Journal of Non-Crystalline Solids 354 (2008) 5408–5420

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Fluorine incorporation in silica glass by the MCVD process: Study of fluorine incorporation zone, evaluation of optical properties and structure of the glass

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ARTICLE INFO

Article history:
Received 17 March 2008
Received in revised form 28 August 2008
Available online 24 October 2008

PACS:
42.70.C
42.81
52.75.R,81.15.G
82.60:61.18.F
78.20.C

Keywords:
Oxidation reduction
Optical fibers
Chemical vapor deposition
Vapor phase deposition
Laser–matter interactions
Nuclear magnetic (and quadrupole) resonance
Optical spectroscopy
Defects
Absorption
Photoinduced effects
Silica
Silicates
NMR
MAS-NMR and NQR
Thermodynamics
Structural relaxation
Viscosity

ABSTRACT

A theoretical approach was made to find out a complete fluorine incorporation zone on a ternary diagram which serves as a useful graphical representation to select the flows of the supplied reagents for incorporation of the suitable amount of fluorine into cladding glass of optical fiber preform made by the MCVD process using CCl_2F_2 as a source of fluorine under oxygen abundance, oxygen deficiency and intermediate oxygen state conditions. The possible mechanism for incorporation of fluorine into cladding glass of optical fiber is also evaluated on the basis of the thermodynamical data. The fluorine incorporation mechanism in silica glass by the MCVD process is found to be dependent on the $CCl_2F_2/SiCl_4$ ratio in the input gas mixture. Fluorine doping is found to be effective for removing the strained Si–O–Si bonds, which govern the optical transparency in deep ultra-violet (DUV) and vacuum ultra-violet (VUV) regions. The maximum refractive index depression of -0.5×10^{-3} is obtained with incorporation of fluorine into silica cladding glass by the MCVD process using CCl_2F_2 as a dopant precursor with suitable flow of $SiCl_4$ vapor along with O_2 through backward deposition pass. The structure of fluorine doped silica glass preform samples containing 1.70–1.79 mol% fluorine incorporated by the MCVD process based on the analyses of ^{19}F MAS spectra done by high-resolution ^{19}F NMR spectroscopy reveal the presence of two distinct types of fluorine environments. The majority of the fluorine environments are formed in $SiO_{1.5}F$ polyhedral and less abundant species is observed to be highly unusual, yielding a fivefold coordinated silicon of the type SiO_2F polyhedral which become increased with increasing the fluorine content.

1. Introduction

Fluorine is a very useful dopant for silica based optical fibers because of its refractive index lowering property without an increase of any additional optical loss [1]. Several fluorinated reagents such as SF_6, SiF_4, CF_4 and CCl_2F_2 are used for this purpose [2–6]. Fluorine incorporation into silica glass using chlorofluoromethane (CCl_2F_2-12) as a source of fluorine has been studied under different deposition conditions and methods [7–13]. Fluorine incorporation into silica glass specifically using CCl_2F_2-12 does not show any fixed deposition condition. Therefore it is necessary to find out a complete deposition zone of fluorine into silica glass. Some works have already been done for determination of fluorine incorporation zone into silica glass [14]. Cocito et al. have evaluated a complete non-deposition zone of fluorine on the basis of the stoichiometry of the two main reactions for $Si_2O_3F_2$ and SiF_4 formation under both oxygen abundance and small oxygen deficiency conditions. The maximum value for lowering of refractive index relative to silica was reported as -4.9×10^{-3} at the flow of $SiCl_4$ of 26.7 mol%, CCl_2F_2 of 39.8 mol% and O_2 of 33.5 mol%.

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doi:10.1016/j.jnoncrysol.2008.09.020

However in addition of SiF_4 other products such as chlorofluorosilanes are formed during fluorine incorporation. Evaluation of the fluorine incorporation zone in terms of the percentual values of the flow of the supplied reagents into silica glass is necessary on the basis of a complete thermodynamical equilibrium of all the possible reactions, including the chlorine dissociation occurring within a gaseous mixture of $SiCl_4$, chlorofluorosilanes, SiF_4, CCl_2F_2 and O_2. It is possible to get an idea of possible maximum lowering of refractive index into silica glass from this fluorine incorporation zone under certain percentual values of $SiCl_4$, CCl_2F_2 and O_2. The optical properties of the fluorinated preform and fibers are studied with variation of the fluorine content to understand the optical transparency specifically below 250 nm wavelength. The structure of fluorinated silica compound incorporated in silica glass of Fluosil preform made by the CVD process using SiF_4 as a source of fluorine and $SiCl_4$ as the silica precursor with methane/oxygen burner is observed by ^{19}F NMR spectroscopy [15–17]. We have focused about the possible structure of fluorinated silica cladding layer using CCl_2F_2 as a source of fluorine incorporated by the MCVD process. The structure of fluorinated compound incorporated in silica cladding glass was evaluated at different flow ratio of $CCl_2F_2/SiCl_4$ on the basis of ^{19}F NMR spectroscopy study.

2. Experimental procedure

Fluorine doped silica layers have been deposited from the gas phase on the inner wall of high purity silica tubes (Suprasil F 300) by means of the well known MCVD (modified chemical vapor deposition) process [18–21]. Tubes with outer and inner diameter of about 20 and 17 mm respectively having 50 cm length were rotated in the MCVD lathe and heated to temperature of 1825 °C by a H_2/O_2 silica burner slowly traversing the tube with a velocity of 12.5 cm/min. After the deposition of several layers, the tubes were collapsed at temperature of about 2250 °C to a solid rods known as optical preform, where the deposited layers formed the preform core with a thickness of about 1–1.5 mm and the carrier tube formed the cladding with an outer diameter of about 10–12 mm. As starting gaseous compounds we used $SiCl_4$, CCl_2F_2 and O_2, in all cases with O_2 as carrier and reactive gas. The refractive index of the deposited layers in the preform core was determined by the Preform Analyzer.

Several preforms are fabricated by the above process with deposition of the barrier layer of SiO_2 + F composition using CCl_2F_2 as a source of fluorine at different flow of CCl_2F_2 against constant flow of $SiCl_4$ and O_2 in order to evaluate the deposition limit of fluorine incorporation into silica glass as well as the etching conditions. The deposition of barrier layers was done at 1825 °C under forward passes as well as under backward passes. The cross-sectional view of the different fluorine doped deposited layers of small hand-drawn preform section are shown in Fig. 1. To identify the fluorine doped layers of different fluorine content, pure SiO_2 layer was deposited in between every two different fluorine content layers. The RI profiles of two fabricated fluorine doped preforms are given in Figs. 2(a) and 2(b) made by backward pass and forward pass

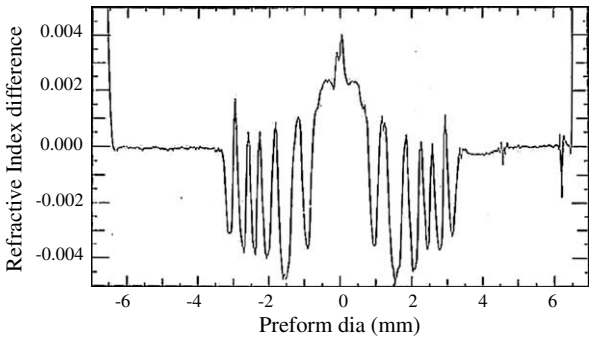

Fig. 2(a). Refractive index profile of fluorine doped different layers deposited along backward direction measured by preform analyzer.

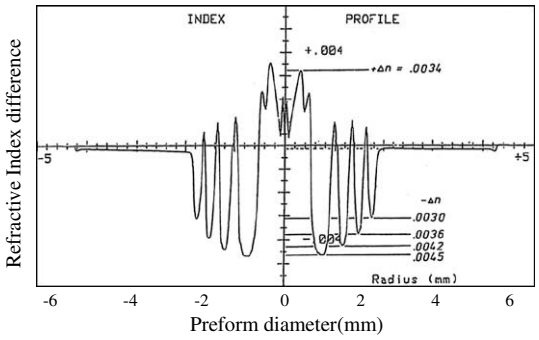

Fig. 2(b). Refractive index profile of fluorine doped different layers deposited along forward direction measured by preform analyzer.

deposition process respectively. Some preform making runs are also carried out with continuous change of the flow of $CCl_2F_2$with respect to a constant flow of $SiCl_4$ and O_2 from every three passes along both forward and backward direction without deposition of pure SiO_2 layers in between two different fluorine content layers. Such fluorine doped cladding layer behave like a depression of RI profile of the graded-Index nature. The RI profiles of such four fluorine doped preforms (two for forward deposition pass and two for backward deposition pass) are given in Figs. 3(a), 3(b) and 4(a), 4(b). The fluorine incorporation into silica glass was identified from the refractive index-profile of the preforms taken by the preform analyzer. Some fibers are drawn from such fabricated preforms with an on-line resin coating. RI profile of fibers drawn from the two fabricated preforms made by backward deposition and other through forward deposition pass are shown in Figs. 5(a) and 5(b) respectively. The fluorine content into silica glass was measured from the refractive index depression value of -2.792×10^{-3} per mol% of fluorine incorporation relative to silica [22]. The transmission spectra of fluorine doped preform and fiber samples are measured in VUV and DUV regions. To estimate the OH content of two such fluorine doped fiber preform samples their transmission spectra are taken in IR region. The transmission spectra of the preform

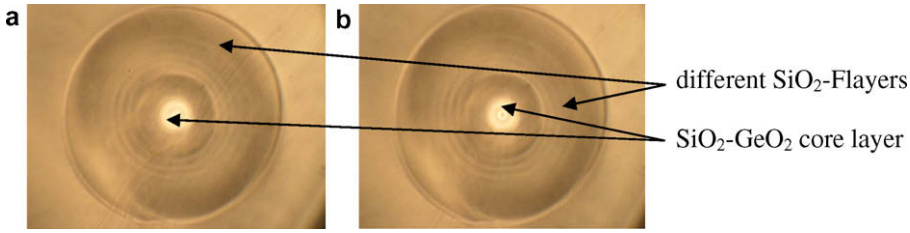

Fig. 1. Cross-sectional view of different fluorine doped silica layers of two fiber preform samples containing (a) 1.70 mol% and (b) 1.79 mol% fluorine.