PROPERTIES OF GE-DOPED SILICA PREFORM BY RAMAN SPECTROSCOPY

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ABSTRACT

In the present work, the structural modifications of Ge-doped silica preforms due to $\gamma$-irradiation at room temperature have been investigated using Raman spectroscopy. The MCVD fabricated preforms labelled as P1 and P2 are distinguishable by the oxidation and thermal history during the fabrication process, in which related to the oxygen bonding of SiO$_4$ tetrahedral. From Raman analysis, the 480 cm$^{-1}$ (D1) and 609 cm$^{-1}$ (D2) peaks are the main network features of pure and doped silica glass, suggest the formation of defect centers in the preforms. The structural modifications of this defects centers are more sensitive in P2, due to the oxygen deficient state of the preform.

Keywords: Ge doped silica perform, raman spectroscopy; MCVD, oxygen-deficient.

INTRODUCTION

Recent study shows that under certain circumstances of fabrication parameter (i.e. pressure, precursor flow, temperature and collapse speed), specific defect condition can occur (Lü et al. 2014; Salh, 2011; Shen et al. 2013). The condition for defect to form is mainly determined by the oxidation (annealing) environment during the process which later can be classified into oxygen rich or oxygen deficient center (ODC) (Ballato and Dragic, 2013; Pasquarello and Car, 1998). The ODC is responsible for many photo-induced transformations that is significant to the development of electronic and optical devices (Salh, 2011; Skuja, 1998). The understanding in the effect of ODC in glass is limited, due to the nature of this defect as it is diamagnetic and hindered by electron-phonon interaction (Skuja, 1998). When the ODC is bleached by photon, this center transforms from diamagnetic into paramagnetic. This rearrangement of electron together with the atomic relaxation, results in the increasing of polarizability. For further investigation, we exposed our sample to gamma- irradiation in order to induce microstructure damage allowing the Si-O-Si coordination to be identified and studied. The structural modification of Ge-doped silica preform have been investigate using Raman spectroscopy.

Structural modification such as symmetric stretching and breathing motion in ring have been reported to be Raman scattering active (Pasquarello and Car, 1998; Salh, 2011; Shen et al. 2013). The number of Si-O-Si rings and their correspondants to the distribution under $\gamma$ irradiation will be quantitatively investigate to understand the effect of preform quality on two different fabrication process.

EXPERIMENTATION

Preformed fabrication via MCVD

The preforms have been fabricated using modified chemical vapor deposition (MCVD) technique labelled as P1 and P2. The MCVD process utilized vapor mixture of highly purity Silica Tetrachloride (SiCl$_4$) and Germanium Tetrachloride (GeCl$_4$) as starting material (Nagel et al. 1982; Wood et al. 1987). The mixture are oxidised by O$_2$ gas being heated with external high temperature oxy-hydrogen flame to form a fine glass particle ‘soot’. The vapor mixture flowed into a silica glass tube which also serve as a substrate. The ‘soot’ are then deposited on the inside walls of the glass tube at downstream of the flame moving direction due to the thermophoresis phenomena (Simpkins et al. 1979). The soot is immediately sintered to transparent, bubble-free high quality glass layer as the flame traverses over that soot position. By repeating the traversal process again, the build-up of the glass layer is done. When the required glass thickness is attained, the tube substrate is heated closed to silica glass fictive temperature (1900 – 2100 $^\circ$C) which reduced the tube diameter slowly (collapse process) and finally produced a solid glass rod known as preform. During collapse process, O$_2$ flowed into the substrate tube to preserve its inner pressure and to avoid volatilization of GeO$_2$ from the core. The O$_2$ flow rate are gradually reduced as the tube diameter decreased and finally stop when the tube inner diameter started to fuse. This MCVD technique are widely exploit in optical fiber fabrication due to the highly pure starting precursor with low impurities (i.e. transition metal ions and OH-ions) glass for long distance optical communication network (Bubnov et al. 2004; MacChesney, 2000). The final quality of the optical glass
such as optical loss/attenuation, refractive index and shape can be controlled by varying the precursor flow and process temperature (i.e. oxidation and annealing) (Ainslie et al. 1982).

In the present work, two types of sample are employed with the precursor flow rate and deposition temperatures are shown in Table-1. The collapsing rate is defined as the speed of the hydrogen-oxygen torch moving from end to end of the preform and the collapse temperature is fixed similar to oxidation temperature. Due to high temperature, substrate tube experienced stronger distortion and also greater GeO2 volatilization rate (Bubnov et al. 2004; MacChesney, 2000; Nagel et al. 1982; Simpkins et al. 1979; Wood et al. 1987). The final solid glass rod is cut to small glass disk (thickness about 2.0 ± 0.2 mm) and polished for optical quality using diamond sand paper. The GeO2 concentration, distribution and also refractive index (RI) were determined using x-ray energy dispersion technique (FEG Quanta 450, EDX Oxford) and preform profiler (Photon Kinetic PK 104).

**Table-1.** Precursor flow rate and deposition temperature.

<table>
<thead>
<tr>
<th>Precursor/Process</th>
<th>Sample P1</th>
<th>Sample P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl4 vapor flow</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>GeCl4 vapor flow</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>O2 flow</td>
<td>1400</td>
<td>1600</td>
</tr>
<tr>
<td>Oxidation temperature (°C)</td>
<td>2100</td>
<td>2200</td>
</tr>
<tr>
<td>Collapsing rate [mm/min]</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

**a) Raman spectroscopy**

Raman scattering measurements were carried out for all preforms by using Renishaw inVia Raman spectrometer in room temperature. The excitation laser was focused to the sample with 50x objective lens from 532 nm (DPSS) laser with power of 25mW. The scattering intensity light collected at 90° to the excitation beam are dispersed with 1800 lines/mm dispersive grating through a 65 um pin-hole then detected using pelter-cooled CCD. The spectral resolution of the dispersive spectrometer is 1.1 cm⁻¹. All the Raman intensity have been corrected for temperature dependence, as shown in equation (1), using Bose-Einstein equation (2) [27].

\[
I_{corrected} = \frac{I_{observed}}{n(\omega) + 1} \quad (1)
\]

\[
n(\omega) = \exp \left( \frac{\hbar \omega}{\kappa_B T} \right) \quad (2)
\]

\[I_{corrected}\] = measured intensity in Raman spectra
\[h\] = Plank’s constant
\[\omega\] = wavenumber in Raman spectra
\[T\] = measurement temperature in Kelvin
\[\kappa_B\] = Boltzman’s constant

The Raman spectra are then normalized to the Si-O-Si symmetric stretching of bridging oxygen (BO) dominant band around 440 cm⁻¹ where this band are predominant for 6-membered SiO₄ (Vaccaro et al. 2010).

**RESULTS AND DISCUSSION**

**Fiber analysis**

The refractive index profile (RIP) are then measured by using a preform profiler (Photon Kinetic PK104) to see the Ge mol% concentration in the preforms. Note from Table-1, the germanium has been proved to have the ability to increase the RIP of the silica. The cladding part of the preform consist only silica, while the core consist both of silica and germanium. The index difference between the core and the outer layer are about 1.44% (P1), and 0.72% (P2). The high index difference in the core shows that the germanium is highly doped in the core during the fabrication process.

**Table-2.** Refractive index profile (RIP) for sample P1 and P2.

<table>
<thead>
<tr>
<th>Analysis on the fiber have been carried out using x-ray energy dispersion analysis (EDX) to see the distribution of all elements in the preforms.</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a) P1</td>
<td></td>
<td></td>
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<tr>
<td>b) P2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By using mapping technique, Figure-1 shows the homogenous distribution of Silica, Oxygen and Germanium element in the core and cladding part for both
preform. This result agree with the RIP profile (Table-2), showing Ge is highly distributed in the core.

a) Raman Spectroscopy

The Raman spectra of both sample before and after radiated with γ irradiation of 10 Gy is given in Figure-2 (a) and (b). Before radiation, both sample produces similar Raman peak wavenumber at ~440, ~480, 600 and 800 cm⁻¹. It has been reported that the broad region around 400-500 cm⁻¹ consist two main peaks situated at 440 cm⁻¹ and 480 cm⁻¹ (D1) [(Galeener, 1979; Vaccaro et al. 2010)]. Peak at 440 cm⁻¹ peak represents the symmetric stretching of bridging oxygen atoms with silicon (Si-O-Si)ₙ with ring number of n=6 (Baur, 1980; Pasquarello and Car, 1998). The 480 cm⁻¹ (D1) is a defect mode, assigned to breathing motion of bridging oxygen in 4-membered SiO₄ rings (Baur, 1980).

From peak deconvolutions at this region, the Raman peaks were observed at 451 and 485 cm⁻¹ with the half width between 93 to 106 cm⁻¹. The Raman shift have been shifted to higher wavenumber around ~12 cm from peak at 440 cm⁻¹ and it is dominated by the changes of bond length (compared with bond angle) which can be refer to the existence of tensile strain between Si-O bond and also phonon confinement effects (Galeener, 1979; Revesz and Walrafen, 1983; Sato and Suda, 1998). Peak at this region also represent strong, narrow and polarized GeO₂ raman scattering at 440 and 456 cm⁻¹ which is capable to shift the peak center wavenumber (Gillet et al. 1990; Sato and Suda, 1998). The dispersion of the peak half width about ~13 cm⁻¹ from usual (Si-O-Si) symmetric stretching mode of bridging oxygen is also related to the incorporation of Ge atoms into Si-O-Si network (Gillet et al. 1990; Martinez et al. 2003).

As reported in (Revesz and Walrafen, 1983), peak at 480 cm⁻¹ (D1) is immune to particle irradiation thus no/small significant observation was found. The peak at 609 cm⁻¹ (D2) is clearly observed on both sample arise from symmetric stretching vibration of oxygen in a planar three membered (Si-O)₃ ring structures (Baur, 1980; Pasquarello and Car, 1998; Shen et al. 2013). The intensity of this band was found higher for sample P2 compared to P1 suggesting an enhancement of the (Si-O-Si)₃ ring structure. The enhancement is suspected from high mobility of Ge atoms during high temperature oxidation process that broke long-range SiO₄ tetrahedral structure. Later, when the sample cooled down to room temperature, the Ge atoms bond and forming a short bond with O atoms thus left down the (Si-O)₃ ring structure. From structural relaxation study shows this phenomenon might increase the material fictive density and the symmetric cooperative vibration (Jr. and Galeener, 1980).

The Raman spectra of both sample before and after radiation b) after γ-irradiation with 10 Gy is given in Figure-2 (a) and (b). Before radiation, both sample produces similar Raman peak wavenumber at ~440, ~480, 600 and 800 cm⁻¹. It has been reported that the broad region around 400-500 cm⁻¹ consist two main peaks situated at 440 cm⁻¹ and 480 cm⁻¹ (D1) [(Galeener, 1979; Vaccaro et al. 2010)]. Peak at 440 cm⁻¹ peak represents the symmetric stretching of bridging oxygen atoms with silicon (Si-O-Si)ₙ with ring number of n=6 (Baur, 1980; Pasquarello and Car, 1998). The 480 cm⁻¹ (D1) is a defect mode, assigned to breathing motion of bridging oxygen in 4-membered SiO₄ rings (Baur, 1980).

As the effect of γ-radiation, the glass atomic structure is deformed and producing a point defect (Friebele et al. 1979). From quantitative studies of the Raman peak, the defect can be identified and their respective phonon interaction, bonding characteristics and strain can be analyzed. Note from Figure-1. (b), after irradiation, more Raman modes appear at 700, 800 1060, and 1230 cm⁻¹ region. The increasing number of these modes can be related to the deformation of Si-O-Si, Ge-Si, Ge-O and Si-Si bond (Gillet et al. 1990; Martinez et al. 2003; Sato and Suda, 1998). At region 600 cm⁻¹, the peak is splitting and broaden slightly to higher wavenumber with decreasing intensity due to Ge-O-Ge bending modes. The weak band at 1060 and 1230 cm⁻¹ which are only apparent in the irradiate sample is assigned to Si-O-Si transverse-optical (TO) and longitudinal-optical (LO) symmetric-stretching and asymmetric stretching respectively with one, two, three and four non-bridging oxygen (Galeener, 1979, 1982; McMillan et al. 1994). While peak at 1230cm⁻¹ shows the breakage of SiO₂ to metasilicate, Si₂O₆ (Chmel and Sochivkin, 1986; McMillan, 1980).

Figure-3 is the absorption spectra reported by Shafiqah et al on the same sample used in this study. The result shows only in P2 sample, peak at 5.1 eV which assigned to the germanium oxygen-deficient sample (GODC) can be clearly observed. This result indicate that
the P2 is an oxygen deficient state while P1 is in an oxygen rich sample. Our results from Raman spectroscopy reveals the oxygen deficient samples are more sensitive to the structural modification by $\gamma$-irradiation, showing larger Raman intensity compared to the oxygen rich.

**CONCLUSIONS**

In summary, we have examined the Raman scattering of Ge-doped SiO$_2$ optical preform fabricated by MCVD technique. Two types of sample were fabricated to study the influence of oxidation process parameter by adjusting the precursor concentration and process temperature. Although their final concentration is almost similar, oxygen-deficient sample is more sensitive to structural modification by $\gamma$-irradiation thus produces significant Raman scattering.

**ACKNOWLEDGEMENTS**

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