Ultraviolet absorption in modified chemical vapor deposition preforms

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Using a simple and effective technique, we have systematically studied the UV absorption in a number of fiber preforms made by modified chemical vapor deposition. The 242-nm absorption band due to germanium-related oxygen-deficient centers (GODC's) is found to be approximately linearly dependent on germania concentration and, after a small initial increase, is almost constant throughout the preform collapse process. However, we found that the band can be increased by 700% when a reducing atmosphere (He + 1%D_2) is substituted for O_2. Several codopants have been evaluated to determine their effect on the GODC concentration. Phosphorus, boron, aluminum, and fluorine all reduce the 242-nm band; phosphorus causes the largest change.

BACKGROUND

Since the discovery of photosensitivity in germanosilicate fibers by Hill *et al.*,[1] there has been a considerable amount of research on optimizing and understanding the effect. The absorption band at 242 nm, which arises from germanium-related oxygen-deficient centers (GODC's) in these fibers, is found to be critical for the effect, its strength ultimately determining how much UV light will be absorbed when the fiber is transversely illuminated by the use of the grating writing configuration first demonstrated by Meltz *et al.*[2] Photobleaching of the band in UV-exposed fiber samples has been observed by some researchers.[3,4] The cause of the index change forming the gratings may be a combination of color-center related changes in UV absorption together with a change in the glass transition temperature T_g caused by annealing (the temperature during grating writing is estimated to be well over 1000 °C in some cases). For an enhanced effect, high GODC levels are required in fibers. These levels have been achieved by resorting to fibers with high germania content or by flame brushing.[5] An enhancement in the 242-nm band has also been observed by several researchers[6–8] when a helium and hydrogen atmosphere is used at the preform collapse stage instead of conventional oxygen. It is generally believed that the GODC levels are critically dependent on several preform fabrication parameters, in particular the collapse procedures, the atmosphere during collapse, and codopants in the fiber cores. To our knowledge, there has not been a systematic study of these important aspects.

We have used the strength of the GODC absorption band at 242 nm to evaluate the levels of GODC in preforms, which was found to be similar to those in the resulting fibers by Gallagher and Osterberg.[9] UV absorption in preforms with germanosilicate cores has been studied by several researchers using polished preform disks with only the core illuminated.[3,8] However, we have devised a simpler and accurate method for obtaining UV absorption of glass made by modified chemical vapor deposition (MCVD). This method involves cutting samples from an uncollapsed MCVD preform tube and measuring the transmission through the deposited film on a standard spectrophotometer. The silica substrate tube has negligible loss in the wavelength range of interest. The core deposit of tens-of-micrometers thickness on the uncollapsed preform tube can be measured, allowing for accurate resolution of the GODC band at 242 nm. We have used this method to investigate the evolution of the GODC population during preform collapse and the dependence of the GODC on germania concentration, collapse conditions, and codopants.

EXPERIMENT

A silica substrate tube is first washed in water before further cleaning by gaseous etching with SF_6 and fire polishing at ~1700 °C. Using a MCVD technique (the process is reviewed in Ref. 10), we first deposit a layer of pure silica to calibrate the system and to provide a barrier layer of high-purity silica between the substrate tube and the deposit to be studied. Three to five layers of germanosilicate glass are then deposited. The collapse process is conventional except that different parts of the preform are collapsed or partially collapsed in different ways. To study the evolution of the GODC population during collapse, we change the starting position of the burner at each collapse pass, thus leaving a section of the preform unaffected by the subsequent process. This step permits evaluation of samples at different stages of collapse.

The preform refractive-index profile is then taken from a totally collapsed section of the preform to establish the core size and germania concentration (a molar refractivity of 1.32×10^{-3} index change/mol% GeO_2 is used, from Ref. 11). A typical preform collapse log is shown in Table 1. Samples at different stages of the collapse process are obtained from the sections of preform tube left as the burner pass was shortened. The thickness of the layers of germanosilicate glass on the inner surface depends on the extent of the tube collapse. The thickness of the film is calculated from the measured core size

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Table 1. Typical Collapse Log

Collapse Pass Number	$GeCl_4$ (cm^3/mim)	O_2 (cm^3/min)	Burner Speed (mm/min)	Temperature (°C)
0	~5	600	100	1800
1	~5	600	80	~1900
2	~5	200	60	~1900
3	~5	200	40	~1900
4	~5	200	Reverse 30	~1900

in the totally collapsed preform and the inner diameter of the tube. An ~20-mm length of the tube is then cut in two with a semicircular cross section, and the resulting samples are measured on a Perkin-Elmer spectrophotometer (Lambda 9) with an ~1-mm-wide beam traversing through the face of the sample.

A fresh substrate tube (WG tubes from Heraeus Silica and Metals Ltd.) was tested first. An absorption tail below 230 nm was observed with ~1 dB/mm measured at 200 nm. A small band at ~242 nm (~0.1 dB/mm at the peak) is also seen. This band is due to the well-known oxygen-deficient centers at silicon sites in silica (the equivalent of GODCs; see Refs. 6 and 12). This loss in the substrate tube (~1-mm thickness is normally used) would contribute as much as ~15-dB/mm loss at 200 nm in our preform measurements after normalization against the thickness of the deposited film. This value is significant for our measurements because the loss in the deposited layers can be as low as tens of decibels per millimeter around 200 nm. So, to reduce the error, a fresh substrate tube of a similar thickness is always used as a reference in the spectrophotometer.

The measured loss in germanosilicate glass reported here is similar to that obtained by other researchers[3,4,8,9] with a band at 242 nm and a UV tail below 210 nm. In samples with high GODC concentrations, the peak of the 242-nm band cannot be resolved owing to background fluorescence at ~400 nm emitted from the excited GODCs (a filter can be used to block the fluorescence to improve the measurements). In these samples we estimated the loss at 242 nm by filling in the missing section of the spectrum by a fit of the resolved section to a fully resolved spectrum obtained in a sample with low GODC concentration.

The 242-nm band at different collapse stages was studied for three preforms with different germania concentrations. Figure 1 gives the peak value of the 242-nm band at the beginning of the each collapse pass for the three preforms. At the end of pass 4, the preform is totally collapsed, and UV loss spectrum is measured on a slice of preform (~100 μm thick) with the cladding around the core masked off. An increase (20–30%) in the 242-nm loss was observed after pass 2. Thereafter the loss remained approximately constant. The evaporation of the germania film at the surface during collapse is thought to affect less than 10% of the total thickness of the deposited film, according to the refractive-index profile of the totally collapsed preform, and, therefore, introduces an error of only a few percent in these measurements.

Preforms with different germania concentrations were fabricated and measured to determine the dependence on the strength of the 242-nm band. This result is shown in Fig. 2. The squares were measured from as-deposited films (at the beginning of collapse pass 0 in Table 1). The circles were obtained from samples after two collapse passes. The losses at 242 nm in as-deposited films are generally smaller than those in samples after two collapse passes. A straight line is fitted to the circles by the use of the equation

$$\alpha_{242} = K\rho_{GeO_2}, \tag{1}$$

where α_{242} is the absorption in decibels per millimeter at 242 nm, $K = 36$ dB/(mm × mol% GeO_2), and ρ_{GeO_2} is the concentration in mole percent of GeO_2. A much smaller loss [10 dB/(mm × mol% GeO_2)] was reported in Ref. 8. The discrepancy may be explained by differences in preform process conditions. The linear dependence of the 242-nm band on the germanium concentration indicates

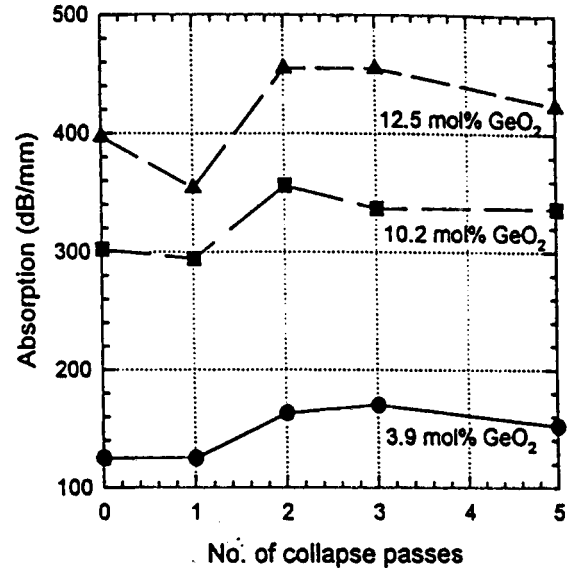

Fig. 1. Peak of the 242-nm band at different stages of collapse for three germanosilicate preforms. (See Table 1 for collapse procedures.)

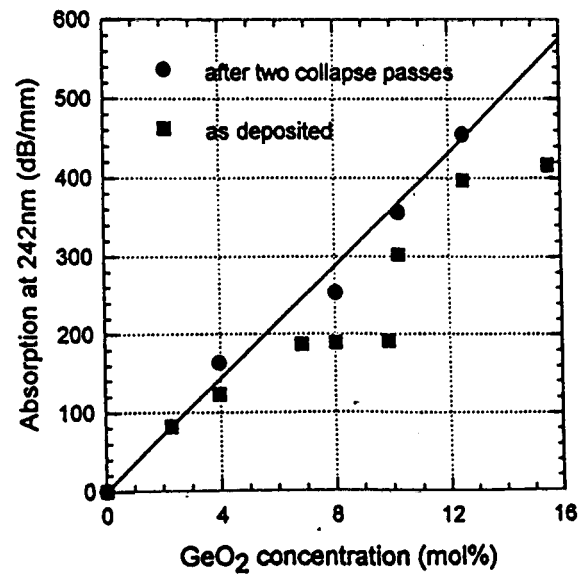

Fig. 2. Peak of the 242-nm band versus germania concentrations in germanosilicate preforms. The squares are from as-deposited samples, and the circles are from the sample after two collapse passes.

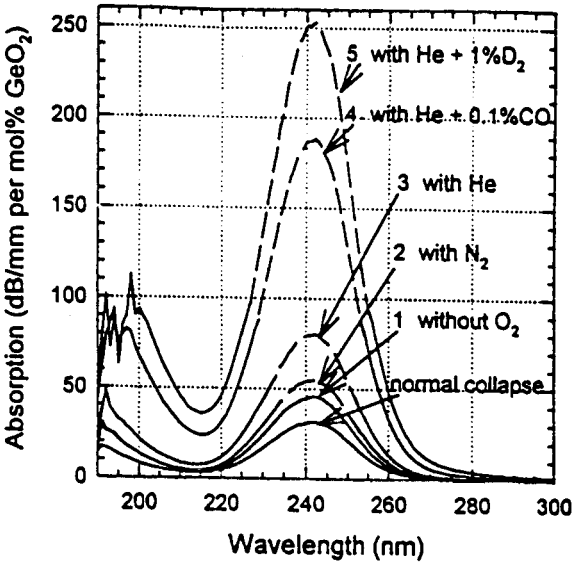

Fig. 3. Effect of collapse conditions on the 242-nm bands.

that it is not due to Ge–Ge wrong bonds, for a quadratic dependence would then be expected.

The effect of collapse conditions was also investigated in five preforms following a collapse procedure similar to that in Table 1, but with the following modifications. In the first preform, the O_2 was switched off during collapse. The same total volume flows of N_2 and He were substituted for O_2 in the second and the third preforms, respectively. Carbon monoxide (0.1%) and deuterium (1%) were added to He in the fourth and fifth preforms, respectively. Figure 3 gives the resulting UV absorption spectra measured on the five preforms. All the samples were taken after two collapse passes. A spectrum from a conventionally collapsed preform is also plotted for comparison. The spectra are normalized with respect to germania concentration for ease of comparison. the 242-nm band in preforms collapsed 1, without O_2; 2, with N_2; 3, with He; 4, with He + 0.1% CO; and 5, with He + 1% D_2 show ~40%, ~70%, ~150%, 500%, and 700% increases, respectively, over that found in a conventionally collapsed preform. In preform 3 the peak loss at 242 nm was measured to be ~80 dB/(mm × mol% GeO_2) in a 8 mol% germania preform. This result agrees with that reported in Ref. 8 for a preform made under a reducing atmosphere.

We have also investigated the effect of codopants on the 242-nm band. Phosphorus, boron, and fluorine were introduced separately in germanosilicate preforms by the MCVD process. Aluminum and sodium ions were incorporated separately by solution doping. In cases other than the F-doped cases, a doped silica preform was made in the absence of germanium to check the UV absorption and to permit the codopant concentration to be estimated from the change in refractive index from that of silica. This concentration was then later used to estimate the codopant concentration after germanium had been added. The germania concentration in these codoped samples was determined after subtracting the index change caused by the codopant. In the F-doped cases, the deposition condition was almost identical to that when the same amount of $SiCl_4$ and $GeCl_4$ was used but without F doping, as the amount of F involved was small. In this case, the germanium content was determined first from the sample without F doping, and the F concentration is then estimated after subtracting the index change caused by the germanium. The following values were used in the index calculations: 5.7×10^{-4} index change/mol% P_2O_5, -4.65×10^{-4} index change/mol% B_2O_3,[11] 1.90×10^{-3} index change/mol% Al_2O_3, and -4.5×10^{-3} index change/mol% F.[13] Table 2 gives the compositions of all the preforms. All the samples were taken after two collapse passes except the phosphorus-doped sample, which was evaluated as deposited.

The UV absorption spectra were measured on all the samples, and the results are shown in Figs. 4–7. The loss at 242 nm as a function of the ratio of the number of codopant atoms to germanium atoms for all the codopants is given in Fig. 8. Phosphorus gives a larger reduction of the 242-nm band than any of the other codopants (Fig. 4), with ~80% reduction when less than one P atom for every 2 Ge atoms is present in the glass. The virtual disappearance of the 242-nm band in P-doped germanosilicate preforms explains the failure to write Bragg gratings in these fibers with a writing wavelength at approximately 242 nm without use of the hydrogenation technique (see Ref. 14 for the technique). We have not observed any UV absorption bands (down to 190 nm) in the pure P-doped

Table 2. Samples Used in the Study of the Codoping Effect

Code	ΔN	GeO_2 (mol%)	P_2O_5 (mol%)	B_2O_3 (mol%)	F (mol%)	Al_2O_3(mol%)	Deposition Temperature (°C)
1	0.0032		5.6				1530
2	0.0125	8.8	1.6				1600
3	0.0138	9.0	3.4				1500
4	0.016	9.7	5.6				1500
5	−0.0098			21.1			1230
6	0.017	16.6		10.6			1350
7	0.0164	16.9		12.3			1300
8	0.0155	17.7		16.9			1250
9	0.0138	17.9		21.0			1220
10	0.004	6.8			1.1		1680
11	0.00065	6.8			1.9		1680
12	0.0026					1.4	
13	0.0075	4.5				0.8	
14	0.0096	4.5				1.9	

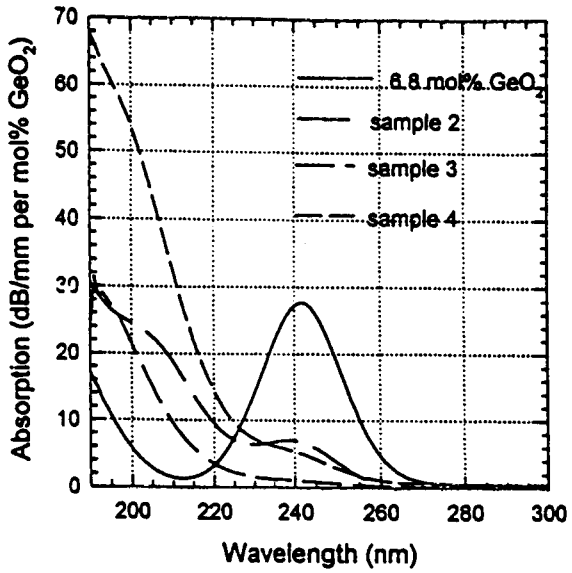

Fig. 4. Effect of phosphorus codoping on the 242-nm band. (See Table 2 for compositions.)

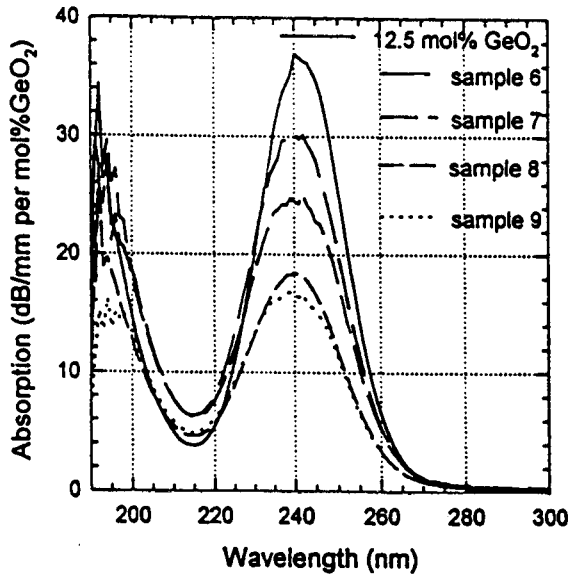

Fig. 5. Effect of boron codoping on the 242-nm band. (See Table 2 for compositions.)

silica preform (sample 1 in Table 2), which indicates that these fibers have a much better UV transmission compared with that of germania-doped silica fibers. In addition to the reduction of the 242-nm band, there is also a large increase in the UV absorption tail below 220 nm and an appearance of a weak band around 210 nm in the P-doped germanosilicate fibers. The 210-nm band is seen most clearly in sample 2 in Fig. 4.

A small amount of boron codoping (<10 mol%) hardly affects the 242-nm band (see Figs. 5 and 8), and more than 10 mol% of boron actually reduces its strength. We find this curious since boron is known to enhance the photosensitivity of germanosilicate fibers.[15] Enhanced photosensitivity in boron codoped fibers has also been confirmed by us in fibers prepared under similar conditions to those for the boron codoped samples. A possible explanation is that boron increases the stress in the fiber. In the pure boron-doped silica preform (sample 5), no absorption bands down to 190 nm were detected.

The presence of fluorine decreases the 242-nm band (Fig. 6). The aluminum-doped germanosilicate preforms give slightly different spectra (Fig. 7). In addition to the reduction in the 242-nm band when aluminum was introduced, a strong band develops at 205 nm, which was not observed in other samples. A similar band has been reported in germania films deposited onto glass substrate.[16] The pure aluminum-doped silica preform (sample 12) exhibits a strong UV tail below 230 nm (Fig. 7).

The incorporation of small amounts of sodium (it has not been possible to determine the exact concentration in this preform) does not have much effect on the 242-nm band. A broad-band absorption appears, however, which tails off at longer wavelengths. This contributes a large

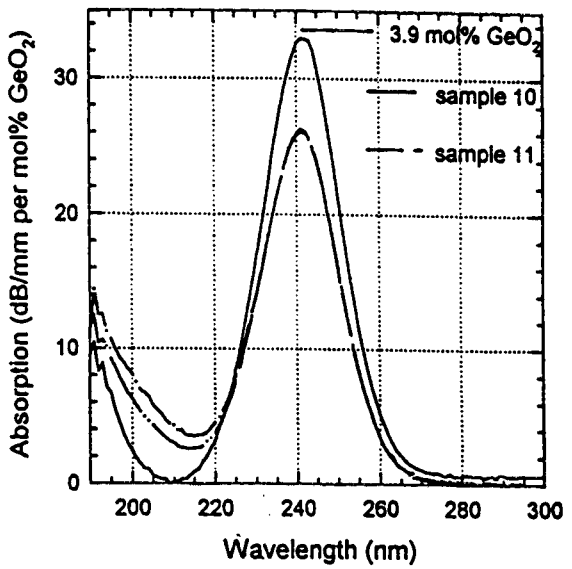

Fig. 6. Effect of fluorine codoping on the 242-nm band. (See Table 2 for compositions.)

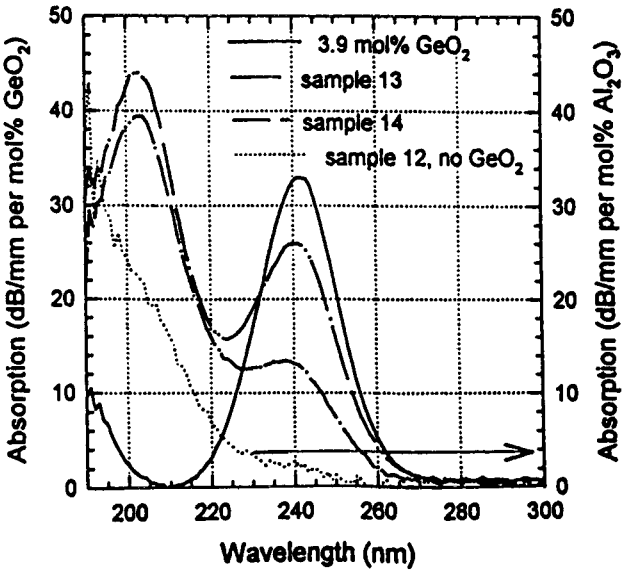

Fig. 7. Effect of aluminum codoping on the 242-nm band. (See Table 2 for compositions.)

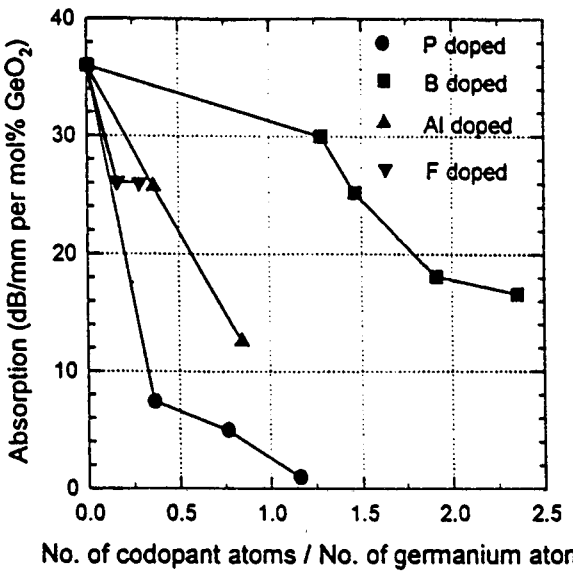

Fig. 8. Peak of the 242-nm band versus the ratio between the number of codopant and germania atoms.

absorption at infrared wavelengths when measured in the fibers.

DISCUSSION

The formation of GODC in germanosilicate preforms is governed by the following equilibrium:

$$GeO_2 \rightleftharpoons GeO + \frac{1}{2} O_2. \quad (2)$$

The reduction in the 242-nm band with the introduction of codopants is difficult to explain with a modification of the local lattice by the codopant atoms, particularly in the case of phosphorus doping, where a large reduction of the band has been seen with small amounts of codopants. A more valid explanation may be a change in the physical properties of the deposited glass when a codopant is introduced. All the codopants that we have used are known to soften the glass; phosphorous gives the largest effect. This softening is evident as sintering temperatures of the codoped glasses are lowered. A softer glass will help the movement of gases in and out of the glasses during sintering and collapsing. With a larger amount of O_2 present in the glass during the sintering and collapsing process, the equilibrium in Eq. (2) will be pushed to the left to reduce the GODC concentration in the glass. Sintering is critical for the formation of GODCs because as the deposits are not totally solidified at the beginning of the sintering, they are, therefore, much more exposed to the gas atmosphere. The slightly higher GODC concentrations after two collapse passes shown in Fig. 1 are explained by the equilibrium in Eq. (1) shifting to the right when process temperatures are raised.

The reducing atmospheres introduced during collapse have been demonstrated to have a large effect on the GODC concentrations, as expected. A significant amount of germanium has been seen to be burnt off from the surface during collapse owing to the instable nature of the reduced GeO_2 at the process temperatures. The GODCs may consist of two different defect centers, as reported in Refs. 6, 17, and 18.

CONCLUSIONS

The strength of the GODC absorption band at 242 nm in germanosilicate preforms is found to be linearly dependent on germania concentration. The GODC absorption band's strength is also found to increase slightly after the first two collapse passes, remaining almost constant thereafter during standard collapse conditions with an oxygen flow through the preform tube. The 242-nm band is enhanced by the use of reducing atmospheres during collapse with an increase of ~700% when O_2 is substituted by He + 1% D_2. Phosphorus, boron, aluminum, and fluorine are all found to reduce the 242-nm peak; phosphorus gives the largest reduction.

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