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Improved all silica fibers for deep UV-application

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ABSTRACT

Deep UV application of optical fibers has been restricted due to the strong photodegradation in silica fibers transmitting deep UV light. We have developed an improved all silica preform for the production of multimode fibers with drastically improved resistance to UV-light. Two key experiments have been performed in order to characterize the solarization behavior of such fibers: 1) ArF-excimer laser and deuterium lamp photodegradation spectroscopy enables the in situ observation of defect center creation. 2) Long time photodegradation excimer laser experiments (ArF and KrF) are a good tool to predict the fiber's lifetime for applications with such lasers. Compared to standard high OH all silica fibers the optimized fibers show an exceptionally low creation of E'-centers (215 nm). Hydrogen doping of such fibers further increases the UV-resistance: Even after prolonged excimer laser irradiation (ArF: 20×10^6 pulses, 5 mJ/cm^2, 400 Hz; KrF: 20×10^6 pulses, 50 mJ/cm^2, 500 Hz) these fibers maintained their very high initial transmission, neither E'-center nor NBOH-center (265 nm) absorption could be observed.

Keywords: silica glass, optical fiber, UV-resistance, deuterium lamp, ArF-excimer, KrF-excimer, hydrogen doping

1. INTRODUCTION

Optical fibers are made by drawing a preform through a furnace; the diameter of the preform is typically reduced by a factor of several hundred times to the final diameter. Preforms for multimode all silica fibers which are used in medical applications like spectroscopy and laser power transmission consist of a core of pure silica and a thin cladding of doped silica with a index of refraction lower than that of the core material to ensure total reflection of the guided light in the fiber. The spectral attenuation of these fibers is mainly determined by the properties of the silica in the core. In state of the art silica fibers high purity synthetic silica is exclusively used as core material. Synthetic silica is generally made by the flame hydrolysis of a silicon containing compound by producing SiO_2 particles and depositing them and vitrifying them on a substrate. The vitrification of the SiO_2 particles can be performed directly during its deposition on the substrate (**DQ**: direct quartz), or in a separate sintering process as in the case of the so called **soot** process. In general the core materials are classified in low and high OH silica, at which low OH silica is predominantly made by a soot process.

All silica fibers with high OH core are in principle well suited for deep UV applications due to their high initial transmission in the UV, which is due to the smaller concentration of intrinsic defects like oxygen deficiency or peroxy linkage in high OH silica than in low OH silica. The transmission of state of the art fibers with high OH, DQ core material is mainly restricted by light scattering, whereas in fibers with low OH, soot core material in addition typical UV absorption bands can be observed (Fig. 1). These additional UV-losses of soot-fibers rule out their deployment for deep UV-applications. For an overview of the preform/fiber types discussed in this article see Table 1. A detailed discussion of possible defects in fused silica can be found in Griscom[2].

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Table 1 All silica preform types

FLUOSIL preform type	**OH content of core silica [ppm]**	**Production method of core silica**	**Characteristics**
SWU	<1	Soot	Low OH core material; high IR transmission
STU[3]	<20	Soot	Low OH; reduced chlorine; for broadband application
SSU	~700	DQ	Standard high OH preform; high UV transmission
SBU	~700	DQ	Newly developed high OH preform; high UV transmission; low solarization

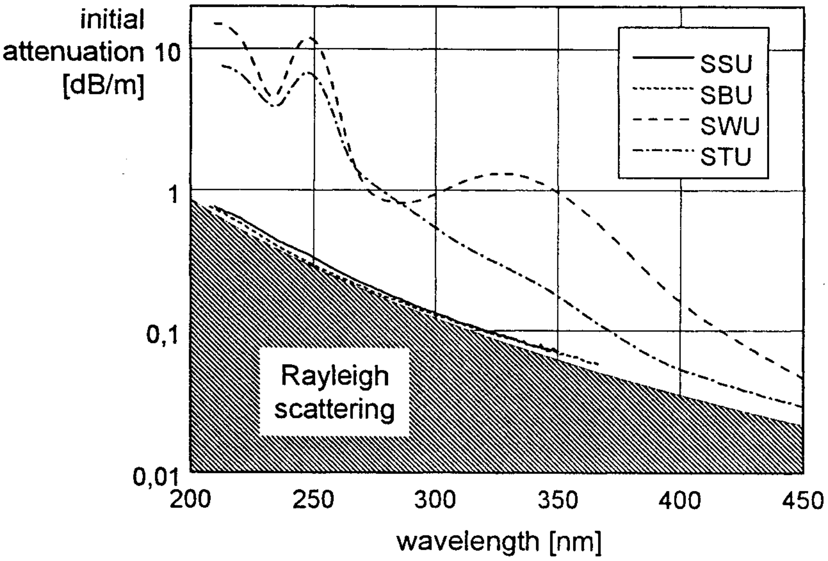

Figure 1 Initial UV-attenuation of different fiber types. **SSU, SBU**: DQ-core, high OH; **SWU**: Soot-core, low OH; **STU**: Soot-core, low OH, reduced chlorine content.

Despite high initial UV transmission the application of high OH fibers was limited due to strong induced absorption by UV irradiation. The induced absorption is caused by the creation of intrinsic defect centers[1]. In high OH silica the most relevant centers for application below 300 nm are the E' center at 215 nm and the NBOH center at 265 nm (Fig. 2).

Therefore the basic approach to improve UV resistance of fibers is to optimize the core material properties in that way, that after drawing a fiber from the preform, the defect center creation due to UV-irradiation in the spectral region of interest is minimized. A second approach which leads to an enhanced UV-resistance is hydrogen loading of fibers[4,5], because hydrogen is able to anneal induced defect centers which otherwise would lead to induced absorption (see also section 3).

In the next section we will explain the experimental techniques to determine the photodegradation of fibers under excimer laser or deuterium lamp radiation. In section three results on fibers drawn from the newly developed preform SBU with and without hydrogen doping the fibers are presented and compared to state of the art SSU fibers.

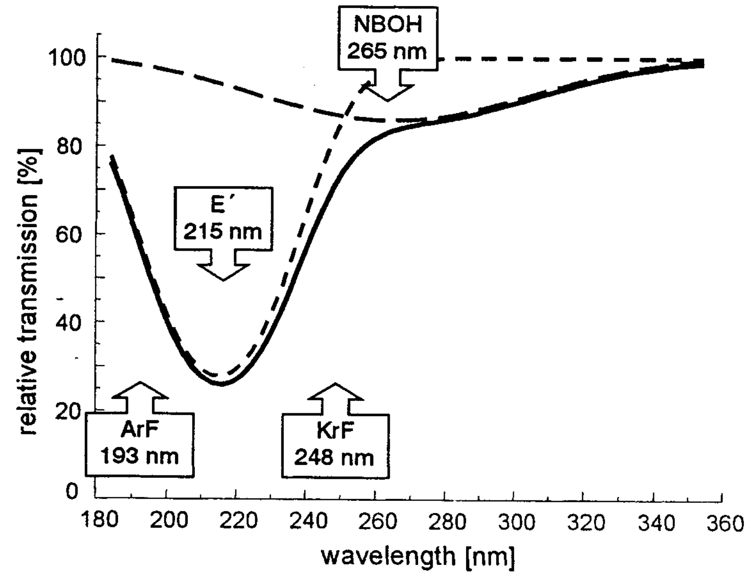

Figure 2 Typical excimer laser induced damage to an high-OH all-silica fiber. Induced transmission loss (solid line) is a superposition of strong E'-center absorption (short dash) and a broad NBOH band (long dash). Both bands have to be considered for KrF-applications (248 nm). For ArF-applications (193 nm) the main problem is E'-center creation.

2. EXPERIMENTAL

All experiments were performed with optical fibers drawn from FLUOSIL[6] preforms. As core material two different high-OH synthetic silica grades were used. The preform cladding consisted of highly fluorine doped fused silica manufactured with a plasma outside deposition process. The fiber core/cladding diameter was generally chosen to be 200/220 µm and the numerical aperture were about 0.22. For the experiments the acrylate fiber coating was removed with a suited solvent and the fibers were cleaved with a standard fiber cleaver.

Three different experiments were carried out in order to characterize the UV performance of the fibers: Excimer laser (ArF) and deuterium lamp (D_2) photodegradation spectroscopy enables the in situ visualization of defect center creation and recovery, particularly of the crucial E'- and NBOH-centers (Fig. 3A, 3C). Longtime excimer laser photodegradation experiments (ArF, KrF) are a good tool to predict the fiber's lifetime for applications with such lasers (Fig. 3B).

For the excimer laser photodegradation spectroscopy the ArF laser beam was coupled into 1 m of fiber through a conventional fused silica lens (Fig. 3A). In addition to the laser beam, light from a low power deuterium lamp was focused into the fiber. In-between two laser pulses the transmitted D_2-spectrum was recorded with an optical multi-channel analyzer (OMA), thus allowing the measurement of the laser induced defect center creation during irradiation. The energy density of the laser was set to $\varepsilon = 50$ mJ/cm^2, the repetition rate was 10 Hz, pulse length $\tau = 15$ ns. After 1000 laser pulses the excimer laser was switched off, the spectral recovery of the fiber could now be recorded as a function of time.

The experimental setup for the ArF and KrF longtime excimer laser photodegradation experiments is basically the same as the one described above (Fig. 3B). Since no spectral information is needed, only the excimer laser light was coupled into the fiber. The standard in-coupled energy density was 5 mJ/cm^2, but it could be raised up to 100 mJ/cm^2 for particular experiments. The out-coupled pulse energy was detected as a function of laser pulses with a pyroelectric joulemeter (*Molectron J3-05*, detection limit: 15 nJ/pulse). The length of the fibers was chosen to be 1 m for ArF (193 nm) and 3 m for KrF (248 nm) in order to obtain a sufficient amount of out-coupled light. With this experiment the total absolute transmission of the fiber is measured, which also includes the Fresnel reflection losses in addition to the fiber's attenuation. The shape of the beam in the coupling plane could be controlled with a CCD-camera and the energy density was set by a computer driven variable beam-splitter. For standard measurements in which the fiber was irradiated for several million pulses at 400 Hz (ArF) and 500 Hz (KrF) respectively it was necessary to control the in-coupled energy density in order to level out laser fluctuations. This was done by measuring the energy density with a reference detector and a subsequent automatic adjustment by turning the variable beam splitter.

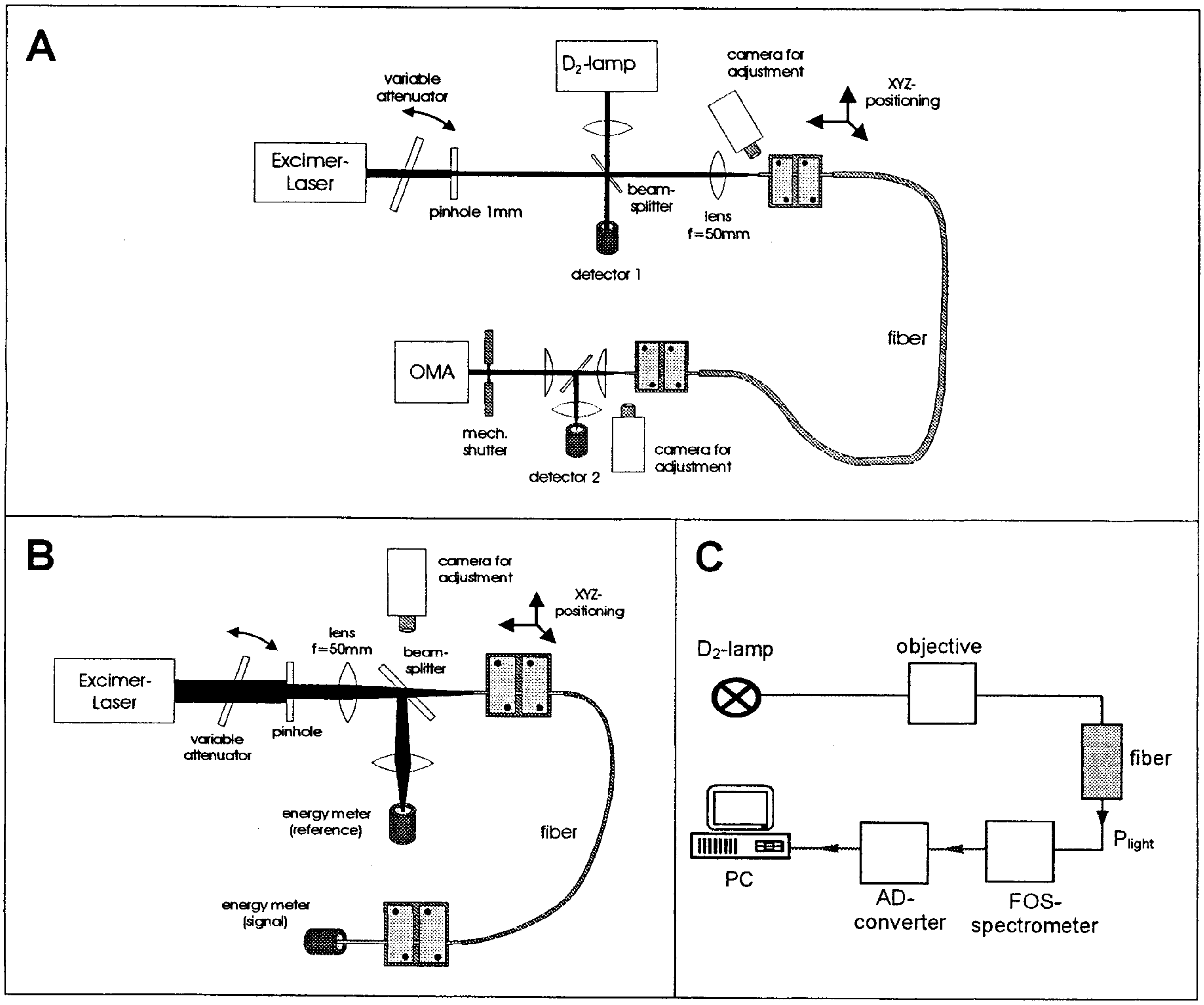

Figure 3 Experimental setups: **A** – Excimer laser photodegradation spectroscopy, **B** – Excimer laser long time photodegradation experiment, **C** – Deuterium lamp photodegradation spectroscopy.

For the D_2-lamp photodegradation spectroscopy the UV spectrum of a deuterium lamp was coupled into the fiber through two fused silica lenses (Fig. 3C). The spectral input power was 70 nW/nm at $\lambda = 215$ nm. The out-coupled light was analyzed with a fiber-optic spectrometer (FOS) in the spectral range between 190 nm and 350 nm and subsequently read out by a standard PC. During this experiment the 2 m long fibers were irradiated for 2 hours followed by the observation of the fiber's recovery for another 3 hours.

In order to study the influence of molecular hydrogen on the defect center generation, fibers were also loaded with hydrogen yielding H_2-concentrations in the order of 10^{19} cm^{-3}. To load the fibers with hydrogen they are stored for several weeks in a high pressure cylinder containing the gas.

3. RESULTS AND DISCUSSION

Figure 4 (left) depicts the relative transmission spectrum of a state of the art high OH fiber (SSU type) after ArF laser irradiation. The core material of this fiber is manufactured by the DQ method, yielding an OH-content of approximately 700 ppm. The exposure to such an intense UV light leads to a very strong increase of E'-centers (215 nm), nevertheless only a slight NBOH center (265 nm) creation can be observed. A possible explanation of this behavior is the presence of non-absorbing precursor defects in the core of the fiber that are transformed into E'-centers during irradiation[4,7,8,9]. Among others these precursor defects could be strained Si-O bonds (1), Si-Cl (2) or Si-H bonds (3). A single UV-photon would have sufficient energy to cut one of the mentioned bonds resulting in a E'-center and an NBOH center, atomic chlorine or hydrogen respectively.

$$\equiv\text{Si}\text{—O—}\text{Si}\equiv \;\rightarrow\; \equiv\text{Si}\cdot + \cdot\text{O–Si}\equiv \tag{1}$$

$$\equiv\text{Si-Cl} \;\rightarrow\; \equiv\text{Si}\cdot + \cdot\text{Cl} \tag{2}$$

$$\equiv\text{Si-H} \;\rightarrow\; \equiv\text{Si}\cdot + \cdot\text{H} \tag{3}$$

Only an insignificant recovery of the fiber occurs after the laser is switched off. It is widely accepted, that the recovery of E'-centers and NBOH centers is mainly affected by the presence of molecular hydrogen[1], which is capable to transform the absorbing centers into their non-absorbing counterparts:

$$\equiv\text{Si}\cdot + \tfrac{1}{2}\,\text{H}_2 \;\leftrightarrow\; \equiv\text{Si-H} \tag{4}$$

$$\equiv\text{Si-O}\cdot + \tfrac{1}{2}\,\text{H}_2 \;\leftrightarrow\; \equiv\text{Si-OH} \tag{5}$$

The lack of recovery in the SSU fiber is a strong indicator that the concentration of molecular hydrogen is very low.

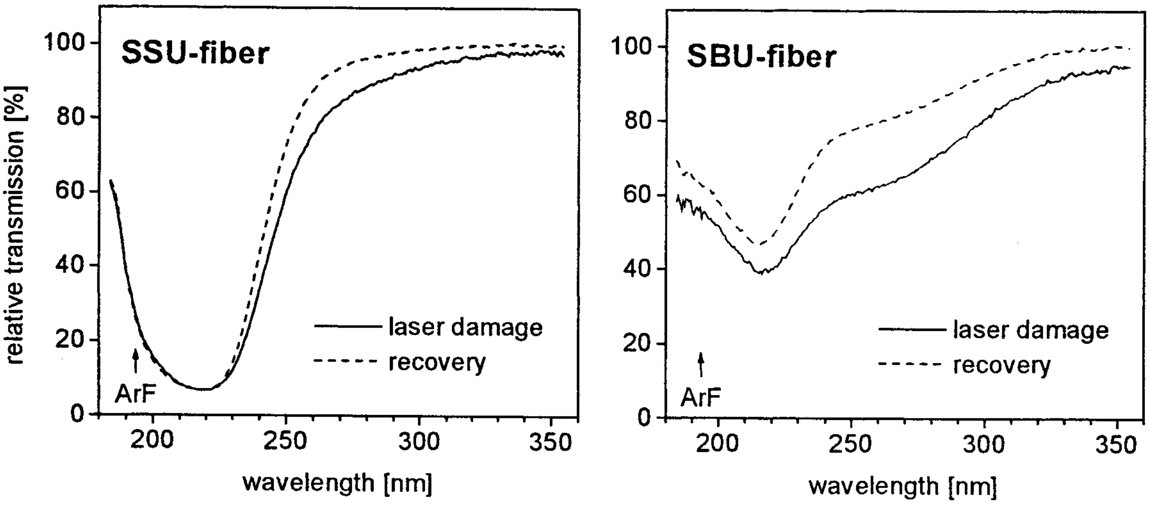

Figure 4 Photodegradation spectroscopy of SSU 1.1 (left) and SBU 1.1 (right) fibers after 1000 ArF laser pulses (solid line) and 10 min recovery (dashed line). Irradiation parameters: 50 mJ/cm^2, 10 Hz, fiber length = 1 m.

The transmission spectrum of a SBU-fiber differs completely from the SSU spectrum (Fig. 4 - right). Both fibers were irradiated under the same conditions. From this photodegradation experiment it is obvious, that the core material of the newly developed high-OH SBU preform has a significantly lower amount of E'-center precursor defects. Nevertheless a stronger increase in NBOH center creation can be observed. For ArF-applications this characteristic behavior represents an obvious advantage since the E'-center generation is dramatically reduced and the NBOH absorption band does not influence the transmission at 193 nm.

A similar result can be obtained from the ArF-excimer laser long time photodegradation experiment (Fig. 5) (ε = 5 mJ/cm^2, ν = 400 Hz, τ = 15 ns, l_{fiber} = 1 m). The SSU fibers are virtually blind after 10^5 laser pulses whereas the SBU fibers have an absolute transmission of about 20% after 10^7 laser pulses. The photodegradation behavior of both fiber types is reproducible from batch to batch.

Remarkably the transmission of the SBU fibers rises in the range of 10^5 to 10^6 pulses. A reason why the defect center creation is slower than defect annealing in that range is up to now unknown.

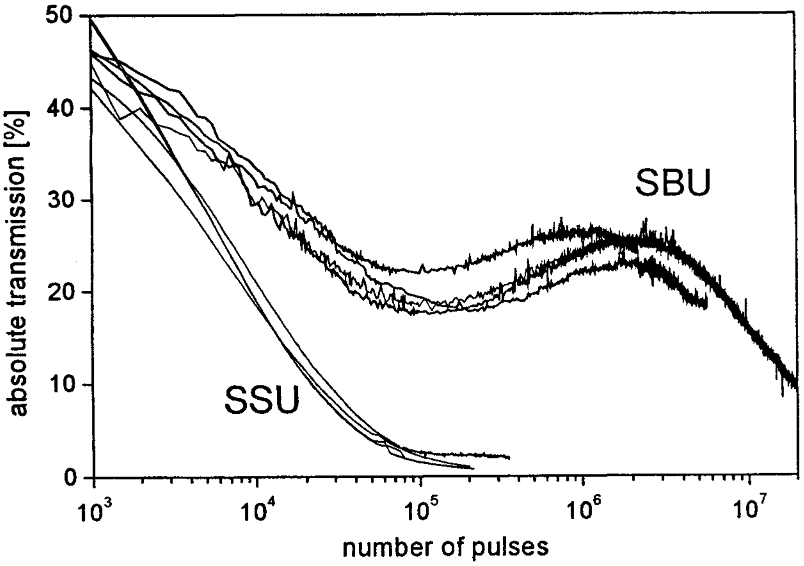

Figure 5 Long-time photodegradation of four different batches of SSU and SBU fibers upon ArF-excimer laser irradiation. Irradiation parameters: 5 mJ/cm^2, 400 Hz, fiber length = 1 m.

The difference in UV-performance between the two fiber types becomes evident when comparing their induced loss at the ArF laser wavelength (193 nm) as a function of energy density per pulse ε (Fig. 6). As described above the increase in E'-center concentration can be isolated from other absorption bands at this wavelength, since only its 215 nm band contributes to additional losses at 193 nm in high OH fibers. For the experiment the increase in absorption of fibers was measured, varying the energy density per pulse from below 1 mJ/cm^2 up to more than 20 mJ/cm^2 (ν = 400 Hz, τ = 15 ns, l_{fiber} = 1 m). The irradiated SBU-fibers degrade at a slower pace than in the case of the SSU-fibers. In Figure 7 the induced attenuation per laser pulse $\Delta\alpha$ at the beginning of the excimer laser irradiation is plotted versus the energy density per pulse. The measured data points of each fiber type are on a straight line. The slope b of this line indicates the nature of the degradation process according to:

$$\Delta\alpha \propto \varepsilon^b. \tag{6}$$

In the case of a one photon process (b = 1) the creation of E'-centers takes place principally through the conversion of non-absorbing precursor defects (reaction scheme (1-3)). Two-photon processes (b = 2) occur when the energy of two photons is needed for the scission of a regular Si-O bond [8]. Since b = 1.2 for a SSU fiber the degradation in such fibers can be predominantly attributed to one-photon processes, whereas in SBU fibers (b = 1.5) the amount of one photon processes (conversion of precursor centers) is reduced.

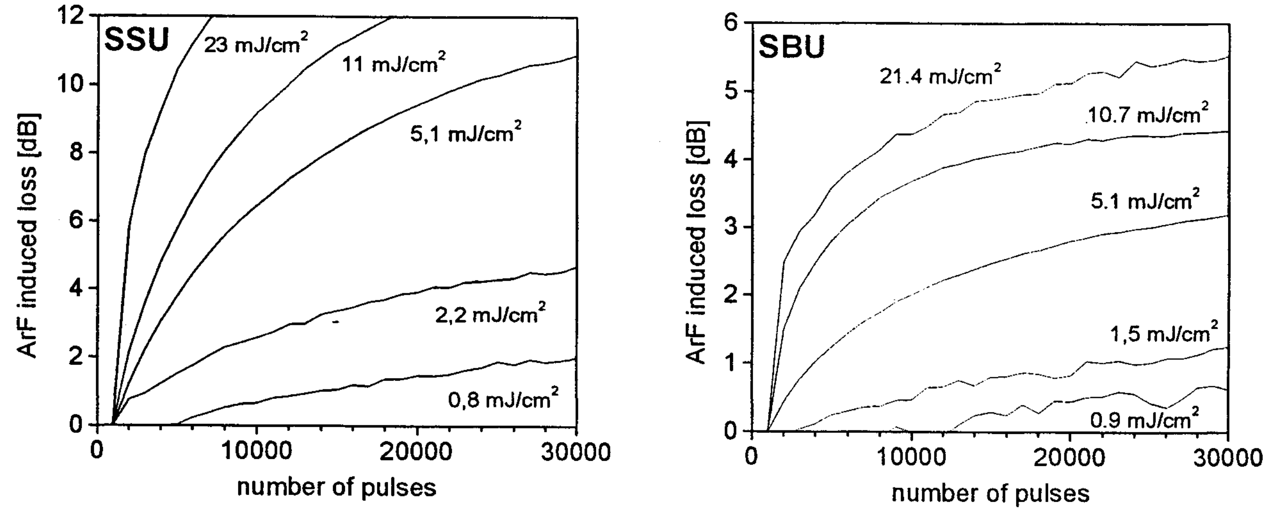

Figure 6 Energy dependence of ArF-excimer laser induced absorption in SSU (left) and SBU (right) fibers. Irradiation parameters: 400 Hz, pulse length = 15 ns, fiber length = 1 m.

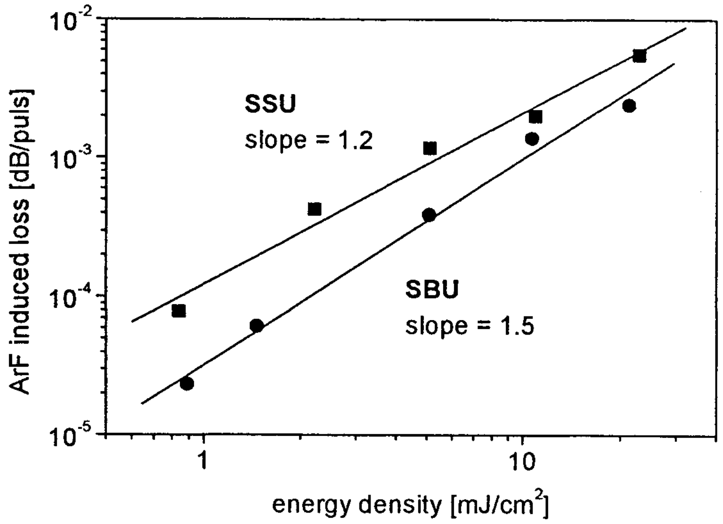

Figure 7 Induced loss per ArF laser-pulse at the beginning of the ArF irradiation of non hydrogen loaded SSU and SBU fibers (length = 1 m) as a function of the pulses' energy density. The slope of 1.2 in the case of the SSU fiber indicates, that the predominant degradation effect is a one photon process caused by the transformation of non-absorbing precursor centers. In the case of the SBU fibers less one-photon processes accompany the solarization, therefore the two photon process becomes more dominant.

A completely different solarization behavior of these two fiber types upon ArF-excimer laser irradiation occurs after loading the fibers with molecular hydrogen (Fig. 8). Although the E'-center creation of a hydrogen loaded SSU fiber is not as strong as in the unloaded one the presence of precursor defects in the SSU fiber leads to a 215 nm band. Due to the restricted mobility of molecular hydrogen within the silica matrix the continuously generated E'-centers cannot be healed instantly (reaction scheme 4), leading to an equilibrium between the creation of E'-centers by UV-photons and the recovery by hydrogen. In the case of the hydrogen loaded SBU fiber the reduced amount of precursor defects leads to a very slight degradation only. After switching off the solarizing laser the molecular hydrogen leads to a complete recovery of the created defects in both fiber types.

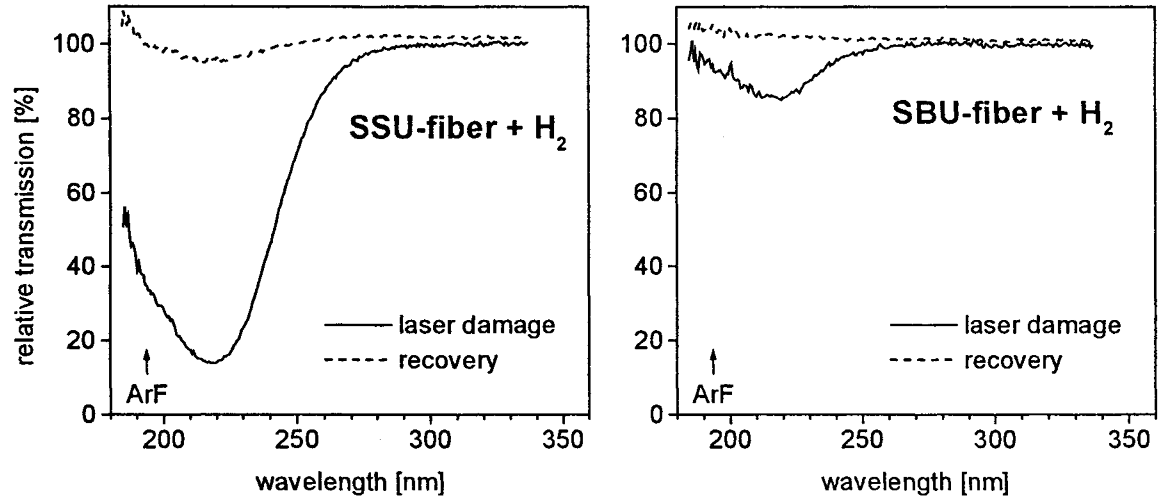

Figure 8 Photodegradation spectroscopy of hydrogen doped SSU 1.1 (left) and hydrogen doped SBU 1.1 (right) fibers after 1000 ArF laser pulses (solid line) and 10 min recovery (dashed line). Irradiation parameters: 50 mJ/cm^2, 10 Hz, fiber length = 1 m.

Long time ArF-excimer laser photodegradation was also performed with hydrogen loaded SSU and SBU fibers (Fig. 9) ($\varepsilon = 5$ mJ/cm^2, $\nu = 400$ Hz, $\tau = 15$ ns, $l_{\text{fiber}} = 1$ m). The fibers show basically the same behavior as already shown in Fig. 8. The hydrogen loaded SSU fiber shows an evident decrease in transmission due to E'-center creation during the first 10^4 pulses. It then saturates at a fixed level, approximately a fourth of the initial transmission. In the case of the hydrogen loaded SBU-fiber no degradation can be observed for 20×10^6 laser pulses.

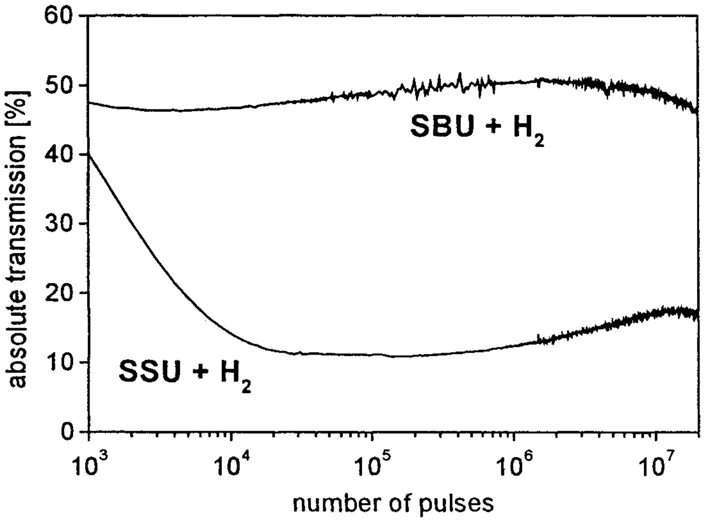

Figure 9 Long-time photodegradation of hydrogen loaded SSU and SBU fibers upon ArF-excimer laser irradiation. Irradiation parameters: 5 mJ/cm^2, 400 Hz, fiber length = 1 m.

The long time excimer-laser photodegradation experiment described above was also performed with a KrF-excimer laser ($\lambda = 248$ nm) (Fig. 10). A 3 m long SSU fiber has an initial absolute transmission of approximately $T_{\text{init}} = 65\%$ (mainly Rayleigh scattering and Fresnel reflection losses) and degrades to a constant transmission level somewhat below 40% ($\varepsilon = 5$ mJ/cm^2, $\nu = 500$ Hz, $\tau = 15$ ns). At the KrF wavelength both, E'-center and NBOH-center absorption contribute to the induced absorption of the fiber. This explains why the SBU fiber's performance under KrF irradiation is inferior to the SSU fiber: according to the ArF photodegradation spectroscopy the creation of NBOH centers in non hydrogen-loaded SBU fibers is higher than in the case of SSU-fibers (Fig. 4).

Nevertheless a hydrogen-loaded SBU fiber does not degrade at all under the same irradiation conditions. This result is also in accordance with the corresponding ArF photodegradation spectroscopy (Fig. 8) and ArF longtime photodegradation (Fig. 9). This experiment was also performed with an energy density of 50 mJ/cm^2, but even at this high fluence the hydrogen loaded SBU fiber showed no degradation at 248 nm.

From this result it can be easily deduced, that the absorption at 248 nm is strongly influenced by the 215 nm E'-center band, since in the case of the hydrogen loaded SSU fiber only E'-centers are created and this fiber shows a significant increase in attenuation at 248 nm. This result is also in accordance with Uhl et al.[8].

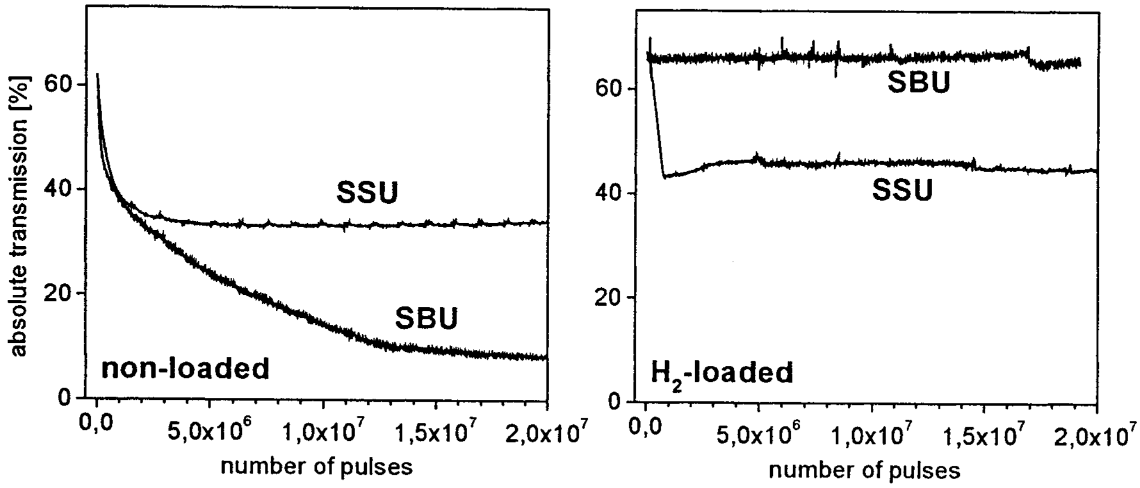

Figure 10 Long time KrF-excimer laser photodegradation of non-loaded (left) and hydrogen loaded (right) SSU 1.1 and SBU 1.1 fibers. Irradiation parameters: 5 mJ/cm^2, 500 Hz, fiber length = 3 m.

Finally photodegradation spectroscopy was also performed with a D_2-lamp (Fig. 11). Basically the results coincide with the excimer-laser spectroscopy described above. In the case of the unloaded SSU fiber irradiation with the D_2-lamp lead to a very strong increase of E'-center concentration and an insignificant NBOH-center creation. A recovery of the E'-centers could not be observed. Corresponding to ArF spectroscopy the hydrogen loaded SSU fiber also showed the characteristic formation of the 215 nm E'-center band during irradiation. However this band healed out completely after the UV-light was switched off.

The unloaded SBU-fiber showed a drastically reduced 215 nm band and a slightly increased 265 nm NBOH band compared to the SSU. In the case of the hydrogen loaded SBU fiber hardly any solarization takes place at all.

As hydrogen out-diffusion occurs, the performance of hydrogen loaded fibers is not stable for a long time. This effect is strongly dependent on the fiber diameter and their working temperature. Fibers with a diameter of 220μm at 20°C with a H_2-concentrations in the order of 10^{19} cm^{-3} just after loading keep enough hydrogen for an improved UV performance for several months[4]. The two main approaches to solve that problem are to reload the fiber or to apply a hermetic fiber coating.

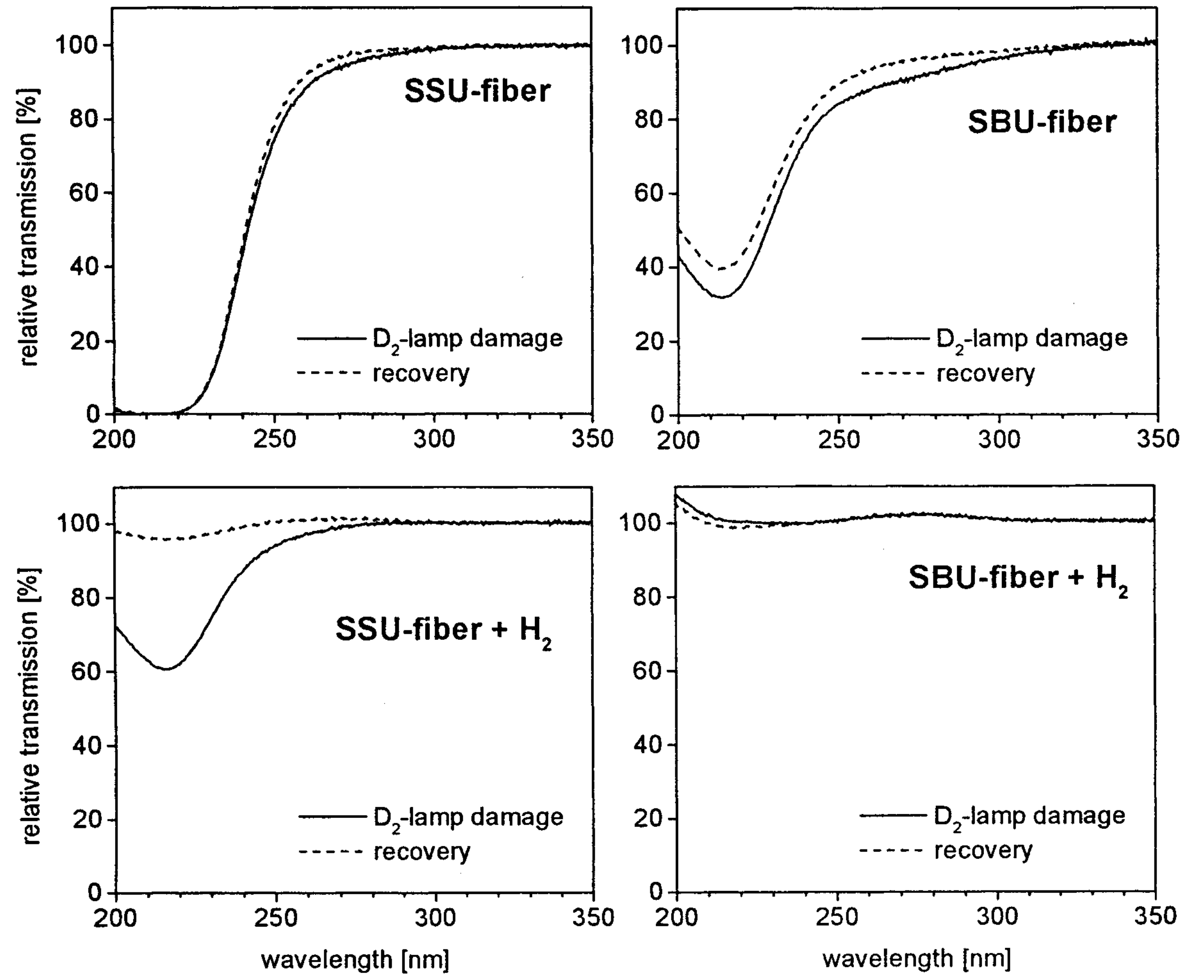

Figure 11 Photodegradation spectroscopy of standard (top) and hydrogen doped (bottom) SSU (left) and SBU (right) fibers after 2 hours of deuterium lamp irradiation (solid line) and 3 hours recovery (dashed line). Fiber length = 2 m.

4. CONCLUSIONS

In addition to a low initial UV-attenuation a major requirement for an optical fiber for an UV application is a strong UV resistance. We introduced an improved preform (SBU) for the production of optical fibers with a drastically reduced photodegradation during transmission of light of a deuterium lamp or an ArF Excimer laser. Photodegradation spectroscopy and energy density dependent photodegradation at ArF laser wavelength (193nm) on SBU fibers in comparison with state of the art SSU fibers indicate that precursors responsible for the E' center creation during UV irradiation are reduced in the SBU fiber. This explains the reduced solarization of SBU at ArF laser and deuterium lamp irradiation as the performance is mainly influenced by E' center absorption.

Hydrogen doping of fibers is well known to improve the UV performance of fibers. Using this technique with the presented new fiber quality nearly no photodegradation is observed under irradiation with deuterium lamp light or ArF **and** KrF Excimer laser. Due to the reduced defect center creation in SBU fibers the presence of hydrogen in the fibers is sufficient to transform nearly all induced defect centers into non absorbing defects. Looking at that strong effect of hydrogen in SBU the problem of hydrogen out-diffusion might be tolerable for applications where extremely low solarization is necessary.

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