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Fused silica fibers for the delivery of high power UV radiation

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ABSTRACT

A set of all silica step index fibers was produced using PCVD and PMCVD methods. The influence of the fiber production technology and chemical composition of silica core on the transmission characteristics of fibers in the UV range, as well as on the processes of color centers formation was studied. The experiments were carried out for the excimer laser wavelengths 308 nm (XeCl) and 248 nm (KrF).

1.INTRODUCTION

Considerable spreading of excimer laser applications in medicine makes a problem of manufacturing of fused silica fibers having damage and transmission properties acceptable for high power UV radiation delivery increasingly actual. Although there are currently a number of commercially available fibers being in use for relatively low intensities of laser radiation the difficulties of high power radiation transport still exist. In order to enlarge the maximum energy density which can be coupled into the fiber the long pulse excimer laser was developed[1,2]. In addition to this some efforts were undertaken to enlarge coupled energy and coupling efficiency by using tapered fibers[1,3]. Therefore the damage problem is not currently the main restriction, at least for XeCl laser wavelength (308 nm). But when handling in pulse repetition rate regime especially with long fibers (10 m and more) another effect begins to limit the transported energy. It is well known that UV radiation can produce color centers in silica glass which have the absorption bands in the UV[4,5]. There have been few investigations concerning the coloration of high-purity silicas by excimer laser radiation[6,7]. It was shown that high power multiple pulse irradiation of silica substrate can produce either stable or unstable defects which influence the UV absorption. There were also few investigations of the induced absorption of silica fibers[8]. Most of these studies dealt with ArF of KrF laser wavelengths (193 and 248 nm respectively). For the XeCl laser radiation (308 nm), which is the most attractive for medical uses, the role of induced absorption is much smaller because of smaller photon energy. Nevertheless, in our previous studies it was demonstrated that transmission of silica fibers at 308 nm also can essentially decrease when working at high repetition rates[9,10]. For OH-rich fibers usually utilized for UV radiation transport the fall of transmission at 308 nm was found to be fully recoverable and dependent on both laser energy density I and repetition rate f. The maximum additional losses are proportional to value $If^{1/2}$ and after the stop of irradiation fiber transmission restores during about 5 minutes[10]. In order to clarify the origin of induced absorption and to establish the role of manufacturing procedure and chemical composition of fiber in this process we have carried out the investigations of transmission and luminescence properties of silica fibers produced by various technologies. It's worth to notice that although the use of 248 nm laser radiation in medicine seems to be doubtful because of its cancerogenioussy, the study of fiber transmission at this

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wavelength should supply an additional information concerning the nature of photoinduced color centers in fibers.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

In our experiments we tested a set of all silica step index fibers produced in Institute of Radiotechnics and Electronics of Academy of Sciences of the USSR. Some of them were manufactured using standard PMCVD method of fluorine-doped silica glass deposition on the inside surface of silica tube and then rod-in-tube method for making a preform. The type and chemical composition of rod were different for different fibers. Characteristics and geometrical parameters of fiber samples are presented in Table 1. For the comparison we tested also two types of commercial fibers - Diaguide ST-U and Optran UV. We also made an attempt to create few experimental samples by means of fully plasma chemical deposition technology. One of them was subjected to additional treatment during one of the technological stages which served to depress the coloration processes in the fiber.

Table 1
Fiber characteristics

Fiber	NA	core diameter (μm)	OH content (ppm)	UV absorption bands (dB/m) 5.1eV	3.8eV
Diaguide ST-U	0.20	600	580	-	-
OptranUV	0.22	600	830	-	-
H700	0.19	520	700	-	-
H970	0.22	400	970	-	-
H1150	0.21	400	1150	-	-
H150	0.20	400	150	12	-
H180	0.20	600	180	?	-
P18M	0.19	400	18	-	1.3
P55	0.26	350	55	-	0.7
P65T	0.20	400	65	-	?

In addition to standard characteristics of fibers such as core diameter, numerical aperture and OH content Table 1 includes the intensities of some typical UV absorption bands 5.1 eV (242 nm) and 3.8 eV (325 nm). Basing on these data we can make an assumption about the structure of silica core, as it was done in Ref.7. In particular, the presence of the band at 3.8 eV which belong to peroxy linkages shows the excess of oxygen in fibers P18M, P55 and P65T produced completely by plasma technology. The origin of 5.1 eV is now under discussion, but it seems to be the sign of hydrogen excess.

The transmission and luminescence properties were investigated using three excimer lasers. Lambda Phisik KrF laser with repetition rate up to 200 Hz and XeCl laser with repetition rate up to 50 Hz were used for the transmission measurements. Optical pulse durations (FWHM) were 25 and 15 ns, respectively. Two pyroelectric energy detectors calibrated with calorimeter at both 248 and 308 nm wavelengths served to detect

energy transmitted through the fiber and to determine input fluences by the way of measuring the energy reflected by the beam splitter placed before focusing lens. The coupling efficiency and single-shot transmission were measured by breaking the fiber near by the input end.

Another KrF (Lambda Physik, pulse duration 25 ns) was explored for luminescence studies. These measurements were made with the aid of optical multichannel analyzing (OMA) system. About 20 mm of fiber coating was removed at the distance of 30 cm from the input end to observe lateral outcoming luminescence light. The diode array examined an entire spectrum in a certain time interval, which could be chosen in the range from 100 ns up to 10 ms. An optional time delay was used to shift the time window from several nanoseconds up to 10 ms after the laser pulse.

3. RESULTS AND DISCUSSION

A. Fiber transmission measurements

As it was shown in previous publications[10,12], the single-shot transmission of silica fibers is significantly restricted at excimer laser wavelengths by two-photon absorption, especially at 248 and 193 nm. In this case the value of transmission T for the fiber of length l is given by

$$1/T = \exp(\alpha_0 l) + \alpha_1 I_0/\alpha_0 \cdot [\exp(\alpha_0 l) - 1] \qquad (1)$$

where α_0 is small signal attenuation coefficient, α_1 - two-photon absorption coefficient. To determine separately α_0 and α_1 fiber transmission was measured as a function of input energy density. Fig.1 represents the results of these measurements for some of fiber samples. The strait line in Fig.1 shows the approximation of transmission by Eq.(1). Table 2 lists the values of one- and two-photon absorption coefficients determined for different samples.

Table 2
Single-shot fiber transmission properties at 308 and 248 nm

Fiber	α_0(308nm),dB/m	α_0(248nm),dB/m	α_1(248nm),cm/MW
Diaguide ST-U (580ppm OH)	0.10	1.0	$2.1 \cdot 10^{-4}$
OptranUV (830ppm OH)	0.10	1.1	$1.4 \cdot 10^{-4}$
H700	0.16	1.0	$1.3 \cdot 10^{-4}$
H970	0.17	1.0	$2.8 \cdot 10^{-4}$
H1150	0.17	1.0	$1.8 \cdot 10^{-4}$
H150	0.33	10.	?
H180	0.33	>20.	?
P18M	1.45	1.9	$7.5 \cdot 10^{-4}$
P55	0.63	1.6	$4.7 \cdot 10^{-4}$
P65T	0.27	1.1	$3.8 \cdot 10^{-4}$

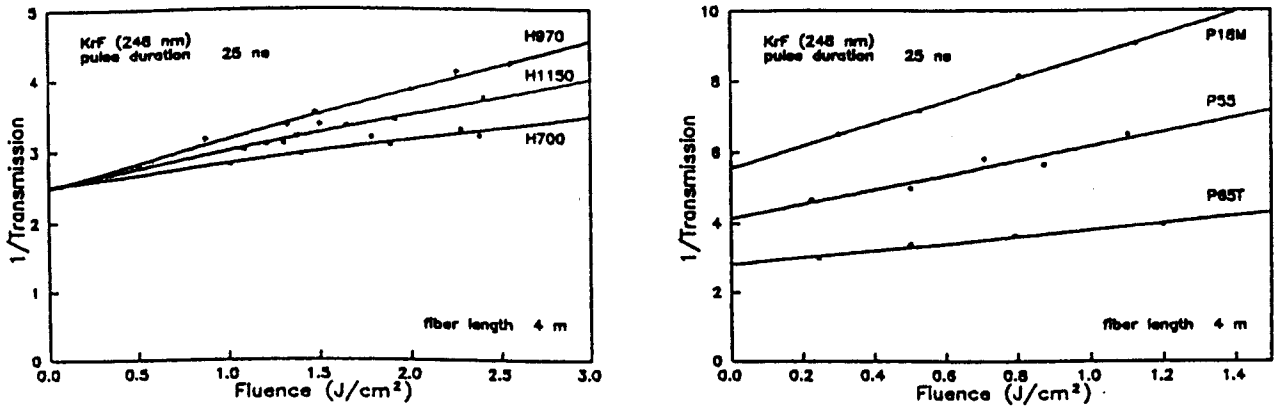

Fig.1 Fiber transmission at 248 nm as a function of input fluence.

One can see that in spite of wide-spread conviction that OH-rich fibers have better transmission performances in the UV some of plasma-produced samples have reasonable absorption at 308 nm and approach the low-signal characteristics of OH-rich fibers at 248 nm. The values of two-photon absorption coefficient are considerably higher for this kind of fibers. We can't infer distinctly about the reason of this difference. Probably it is due to cascade processes with participation of some type of color centers. Two-photon absorption, as well as low-signal attenuation, can be reduced by additional treatment. So further improvement of this technology is of great interest and may open new prospects in developing of delivery systems for both 308 and 248 nm laser wavelengths.

Another obstacle which prevents to use fused silica fibers for short wavelength radiation transport is laser-induced color centers formation. We have explored more carefully multiple-shot transmission of various types of fibers to clarify the role of technological factors in this process.

Fig.2 demonstrates typical dependences of transmission on the number of laser pulses for some OH-rich fibers. Measurements for each fiber were performed at the same conditions, i.e., at the same incident energy density, the same laser repetition rates and for fibers of equal length. Thus the change of transmission in time distinctly represents the rate of color center formation processes. In agreement with our previous investigations fully recoverable decrease of transmission going to some stable level was observed when irradiated by XeCl laser (308 nm). This stable level depends upon the laser repetition rate. It seems natural to ascribe these additional losses to non-bridging oxygen hole centers (NBOHC, -Si-O) which have an absorption band at 4.7 eV (265 nm)[13]. In "wet" silica glasses this type of defects is usually unstable at room temperature. Luminescence measurements (see Chapter 3B) also confirm this assumption. It is commonly assumed that NBOHC is produced by detaching of hydrogen atom from hydroxyl groups. The most surprising fact is that the value of transmission fall does not correlate with the OH content. Moreover, the situation is quite opposite: the fall of transmission, as well as initial rate of this fall diminishes with the rise of OH content.

At shorter wavelength (248 nm) the share of stable laser-induced losses is considerably higher. Its magnitude does not correlate with OH content at all. So far hydroxyl groups are not at least the only precursors of NBOHC.

Measurements with fibers H150 and H200 make this fact more apparent (Fig.3). These samples have few times smaller OH content than of that were discussed above. Nevertheless one of them (H200) demonstrates much faster and only partially reversible fall of transmission even at 308 nm. Another one (P150) shows only small transmission decrease at 308 nm. Moreover, a small enhancement was observed at the initial moment. At 248 nm this sample shows completely recoverable fall of transmission although initial losses are high because of strong absorption band centered at 242 nm.

Plasma-produced fibers are the most sensitive to the multiple-shot irradiation (Fig.4). Created defects are stable either at 308 nm or at 248 nm. However, fibers subjected to additional treatment is less sensitive.

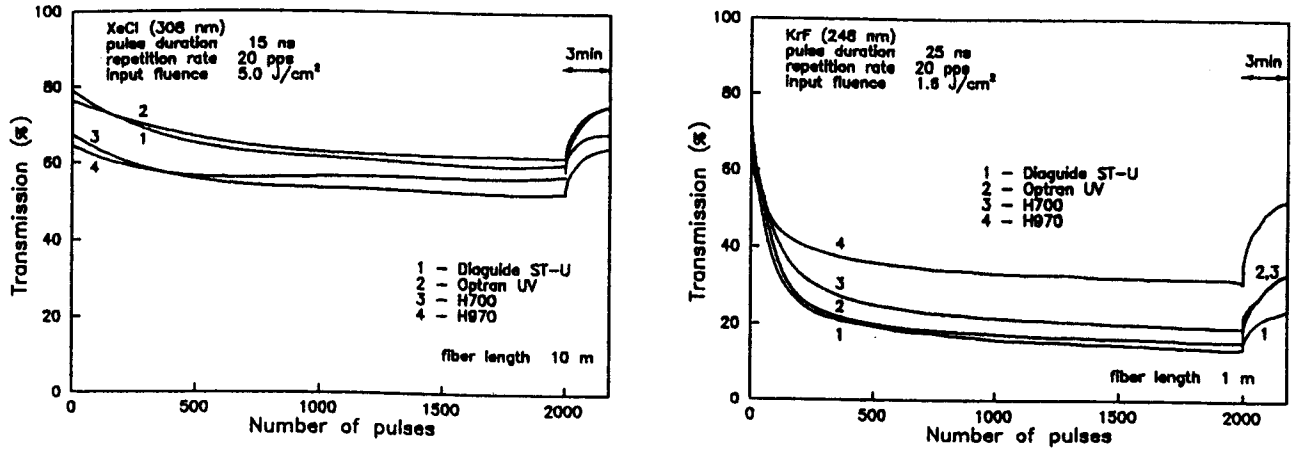

Fig.2 Multiple-shot transmission of OH-rich fibers at 308 nm (left) and 248 nm (right).

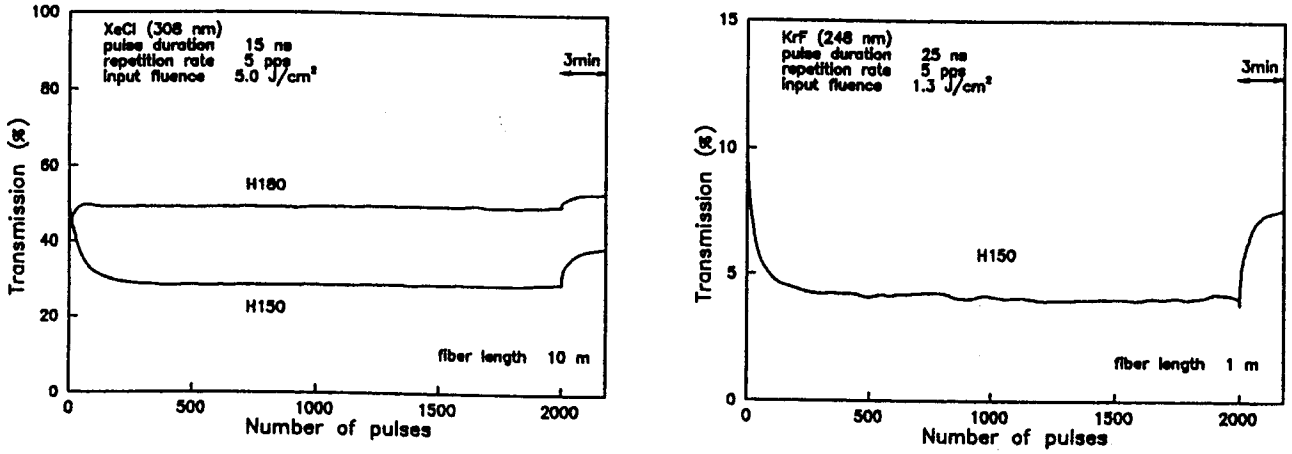

Fig.3 Multiple-shot transmission of fibers H150,H180 at 308 nm (left) and 248 nm (right).

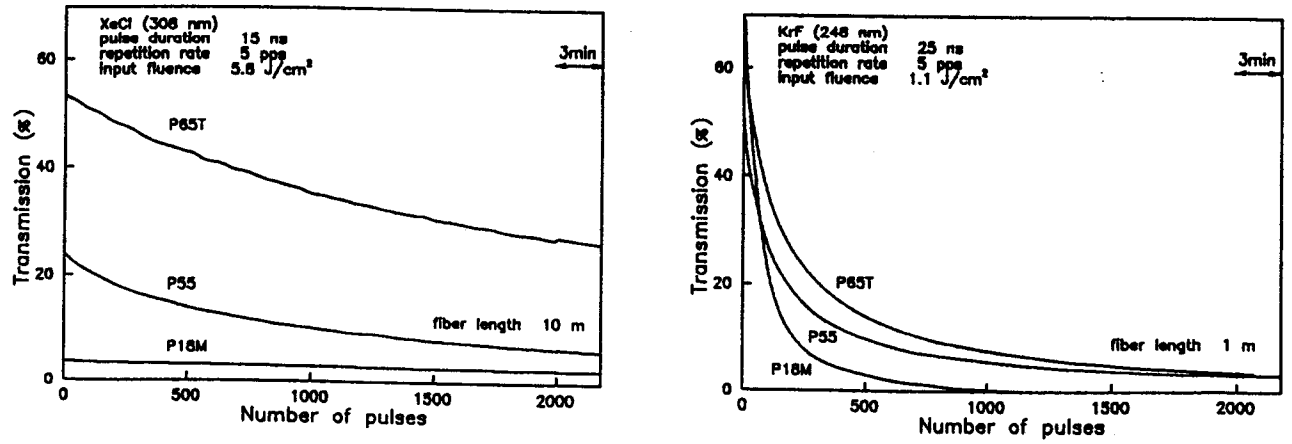

Fig.4 Multiple-shot transmission of plasma-produced fibers at 308 nm (left) and 248 nm (right).

B. Luminescence

In order to determine the type of defects responsible for the single-shot and induced absorption in fibers we have carried out the study of luminescence spectra excited by KrF laser radiation. The experiments were perform with three samples - H200, H700 and Diaguide ST-U. Initial integral spectra of unirradiated fibers are reproduced by Fig.5. One can see that fiber H200 have extremely high luminescent band at 400 nm. The characteristic lifetime of this luminescence measured using various delays of time window was about 100 μs. In addition to this, fast luminescence with the lifetime comparable with laser pulse duration was observed nearby the edge of sensitivity of OMA (about 300 nm). These bands as well as 5.1 eV (242 nm) absorption band considered as a sign of hydrogen excess in "reduced" silica[14,15].

The origin of luminescence at 550 nm in fiber H700 is not clear. The lifetime of this band is 32 μs and in principle it may arise from the casual soiling by cuprum[16].

The only band varying during laser irradiation was that centered at 650 nm. The lifetime is 15 μs and it is undoubtedly well-known luminescence ascribed to non-bridging oxygen[13,17]. Fig.6 exhibits the behavior of luminescence intensity in fiber H700 in comparison with multiple-shot transmission at 248 nm. One can see rather good correlation between luminescence at 650 nm and fiber transmission. A small decrease of luminescence after about 1000 pulses is apparently due to decrease if exciting light intensity at the distance of 30 cm from input end where luminescence was measured.

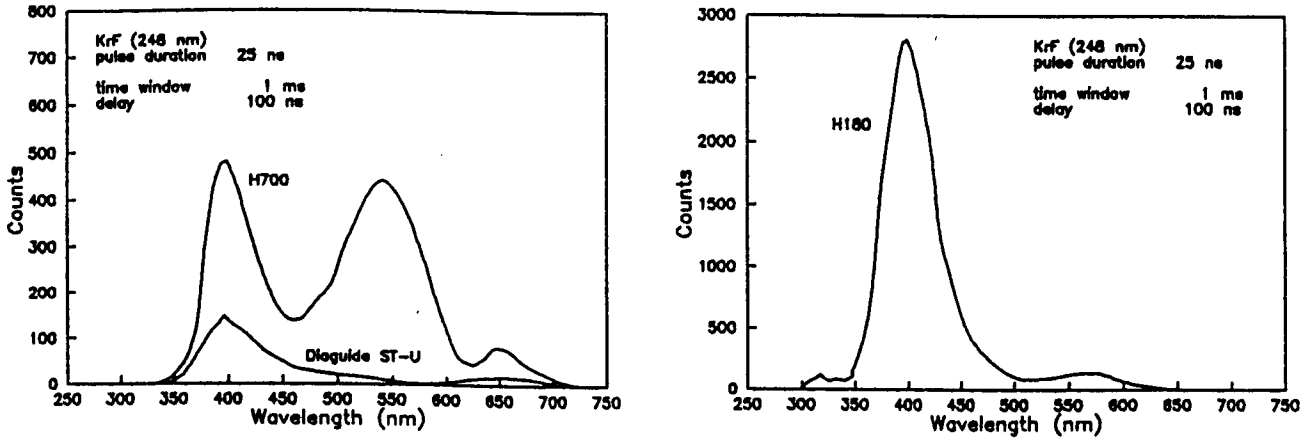

Fig.5 Luminescence of silica fibers excited by KrF laser.

C. Probable mechanisms of color centers formation

The results of luminescence investigations enable us to suggest that nonbriging oxygen is the defect responsible for the multiple-shot transmission properties of tested fibers. The only exception is the fiber H200 (and may be also H150) where the small increase of transmission seems to be caused by destruction of defects responsible for 242 nm absorption band. The smaller magnitude of induced absorption for "wet" fibers with higher OH content and the absence of correlation between OH content and induced absorption in these fibers make us to look for another mechanism instead of generation of NBOHC from hydroxyl groups. Another fact which confirms the assumption of few different mechanisms of NBOHC generation is different ratio of stable and unstable laser-induced losses for 248 and 308 nm. Laser radiation with shorter wavelength produces significantly larger quantity of stable defects. For our opinion, the additional mechanism of unstable color centers generation is the destruction of defects Si-O-OH by breaking the weak O-O bond:

$$\equiv\text{Si-O-OH} \longrightarrow \equiv\text{Si-O}^{\bullet} + \text{OH}^{\bullet} \qquad (2)$$

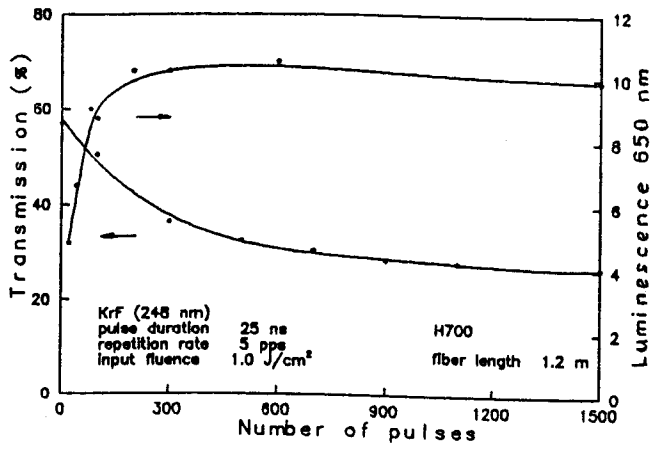

Fig.6 Dinamics of luminescence at 650 nm and transmission at 248 nm during KrF laser irradiation.

Such an assumption about the existence of this mechanism of NBOHC generation was offered in Ref.7 based on the analysis of paramagnetic centers generation in high-purity silica glasses induced by ArF laser (193 nm). Unlike the statements of Ref.7 we consider the reaction (2) as a mechanism of unstable defects formation. Stable NBOHC can be generated by the way of OH groups dissociation:

$$\equiv Si\text{-}OH \longrightarrow \equiv Si\text{-}O^{\bullet} + H^{\bullet} \qquad (3)$$

The energy splitting between σ and σ^* orbitals of bond O-O was calculated by O'Reilly and Robertson[18] to be about 20 eV so only multiphoton destruction of this bond is possible. Some amount of OH groups can dissociate due to the weak tails of σ and σ^* orbitals toward the valence and conduction bands, respectively. Apparently this process should be much more probable for shorter wavelength.

Plasma-produced fibers have an excess of oxygen, what is indicated by the absorption band at 3.8 eV. Taking into account that the hydroxyl concentration is small we suggest that NBOHC in this case is originated from peroxy linkages (the energy splitting between σ and σ^* orbitals is 9.4 eV):

$$\equiv Si\text{-}O\text{-}O\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O^{\bullet} + {}^{\bullet}O\text{-}Si\equiv \qquad (4)$$

Undoubtedly, the mechanism of color center formation has to be investigated more carefully by supplementary methods, e.g., by spectroscopic measurements of induced absorption and luminescence.

4. CONCLUSION

Recently many of excimer laser applications demand the laser beam delivery systems with improved transmission properties at high intensities of laser radiation. For some of them it's necessary to have a long radiation transmitting line, when laser is withdrawn from the operation room. For some others the use of thin fibers is preferable because of their flexibility. By using tapered fibers it's possible to couple at 308 nm up to 20 mJ into the fiber having 300 μs exit core, i.e., up to 28 J/cm^2 (see Ref.1). Our preliminary experiments with tapered fibers showed even higher maximum possible output fluence. One meter long fiber had input core diameter 375 μm, output core diameter 140 μm and was capable to transmit at 308 nm up to 10 mJ, i.e., 65 J/cm^2 (laser pulse duration was 15 ns).

For so high laser intensities, as well as for long fibers two-photon absorption and particularly the processes of color centers formation must be taken into account. As it was shown in present paper, the intensity of these processes in fibers significantly depends upon the fiber production technology and principally can be reduced. So further study of color centers generation mechanism and the search of optimum technology capable to produce fibers having minimum optical losses remains to be of great significance.

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