Germania and Alumina Dopant Diffusion and Viscous Flow Effects at Preparation of Doped Optical Fibers

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Abstract. *We report on germania and alumina dopant profile shift effects at preparation of compact optical fibers using packaging methods (Stack-and-Draw method, Rod-in-Tube (RiT) technique). The sintering of package hollow volume by viscous flow results in a shift of the core-pitch ratio in all-solid microstructured fibers. The ratio is increased by about 5 % in the case of a hexagonal package. The shift by diffusion effects of both dopants is simulated for typical slow speed drawing parameters. Thermodynamic approximations of surface dissociation of germania doped silica suggest the need of an adequate undoped silica barrier layer to prevent an undesired bubble formation at fiber drawing. In contrast, alumina doping does not estimate critical dissociation effects with vaporous aluminium oxide components. We report guide values of diffusion length of germania and alumina for the drawing process by kinetic approximation. The germania diffusion involves a small core enlargement, typically in the submicrometer scale. Though, the alumina diffusion enlarges it by a few micrometers. A drawn pure alumina preform core rod transforms to an amorphous aluminosilicate core with a molar alumina concentration of only about 50 % and a non-gaussian concentration profile.*

Keywords

Alumina, diffusion, doped silica, germania, optical fiber, sensor fiber.

1. Introduction

For about two decades, fibers with extreme refractive index contrast, for instance holey and all-solid microstructured fibers, have been intensively investigated due to their unique optical properties, e.g. unusual dispersion, endlessly single mode transmission, photonic band gap propagation, etc. [1], [2] and [3]. Such fibers are suitable for various sensor applications, e.g. in chemical analytics by absorption, Raman or Brillouin spectroscopy. Fibers with extreme material contrast between core and cladding are also interesting for different applications, e.g. nonlinear devices [4], or sensors for temperature, strain or pressure monitoring with core-inscribed Bragg gratings [5].

The typical fabrication approach for both fiber types follows packaging procedures. The Rod-in-Tube process combines a core glass rod with a different cladding glass hollow cylinder, whereas the Stack-and-Draw method arranges different doped rods or hollow cylinders surrounded by a jacketing tube. The interstitial volume between the mostly hexagonal packaged circular elements is removed at least in the final drawing procedure by evacuation. Alternatively, by drawing at atmospheric pressure the interspace collapse can also be affected by surface tension. The profiles of the doped fibers are smoothed by diffusion, compared to the preform. On the diffusion of GeO_2 in silica matrix by doped layer annealing is reported in [6]. Diffusion and dissociation effects of germania at all-solid fiber fabrication are shown in [7], about the alumina diffusion with low Al_2O_3 concentration reports [8].

2. Simulation of Dopant Dissociation and Diffusion

The germania dissociation is the cause for the development of the central dip in typical gradient and step index fibers. The dissociation can be described by the following simplified reaction:

$$GeO_2(s) \leftrightarrow GeO(g) + 1/2\ O_2(g). \quad (1)$$

Figure 1 shows an exemplary equilibrium partial pressure of the gaseous reaction product GeO starting with a glass composition 10 mol% GeO_2 - 90 mol% SiO_2. The chemical equilibrium was calculated with the program HSC [9]. It demonstrates the high evaporation tendency at fiber drawing temperature of about 1900 °C. The partial pressure of GeO is about 6 % of atmospheric pressure at this temperature. In contrast, for alumina doping no significant vaporous components at this temperature were found. All considered gaseous species, e.g. AlO(g), AlO_2(g), Al_2O(g), Al_2O_2(g), Al_2O_3(g) [10], show an equilibrium partial pressure $p << 10^{-6}$ Pa in the simulation.

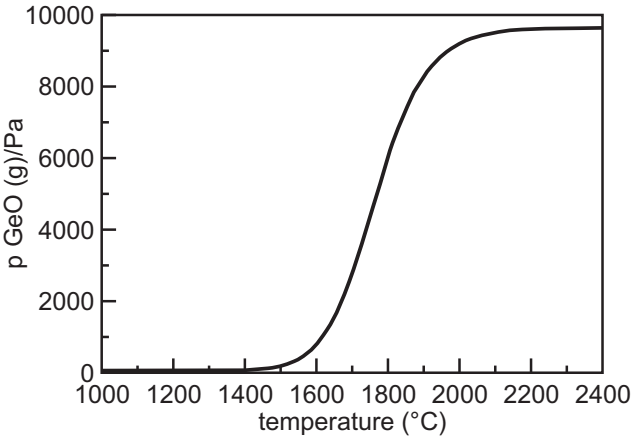


Fig. 1: Calculation of partial pressure vs. temperature for evaporation reaction of germania-silica glass (10 mol% GeO_2), total pressure: 1 bar.

However, in variation to chemical equilibrium consideration the experimental dopant distribution is limited by diffusion effects, depending on temperature and dopant concentration. Figure 2 shows the expected diffusion coefficients at drawing temperature dependent on the dopant concentration. The variation of germania concentration from 1 mol% to 20 mol% at 1900 °C increases the diffusion coefficient by a factor of about 3, from $10^{-10.5}$ cm^2·s^{-1} to 10^{-10} cm^2·s^{-1} [6].

The investigation of annealed aluminosilicate layers by [8] indicates a significantly higher diffusion coefficient with a strong nonlinearity compared to germania doping. In the drawing temperature range (1900–2200 °C) it is expected to be from about

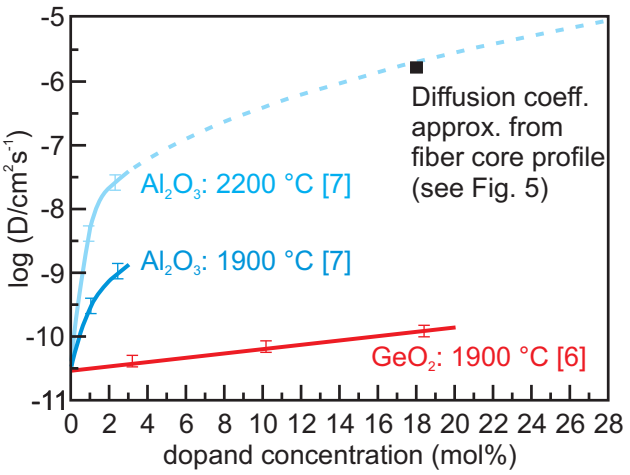


Fig. 2: Approximated concentration dependence of diffusion coefficients for germania (corr. to [6]) and alumina (corr. to [8]) in a silica preform at 1900 °C and 2200 °C, respectively.

10^{-8} cm^2·s^{-1} up to 10^{-9} cm^2·s^{-1} even for low alumina concentration. Though the investigated maximum Al_2O_3 concentration was about 3 mol% in [8].

The effective diffusion time τ_{DF} during fiber drawing was calculated from the axial diffusion zone length z_D and the fiber drawing speed v_F:

$$\tau_{DF} = \frac{z_D}{v_F}. \quad (2)$$

The axial diffusion zone length was approximated from the axial temperature profile, measured along the central axis of the drawing furnace. Based on the equivalent temperature T_{eq} (K), the diffusion zone length z_D can be approximated from the temperature profile (see Fig. 3).

T_{eq} is associated with the activation energy of diffusion E_a given by Eq. (3):

$$\frac{1}{T_{eq}} = \frac{1}{T_{\max}} + \frac{R}{E_a}, \quad (3)$$

where $T_{\max}$ (K) is the maximum temperature of the axial temperature profile and R is the universal gas constant. E_a is given in [6] and [8] presuming an Arrhenius dependence of the diffusion coefficient.

Figure 3 shows the graphically determined diffusion zone lengths with $T_{\max} = 1900$ °C for germania doped fiber drawing and $T_{\max} = 2200$ °C for aluminosilicate fiber drawing. The value of z_D is about 38 mm for a germania doping level between 1 mol% and 20 mol% [7]. For alumina diffusion z_D is approximated to be 52 mm for an Al_2O_3 concentration of 2 mol% and extrapolated to be 60 mm for 20 mol% Al_2O_3.

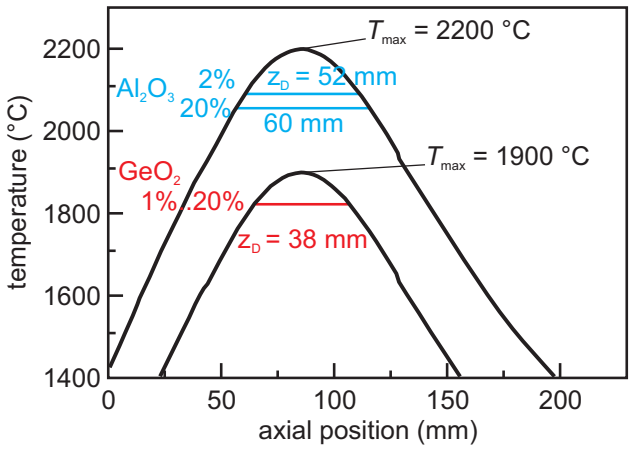
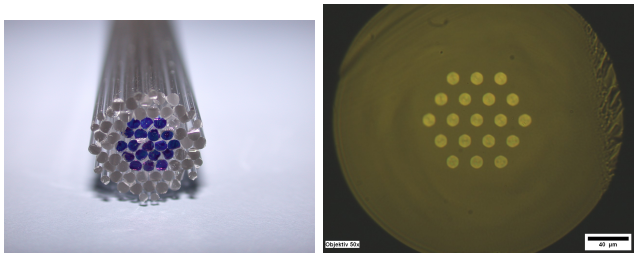


Fig. 3: Approximated effective diffusion zone lengths for alumina and germania doped silica preforms in the drawing furnace.

3. Drawing Experiments

An all-solid microstructured fiber with 19 germanium doped cores (core diameter: $d = 5.0$ µm, pitch: $\Lambda = 10.0$ µm) was manufactured by stack-and-draw technique for a setup in a Coherent Antiresonant Raman Spectroscopic Probe [11]. The preform package arrangement and the drawn fiber are shown in Fig. 4.



(a) (b)

Fig. 4: (a) preform package arrangement of the 19 core fiber. The germania doped rods are marked blue. (b) micrograph of the fiber after drawing.

The shift of the ratio d/Λ was found to be about 5 %. It is caused by the evacuation of the interstitial volume during drawing. The core diameter of the GeO_2 doped preform rods was 504 µm, the outer diameter of 1000 µm, which corresponds to the pitch of the preform arrangement. The GeO_2 concentration was 6 mol%. The core was deposited by Modified Chemical Vapor Deposition (MCVD) with 25 doped layers. After the drawing the core-pitch-ratio has changed from 0.504 (preform) to ratio d/Λ: 0.532–0.533 in the fiber. This corresponds to the expectation by sintering of the interspace volume. The diameter varies over all core elements 5.31–5.57 µm, the pitch: 9.98–10.45 µm, respectively. Due to the relatively low diffusivity of germanium, no significant additional broadening of the core diameter is experimentally observed. The pure silica cladding layer thickness of about 2.35 µm is sufficient for avoidance of bubble formation according Eq. (1).

An aluminosilicate core fiber with extreme high alumina concentration was prepared by RiT technique. A crystalline alumina rod (sapphire) with 2.8 mm diameter was inserted in a silica tube (Heraeus F300) with outer diameter $OD = 30$ mm and central hole diameter $ID = 3$ mm. The preform was drawn with a drawing speed of $v_F = 40$ m·min^{-1} to an UV-acrylate coated fiber with an outer diameter of 125 µm. The drawing furnace temperature, measured with an IR-thermometer, was 2200 °C. The drawing force F was between 0.1 N and 0.17 N. The effective drawing temperature was calculated from the effective drawing viscosity given by Eq. (4) proposed in [12]:

$$\eta(T) = \frac{4F\Delta z_b}{3v_P\left(OD^2 - ID^2\right)\ln\left(\frac{v_F}{v_P}\right)}, \qquad (4)$$

where Δz_b is the axial width of the heating zone for viscous flow in the neck down region of the preform. It is about 35 mm for the used drawing furnace. The approximated viscosity was calculated as about $\log(\eta/Pas) \approx 3$. This corresponds to the measured temperature of the IR-thermometer. It is supposed, that the melting temperature of sapphire (ca. 2050 °C) was exceeded.

4. Results

The dopant concentration profile of the drawn fiber was investigated by SEM analysis. Figure 5 shows the shift of the radial alumina concentration profile from the preform to the fiber. The relative positioning is normalized to the outer diameter of the preform and the fiber, respectively.

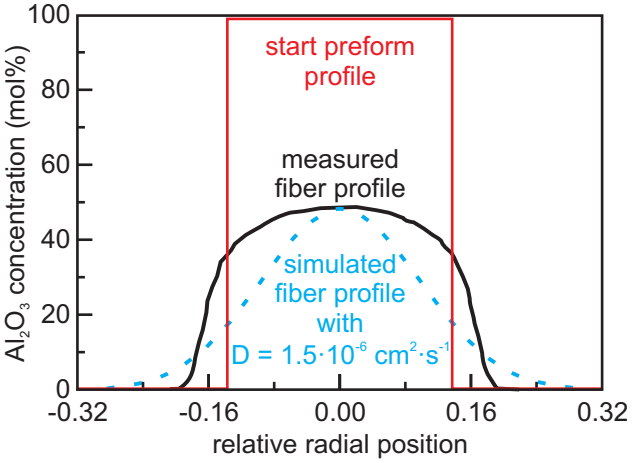


Fig. 5: Alumina concentration profile of the drawn fiber compared to the starting profile of the preform.

The composition of the core changes from pure alumina in the preform to an aluminosilicate glass composition of 50.6 % SiO_2 and 49.4 % Al_2O_3 in the center of the fiber core. The mean diffusion coefficient calculates to be $1.5 \cdot 10^{-6}$ $cm^2 \cdot s^{-1}$ by Fick's law. The approximation is based on an axial diffusion zone length of 60 mm in the drawing furnace and a drawing speed of 40 $m \cdot min^{-1}$. By extrapolating the specified concentration dependence in [8], the found diffusivity corresponds to an aluminosilicate glass with a mean concentration of 18 mol% Al_2O_3 (see Fig. 2). Nevertheless, the experimentally found alumina concentration profile in the fiber cannot be explained only by a simple thermal activated alumina dopant concentration flow balance.

We found structural crystalline changes in the thermal induced transition region from preform core to the fiber core. The investigation of the preform neck-down region by X-ray diffraction analysis shows beside a strong amorphous phase intense peaks of mullite (see Fig. 6). Similar recrystallization effects were also described in [13]. Obviously, the formation of mullite is caused by the long dwell time (approx. 50 min) during passing the neck-down region. After removing the preform out of the drawing furnace it was quenched with natural air convection. The cooling rate is here strong limited by the low surface-volume ratio of the upper neck-down region of the preform. Compared to this low cooling rate under static air quenching conditions, the drawn fiber suffers an extremely high cooling rate by a drawing speed of 40 $m \cdot min^{-1}$. The duration for passing a length of the neck-down region in this case is only 0.05 s.

The investigation of the fiber core (shown in Fig. 7) by electron backscattering shows an amorphous core cross section.

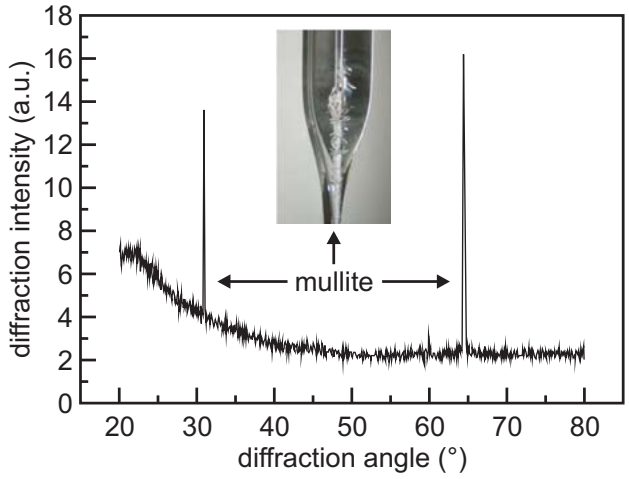
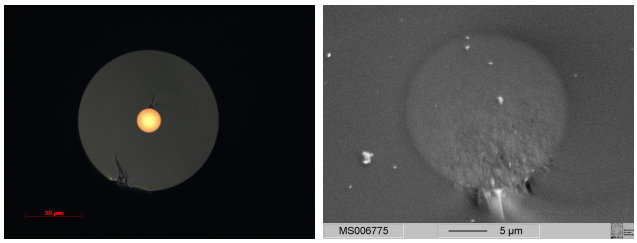


Fig. 6: X-ray diffraction pattern of the core material in the preform neck-down region (inset: photograph of the preform neck-down region, arrowhead shows to the measuring point).



(a) (b)

Fig. 7: (a) white light micrograph of the fiber end face, (b) SEM picture of the fiber core.

We have not found the appearance of any separate crystalline phase in the fiber core. This correspondes with the high transmission and low scattering level of the aluminosilicate core. Figure 7(a) shows the micrograph of the cleaved fiber with white light transmission illumination. The brightness contrast between core and cladding is caused by the high refractive index difference. The SEM picture in Fig. 7(b) demonstrates the excellent homogeneity of the core region. No separate crystals or heterophase separations were observed. The fracture surface at the core cladding interface is caused by the strong tension mismatch between the silica clad and the aluminosilicate core, which has a much higher thermal expansion then silica.

Figure 8 shows the spectral loss of the multimode fiber with a core diameter of 21 µm and a numerical aperture of NA = 0.54.

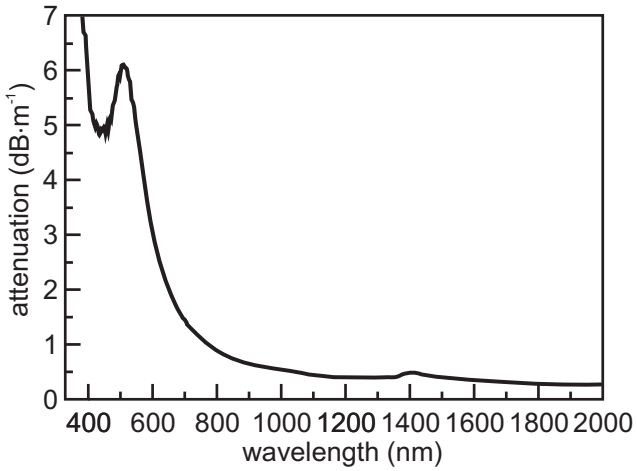


Fig. 8: Attenuation spectrum of the aluminosilicate core fiber.

The minimum loss was found at a wavelength of 1850 nm with 0.27 $dB \cdot m^{-1}$. For a typical application, like Bragg grating inscription at a wavelength of 1550 nm [5], the loss is 0.37 $dB \cdot m^{-1}$. The peak at 550 nm is attributed to impurities of the sapphire starting material.

5. Conclusion

Dopant diffusion combined with thermal induced dissociation can cause variations and disturbances in dopant profiles of all-solid microstructured fibers. For germania doping, a sufficient silica barrier avoids the undesired bubble formation by thermal dissociation. The shift of the core-pitch-ratio by evacuation of the interspace of hexagonal preform packages has to be considered for the design of the final compact fiber. The drawing of a sapphire core in silica cladding does not result in a fiber with a pure alumina core. We found a maximum alumina concentration of about 50 mol% in the fiber core. Obviously, the sufficient softening of the complete preform at fiber drawing presumes the melting of the sapphire rod. The necessarily applied high drawing temperature T > 2050 °C causes an intense reciprocal diffusion of alumina and silica. We found an intermediate recrystallization to mullite in the neck-down region of the preform. The drawn fiber shows an aluminosilicate core with a non-gaussian alumina concentration profile and a maximum Al_2O_3 concentration of about 50 mol%. The diameter of the core is enlarged about by factor 2 compared to the preform cross section. Although the high alumina glasses show devitrification tendency, we found no crystalline phase in the final fiber core. Obviously, the large cooling rate during fiberization of the preform allows overcome the high recrystallization tendency. The fiber core shows a low spectral loss minimum < 1 dB·m^{-1} due to its low scattering and good axial homogeneity. Future applications of this fiber type are to be seen in high temperature sensing and complex all-solid fiber devices, which require a high numerical aperture.

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