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SPEC SHEET

All-Silica, Nonsolarizing Optical Fibers for UV Spectroscopy

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The use of excimer lasers and other strong UV sources in various spectroscopic applications has grown, especially during the past 10–15 years. Because of this growth, the problems associated with the damage and transmission properties of silica fibers in the UV region — particularly for high-power and high-repetition pulsed transmission — need to be addressed. Although a number of fibers that can efficiently handle transmission of relatively low intensities of laser radiation are commercially available, difficulties with high-power radiation transmission still exist. For example, standard synthetic silica optical fibers with high OH levels offer low attenuation and high transmission in the 215–254 nm spectral range, but on exposure to an unfiltered deuterium lamp, these fibers drop to less than 50% of the original transmission within 24 h of continuous irradiation. Similar losses, though less severe and less permanent, have been observed at 308 nm. Also, the standard UV fibers tend to develop significant color centers, visible to the eye, by 10,000 or fewer pulses of excimer laser radiation at 193 nm at fluences of about 50 MW/cm^2. Typically this behavior on exposure to deep UV light is called *solarizing* behavior. Changing transmission capability of the optical fiber during transmission of UV radiation in a spectroscopic measurement creates problems in the analysis of the results, both quantitatively and comparatively.

In the UV spectral region, at wavelengths below 350 nm, synthetic silica optical fibers, having undoped, high-OH cores and fluorine-doped claddings that have a lower refractive index, are the primary candidates. The basic attenuation of these fibers is generally acceptable (1–3). The induced losses primarily arise because of transient or permanent changes in the silica, which are caused by nonlinearities arising from two-photon absorption or simply the creation of defects within the silica. A detailed exposition of possible defects in fused silica was presented by Griscom (4). These losses must be considered and dealt with for transmission of high-intensity UV laser light (5–14), which is required for the developing applications of UV lasers in spectroscopy such as characterization and analysis of materials with excimer lasers and high-power UV lamp sources. These new applications often require high-pulse energies and short-pulse durations, which create very high power densities within the transmission medium and require long-term exposure, either intermittently or continuously.

EXPERIMENTAL

The fibers used in the following experiments were drawn using essentially standard techniques. The basic core/clad structure used a pure undoped silica for the core and a fluorine-doped silica cladding — basically in common with most other all-silica optical fibers. The preforms, however, were made using a proprietary procedure for the modified plasma chemical vapor deposition of silica, different from that of Heraeus or Heraeus-licensed technology. The OH levels for the fibers tested herein were ≥800 ppm. The core diameters of the fibers were generally either 200 μm or 400 μm, with a typical clad-to-core ratio of 1.1 to 1. These fibers are available commercially as nonsolarizing Optran (BioLitec, East Longmeadow, MA 01028) UV optical fibers, for example, as UV400/440P used in the deuterium lamp study presented in Figure 1. The jacket for this fiber is a polyimide coating that has a thickness of about 12 μm. All the results described herein were gathered from tests that were performed by researchers and engineers at unaffiliated clients' facilities.

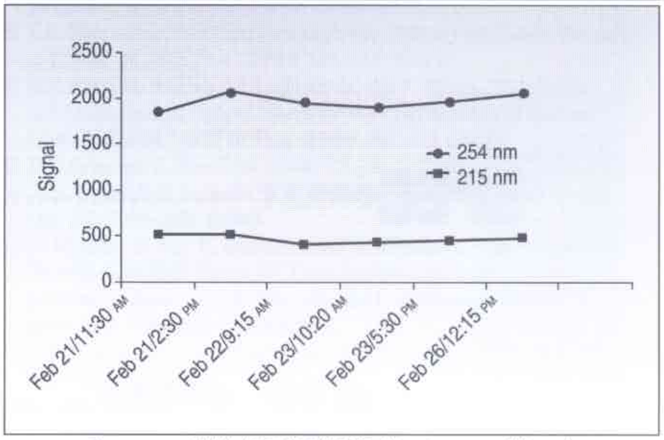

Figure 1. Exposure of UV 400/440/465P fiber to an unfiltered deuterium lamp for five days.

The fiber bundles, used primarily in the long-term exposure to UV light for this paper, were prepared with specially treated terminations in which all organic materials have been removed. The all-silica fibers are fused together to form a pattern of fibers slightly deformed into hexagonal shapes to provide a tight hexagonal packed structure with a minimum of dead space. These specially terminated fiber bundles, PowerLightGuide products (BioLitec), are available in general for high-power transmission, especially when accompanied by high-temperature demands.

The effects of UV light energy at 193, 215, 254, and 365 nm have been observed, as well as additional data at wavelengths ranging from 190 to 450 nm. At 193 nm, an excimer laser source was used. The optical fibers were exposed to pulses of 15 ns duration and input energy of 1.5 mJ. The effects of UV power transmis-

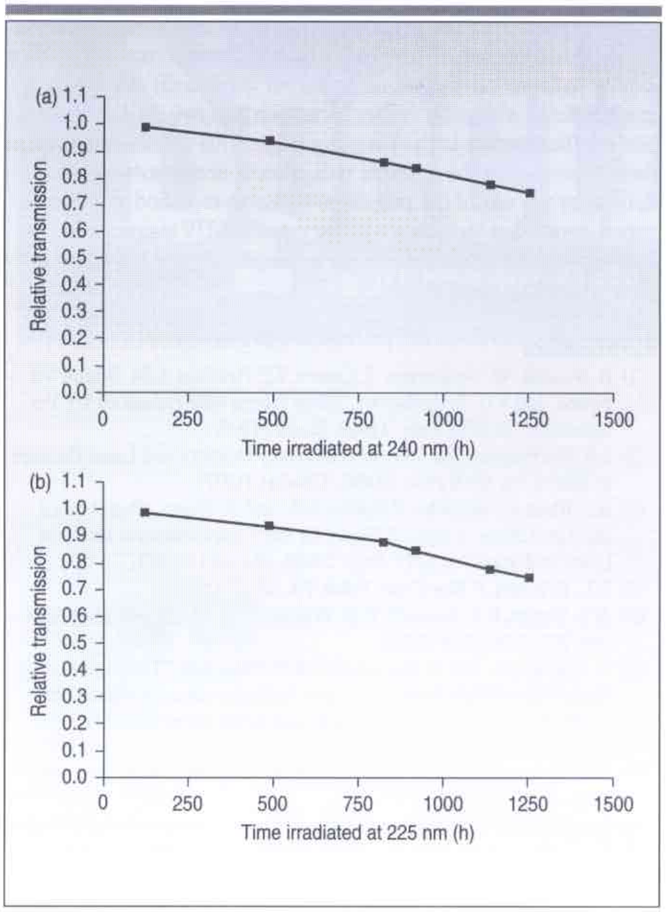

Figure 2. (a) UV fiber transmission stability at 240 nm and (b) UV fiber transmission stability at 225 nm.

sion on optical fibers' transmission behavior at the other wavelengths were observed using continuous radiation sources. These sources were either an unfiltered deuterium lamp or an unfiltered high-pressure mercury lamp. Work on preforms and fibers done earlier in the development of the current plasma chemical vapor deposition process dealt with the fourth harmonic of Nd:YAG lasers, 266 nm (11), and with the 308-nm and 248-nm outputs of XeCl and KrF lasers, respectively (9).

The value of the transmission T for a fiber of length l is given, as in previous publications (7, 9, 10), by $1/T = \exp(\alpha_0 l) + \alpha_1 I_0/\alpha_0[\exp(\alpha_0 l) - l]$, where α_0 is the small signal attenuation coefficient, α^1 is the two-photon absorption coefficient, and I_0 is the input intensity. The coefficients are dependent on wavelength, so fiber transmission at each selected wavelength must be measured as a function of input energy density to obtain their values, as was done in the prior publication (9).

This article's aim is to summarize transmission results obtained over the wide range of deep-UV and near-UV wavelengths; thus, it will not go into a detailed analysis of the components of the transmission.

RESULTS

In Figure 1 the observations of transmission through a UV400/440/465P fiber are presented. As indicated, an unfiltered deuterium lamp was used. The data were obtained over a six-day period. The spectrum was monitored at 253.9 nm and at 214.6 nm. During the 121 h, the transmission through the Optran fiber at 215 nm was substantially unchanged at about 92% of original, while for standard, UV-grade fibers, a drop of 50% was experienced within 24 h. The transmission at 254 nm appears to be slightly improved to about 110% during the 121-h duration of the test. These results are a good indication that essentially no production or growth occurred in the E′-center defect, the absorption peak of which is centered at 215 nm, for the new, nonsolarizing CeramOptec optical fibers.

The Optran UV fiber exposed to repeated pulses of 193-nm laser light was a UV600/660/760/860N fiber. This is an all-silica, 1.1:1 clad/core fiber with the composition and structure indicated in the previous section. It had a 50-μm–thick silicone buffer and a 50-μm–thick nylon jacket. The radiation was focused onto a spot having a 425 μm diameter. The input pulse energy was 1.5 mJ or 1.1 J/cm^2, while the input pulse power was 70 MW/cm^2. The transmission was measured periodically, and the transmission through the Optran fiber was found to be substantially unchanged after 100,000 pulses. In contrast, most standard UV fibers experience significant degradation in transmission in less than 1000 pulses of light at this wavelength and lower input pulse energies. Under the conditions of the 100,000 pulse test, a standard silica/fluorosilica [core/clad] UV optical fiber was found to be colored a deep red by about 10,000 pulses.

The UV transmission stability of a much smaller diameter Optran fiber, UV200/220/245P28, under continuous irradiation by a focused high-power deuterium lamp source was tested across a broad spectrum from 190 to 450 nm. Above 330 nm, no change in spectrum occurred during the 1250 h of continuous irradiation. Results in the UV and deep UV are shown in Figure 2 at 240 nm and in Figure 3 at 225 nm. This fiber also differs from the first examples in that the numerical aperture is elevated to 0.28 compared with the standard 0.22 of most pure silica core all-silica core fibers. The higher numerical aperture is achieved by increasing the fluorosilica content in the cladding. Note in these figures that the transmission at both wavelengths is 99% of the initial transmission after exposure to the deuterium lamp for 120 h. This is very stable behavior, especially at 225 nm, compared with standard optical fiber. Even after 1250 h of exposure the relative transmission at both 240 and 225 nm is still 75%, whereas typical UV-grade fibers have transmission reduced to ≤50% in 24 h or less. Note that, because the lamps are rated for 2000 h, the lifetime of the lamps used was comparable to the extended exposure times and the results were adjusted for change in lamp output over the time of exposure.

Finally, the longest UV exposure testing has been made on specially developed fiber-optic bundles using Optran UV fibers in a fused silica termination. As part of this long-running evaluation of these nonsolarizing fibers, including effects of sustained high temperatures, fiber bundles of 1-m length have been subjected to a range of 500 to almost 40,000 h of continuous radiation at 365 nm. The transmission changed by only about 7% after 200 h and remained essentially constant from 400 h onwards. The radiation source has a measured variability in output intensity of about ± 3%. Comparative measurements were made at several wavelengths as well as for the 360–370 nm range after approximately 1200 h. The results are given in Table I, where the % transmission after 1180 h is the transmission relative to the initial transmission of the sample fiber bundle for the various reported wavelength ranges. All silica fiber bundles from other commercial sources

Table I. Stability of transmission over UV/[near-UV] wavelengths.

Wavelength range (nm)	Transmission after 1180 h (%)
240–250	89.4
310–320	87.9
360–370	86.4
400–410	86.9
430–440	90.1

were found to lose significantly more of their transmission capability and to have a continually increasing loss beyond 400 h. Little or no stabilization was observed at longer times. This application/test also has the problem of high temperatures being present during the operation of the system.

DISCUSSION

Previous workers have determined that the E′-centers and nonbonding oxygen hole center are the primary defects created during high-energy exposure to UV light in medium-to-high OH level silica materials (2–4, 9–11). The growth of absorptions at 163 and 248 nm are now well documented. These detrimental changes in the transmission properties of silica lenses and optical fibers have been called solarization effects. The aims of glass suppliers (15–17) and optical fiber manufacturers (1, 9, 11) as well as silica glass researchers (3, 6, 8, 10, 12) have been to identify the effects, quantify them, and then work to reduce the solarization (16) of these products.

Plasma modified or enhanced chemical vapor deposition processes for creating all silica preforms have done much to improve the quality and reproducibility of the preforms. This processing, though, can introduce some potential sites or nascent defects that can increase sensitivity to solarization. Because most plasmas are oxygen rich, there is a modest probability that, unless special care is taken, peroxy linkages will be incorporated into the preform during its manufacture. This is especially true if the OH level is being held down. Furthermore, most plasmas have intense UV emissions associated with them. These emissions irradiate the silica during the deposition process. This may be more significant during the deposition of the cladding over a solidified core. The exposure may also be enhanced if the consolidation process is carried out more or less simultaneously with the deposition process. The exposure of the preform during its forming may initiate defects or precursors to defects that are activated more easily when, as an optical fiber, they are exposed to laser-generated UV light in a particular spectroscopic application, whether in the medical or industrial areas.

Independent of the general method of fabrication of synthetic silica from $SiCl_4$, the chemistry and physics of the deposition, conversion, and consolidation processes can affect the structure and distribution of intrinsic defects as well as the structure of the glass (18). These can include chemical moieties such as SiOH, SiH, SiCl, O_2, and Cl_2 in addition to the peroxy species mentioned earlier. Interactions between these in the presence of UV radiation have been shown to display a variety of effects on the UV transmission of all silica optical fibers.

The present data are not adequate to allow mechanistic analysis for the latest version of Optran UV optical fibers. Proposed studies similar to those carried out on an earlier version (9) dealing in greater detail with color center formation and two photon absorption coefficients are in the planning stage. This article, however, does demonstrate the possible reduction in precursors for such defects by the use of the proprietary plasma-modified, chemical vapor–deposition techniques in the excellent UV transmission behavior recorded by outside workers, employing the UV fibers in their respective applications.

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