *E'* center (dotted line). These results clearly showed that ODC (I) was created during the fiber drawing process and restricts the transmission of the fiber in VUV region.

It seems to be improved the fiber transmission, if we can suppress the generation of ODC (I). Therefore, we tried to remove ODC in the fiber by annealing the fiber with hydrogen atmosphere. Inset of fig.4 shows the transmission of the fiber piece of before (dashed line) and after (solid line) annealing in hydrogen. Clearly we can observe decrease of absorption from ODC. We examined annealing with hydrogen to also long fiber. The transmission spectra of before (dashed line) and after (solid line) are shown in Fig. 4. The transmission spectra were measured by cutback method. Drastic improvement of transmission in shorter wavelength was observed; transmission at 193nm was increased 65%/m to 80%/m.

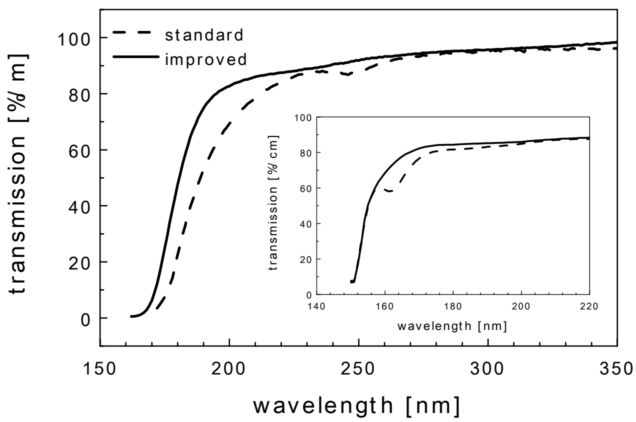


Fig. 4. Transmission spectra of before (dashed line) and after (solid line) annealing with hydrogen atmosphere, witch were measured by cutback method. Inset indicates the transmission of short piece of the fiber.

3.2. Resistance for laser irradiation

A fiber was subjected to ArF excimer laser radiation with a repetition rate of 50Hz and total irradiation of 10^5 doses to examine laser damage in the fluorine doped silica fiber. The power density at the entrance of the fiber was ~20mJ/cm^2. Changes in the transmittance of the fiber were measured *in situ* while irradiating by detecting the output energy using biplaner detectors that were normalized by the input laser intensity. Before and after the irradiation, the transmission spectra of the fibers were measured by a cutback. For comparison, commercially obtained high OH fiber, which contains ~1000ppm-OH and hydrogen, was also irradiated. Before the irradiation, the high OH fiber was treated with hydrogen in the same condition for the fluorine doped silica fiber.

The solid line in Fig. 5 shows the changes in the transmission of the hydrogen-loaded fluorine doped silica fiber at 193 nm when irradiating with an ArF laser. Initially, the transmission slightly decreased, but was quickly saturated at about 90% for the duration of exposure. In addition, after the 10^5 doses of irradiation, the pulse repetition was changed from 50 Hz to 1 Hz and the transmittance was restored as clearly seen in Fig.5. On the other hand, for the high OH silica fiber, the transmission abruptly decreased, but was restored after irradiating (dotted line).

Figure 6 shows the spectra of the fibers before (a) and after (b) the irradiation. In the spectra of high OH silica fiber (dotted line) rapid degradation of the transmission, formation of *E'* center and NBOHC were clearly observed. The hydrogen-loaded fluorine doped silica fiber (solid line), however, did not display significant spectral damage. Table 2 summarizes the concentration of defects in the fibers calculated by Smakula's equation. A slight decrease in the transmission around 220nm and 250nm were caused by the transformation between the small amount of ODC (II) and *E'* center (~10^{13} cm^{-3}) (See solid lines in Fig. 6(a) and (b)). Therefore, degradation occurred in the high OH silica fiber in spite of the hydrogen loading. As seen in Fig 6 (a), it is thought that the high OH fiber contained too many defects and/or precursors to suppress the formation of *E'* center.

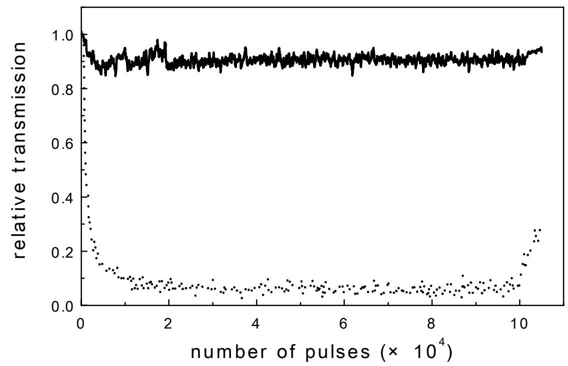
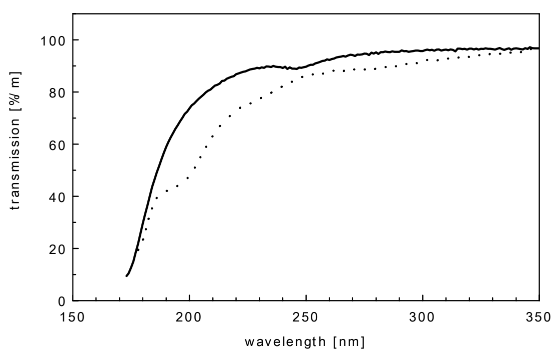
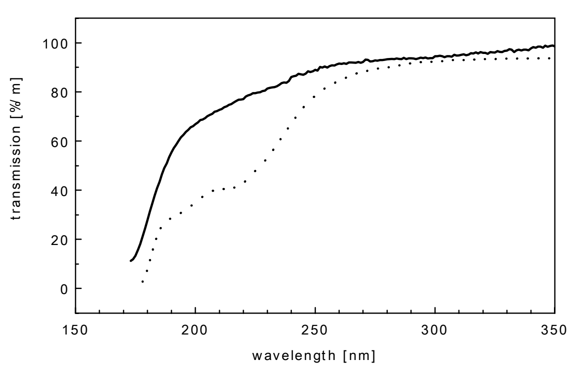


Fig. 5. Changes in the normalized transmittance at 193 nm while irradiating with a laser.
(solid line: fluorine doped silica fiber with H_2 loading, dotted line: high OH fiber with H_2 loading)



(a)



(b)

Fig. 6. Transmission spectra of the fibers before (a) and after (b) ArF laser irradiation.
(solid line: fluorine doped silica fiber with H_2 loading, dotted line: high OH fiber with H_2 loading)

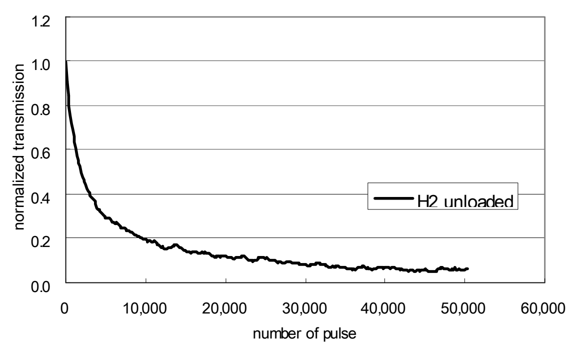
Table 2. Concentrations of defects in the fibers before and after irradiating (See Fig. 6).

Defects [cm^{-3}]		ODC (II)	*E'* center	NBOHC
F-SiO_2:H	before	1×10^{13}	-[a]	-[a]
	after	-[a]	2×10^{13}	1×10^{13}
High OH SiO_2:H	before	-[a]	2×10^{13}	3×10^{13}
	after	-[a]	1.5×10^{14}	6×10^{13}

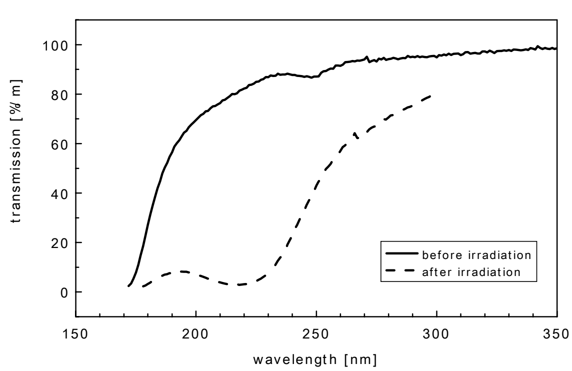
a) Not detectable

3.3 Hydrogen loading and resistivity for irradiation

Hydrogen loading plays an important role to enhance resistivity for laser irradiation. Figure 7 (a) shows change of the transmission of the fluorine doped silica fiber without hydrogen loading during ArF leaser irradiation. The irradiation condition was as below; power density: 20mJ/cm^2, repetition: 50Hz, and total irradiation: $5x10^4$ shots. Abrupt decrease of the transmission was observed in hydrogen unloaded fiber, in contrast with hydrogen loaded fiber that exhibited high resistivity for laser irradiation as shown in Fig. 5. Large number of defect formation was clearly observed in transmission spectra of before and after irradiation (Fig.7(b)).



(a)



(b)

Fig. 7. Change of the transmission (a) and spectra of the fibers before (solid line) and after (dashed line) ArF laser irradiation in hydrogen unloaded fluorine doped silica fiber.

How much hydrogen concentration in the fiber is necessary to maintain strong resistivity for laser irradiation? We examined the change of hydrogen concentration in the fiber during laser irradiation by *in situ* Raman backscatter measurement. Figure 8 indicates the change of transmission and the change of hydrogen concentration during ArF laser irradiation. Irradiation condition was same as the experiment of Fig.5. Hydrogen concentration was determined by ratio of peak intensity at $4135cm^{-1}$ and $800cm^{-1}$ [13]. The sample fiber contains $2x10^{19}cm^{-3}$ of hydrogen, no change was observed during irradiation. In this case, hydrogen concentration seems to be sufficient to suppress defect formations.

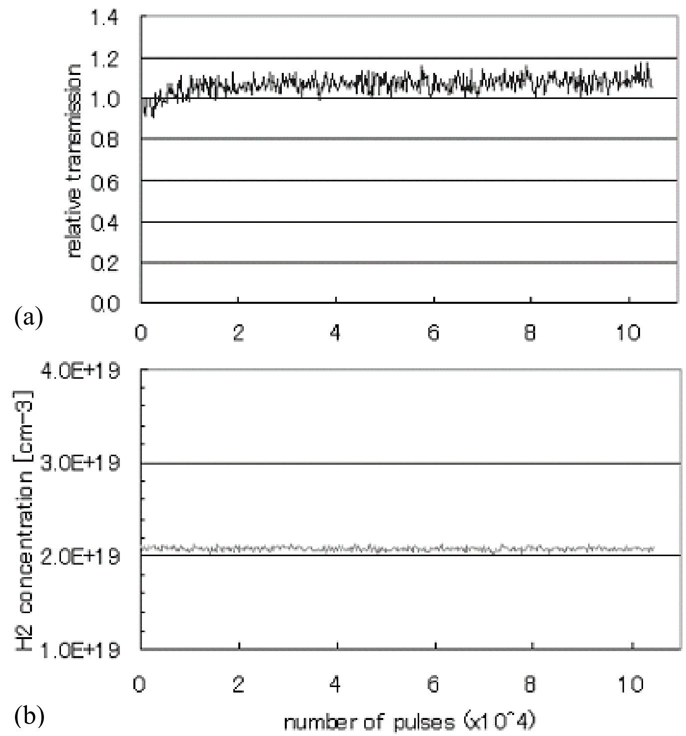
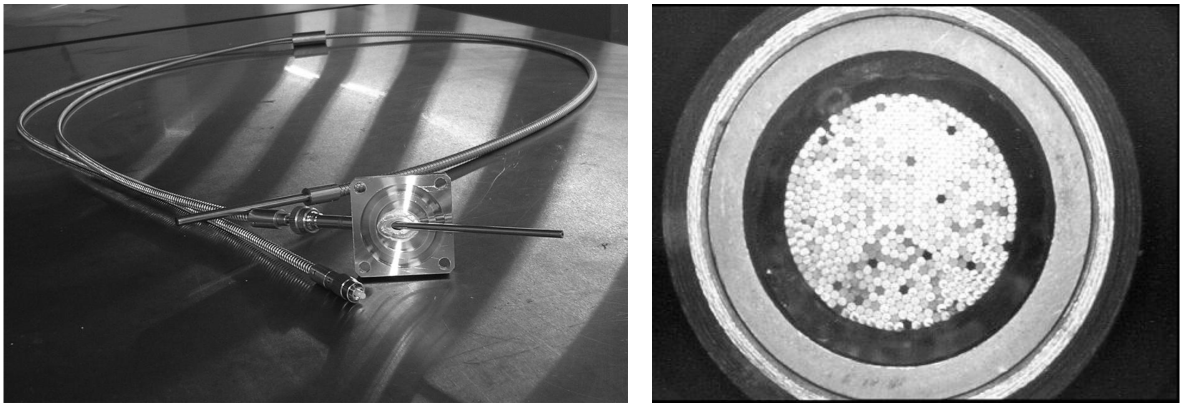


Fig. 8. Change of the transmission and change of the hydrogen concentration during ArF laser irradiation to fiber.

4. APPLICATIONS

Recently, several applications of fluorine doped silica fiber were commercially developed. Figure 9 (a) is a photograph of deep UV light guide propagating to vacuum chamber, which uses for laser ablation and/or spectroscopic measurements. And a photo of resin free fiber bundle for deep UV propagation is shown in Fig. 9 (b), which has strong resistivity for high temperature and high power density of light.



(a) (b)

Fig. 9 Photograph of applications of fluorine doped silica fiber. (a) Deep UV light guide for vacuum chamber. (b) Resin free fiber bundle for deep UV propagation.

5. SUMMARY

Optical fibers for deep UV applications were developed using fluorine doped silica glass. Optimizing the fiber drawing conditions improved the transmission of the fiber in the DUV region. Hydrogen-impregnation into the fibers suppressed the degradation of the transmission due to *E'* center and NBOHC induced by irradiating with an ArF excimer laser. The transmission in deep UV region and resistance for laser irradiation were drastically improved compared to high OH silica fibers. The applications of fluorine doped silica fibers are developing for industrial uses of deep UV power delivery and spectroscopic measurements.

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