Comparative studies on large-core-energy fibres with silica core and fluorine-doped cladding

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Different standard commercial optical fibre samples (silica core with fluorine-doped cladding) were prepared by a modified chemical vapour deposition (MCVD) technique. Their surface and cross-section morphology were characterized by scanning electron microscopy (SEM). Further, X-ray photoelectron spectroscopy (XPS) was used to characterize the compositions, and the chemical environment was also explored by investigating the chemical elements in the samples. The cladding fluorine content for the three fibres is 3.16 wt%, 2.16 wt%, and 1.85 wt% (for fibres A, B, and C, respectively). Moreover, the surface became smoother. Further, the fibre transmission loss corresponding to the fluorine content of 3.16 wt%, 2.16 wt%, and 1.85 wt% was 3.6dB/km, 2.830dB/km, and 2dB/km, respectively. These results indicate that the transmission loss decreases with decreasing fluorine content; thus, fluorine doping affects the optical glass fibre microstructure and transmission loss.

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1. Introduction

An optical fibre or waveguide normally consists of two cylinders having a common centre. The primary one is called core and the secondary one is called the cladding. The first fabrication of the optical fibre was in 1966 and it was used in communication optics [1]. Attenuation in the optical fibre, called transmission loss, is the lowering in the intensity of the light beam with regard to the distance travelled through a transmission medium [2]. The critical attenuation limit of 20dB/km was first realized in 1970 by Schultz, Maurer, and Zimar: they reported a fibre with 17dB/km attenuation by doping titanium in silica glasses. A few years later, they created a fibre with only 4dB/km attenuation using germanium dioxide on the core dopant. Achieving low attenuation is very important in optical fibre telecommunication; this was owing to the significant advancements in the manufacturing techniques and proper material selection and purification [1]. The optical fibre is usually made from insulating materials such as plastic or silica where the core has a refractive index higher than that of the cladding; this is an important condition to consider the total internal reflection [3]. Fluorine is an essential dopant used for preparing a pure silica-core fibre, and unlike boron dopants, it decreases the refractive index of the cladding glass without any additional losses [4, 5]. Fluorine doping have been demonstrated for fibre fabrication by modified chemical vapour deposition (MCVD) [5-8], plasma chemical vapour deposition (PCVD) [9, 10], vapour-phase axial deposition (VAD)[5]and outside vapour-phase deposition (OVD) methods [11, 12].

The applications of the fluorine-doped silica glass as a cladding material for pure silica fibre and its optical properties are significant. Dumas et al. [13] reported the Raman band at 945 cm^{-1} due to Si-F bonds and recommended that a [$SiFO_3$] tetrahedral structure was present in the fluorine-doped glass. Rabinovich[5, 14] recommended that the refractive index reduction in the glass was caused by the fluorine doping, resulting from a substitution reaction of oxygen with fluorine. He also noted that this substitution decreased the non-bridging oxygen defects, which are closely relevant to optical losses in the glass.

However, some works on fluorine-doped silica glasses have reported a structural change in the Si-F bond and exposed some kinds of optical loss closely related to the defects caused by fluorine incorporation in silica glass[15, 16]. For instance, Noguchi et al. [17] reported that there is a slight difference between the wave numbers of the Si-F bond in bulk and fibre glasses. They recommended that this difference was caused by the inside stress applied to the fibre core or by the internal changes respectively to the other dopants. Imai et al. [18] noted that three new Raman bands were observed at 1050–1100,880 and 980 cm^{-1} in fluorine-doped silica glass prepared at a high temperature of 1770 °C.

Hibino et al. [5, 19] considered the optical loss in the fluorine-doped fibres and found that the loss was induced by the drawing fibre process. Yonemori et al. [5, 20] recommended from nuclear magnetic resonance (NMR)

study that fluorine is most likely bonded to the boron in fluorine and boron co-doped glasses. These findings recommended that the optical properties of fluorine-doped glass must be closely related to the fabrication processes, such as the preparation method, purification and stoichiometric controls, and drawing condition. From this point of view, there is still a lack of understanding of the material characteristics of fluorine-doped silica glasses. Consequently, the investigation of the characteristics of the fluorine-doped silica glass is essential [25].

$$\equiv Si - OH\ HO - Si \equiv +2F \rightarrow \\ \rightarrow \equiv Si - O - O - Si \equiv +2HF \uparrow \qquad (1)$$

Fluorine doping in silica decreases the refractive index with no optical absorption in the transmission areas of near infrared, visible, and ultraviolet light [21, 22]. Replacement of non-bridging oxygen with Si-F bonds in the tetrahedral structure have been claimed to give details of the improved optical properties [5].

Consequently, under radiation, a peroxy relation yields two non-bridging oxygen hole centres (NBOHCs) as shown in (1). However, the effect fluorine concentration on the cladding performance and fibre manufactured regimes remains to be elucidated. Comparing the fibres produced under different regimes might provide a deeper insight into the role of fluorine and might allow optimization of the manufacturing regimes [23].

In this study, three kinds of optical fibre with different fluorine content were prepared by modified chemical vapour deposition (samples were prepared by different companies who have not made the details regarding the MCVD method public). The properties and characteristics of fluorine-doped silica glass optical fibres were investigated and a comparative study was performed, which may contribute to improving the fibre performance.

2. Experimental

The fibre structure includes three parts: fibre core (SiO_2), cladding layer (F-doped SiO_2), and coating [poly(methyl methacrylate), $(C_5H_8O_2)n$; PMMA]. The parameters of the fibres are shown in Table 1. In decreasing order of the fluorine content, the fibres are denoted as A, B, and C, respectively.

These fibres were cut for length diameter about 1cm in length for SEM and XPS tests. Then, they were dipped in a dichloromethane solution for1 h to remove the acrylic resin coating from the fibre surface. The samples were put into the beaker containing ethanol in ultrasoundfor30 min to remove surface organic matters. SEM (Model: FEI Quanta 200 FEG) with energy dispersive spectroscopy (EDX) was used to characterize the morphology of the sample. XPS (Model: VG) was used to evaluate the variations in the chemical compositions of the samples. The optical fibre analyser (Model: PK2600) was used to measure the fibre attenuation.

Signal attenuation in optical fibres was determined with the logarithmic unit of decibels. The decibel was used for contrasting two power levels, and has been defined for a particular optical wavelength as the ratio of the output optical power 'Po' from the fibre to the input optical power 'Pi'[2]. The following equation shows how to calculate the attenuation losses:

$$loss(dB) = -10log_{10}\left(\frac{p_\circ}{p_i}\right) = 10log_{10}\left(\frac{p_i}{p_\circ}\right) \qquad (2)$$

The transmission loss is usually expressed in decibels per unit length.

$$\gamma L = -10log_{10}\left(\frac{p_\circ}{p_i}\right) \qquad (3)$$

Here, γ (dB/km)is the signal attenuation per unit length and L (km)is the fibre length.

The details of the material and specifications and compositions of the optical fibres are shown in the Table1.

Table 1. Materials and specifications of the perform optical fibre

Product name parameters	Fibre A	Fibre B	Fibre C
Level of OH	Low	Low	Low
Core diameter (μm)	200 ± 4	200 ± 4	200 ± 3
Cladding diameter (μm)	220 ± 3	220 ± 2	220 ± 3
Numerical aperture (NA)	0.22 ± 0.02	0.22 ± 0.02	0.22 ± 0.02
Material of cladding	Fluorine-doped silica	Fluorine-doped silica	Fluorine-doped silica
Coating	Acrylate	Acrylate	Acrylate
Core material	Pure silica	Pure silica	Pure silica

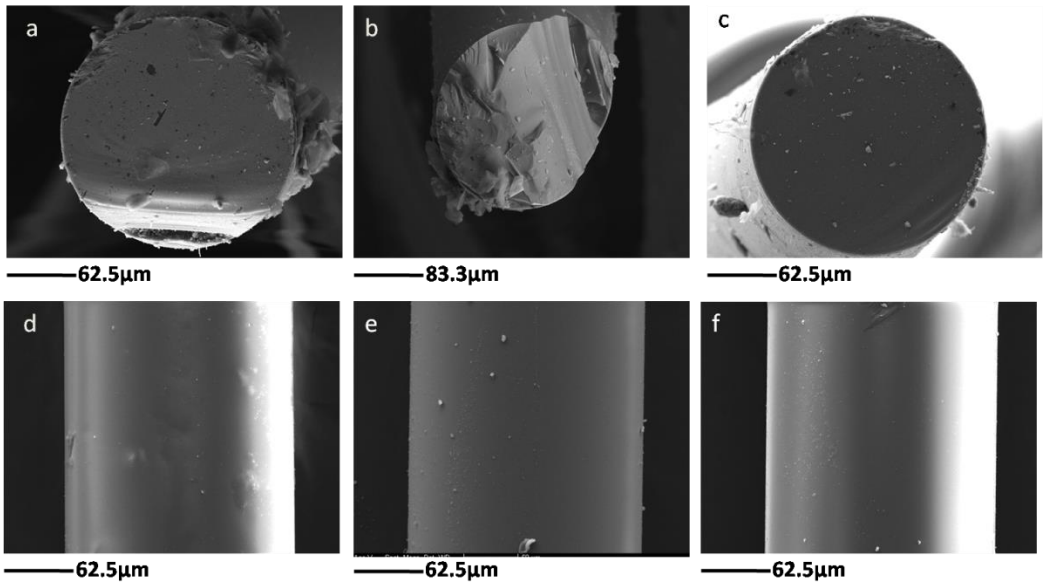

Fig. 1. Cross section and surface morphology for different fluorine concentration. a and d for fibre A, b and e for fibre B, and c and f for fibre C

3. Results and discussion

The core silica energy analysis of the fibre morphology is carried out using samples prepared by different production energy values. The fibre surface and fracture morphology analysis results are shown in Fig. 1, where (a) & (d) correspond to fibre A, (b) & (e) correspond to fibre B, and (c) & (f) correspond to fibre C. Fig. 1 shows an improved surface and cross-sectional scans of the production process parameters and the initial production process parameters for the section scan. In Fig. 1((d), (e) and (f)), a smooth optic-fibre surface with few surface defects and no roughness was observed. Our study results show that the amount of fluorine has no effect on the smoothness or roughness. Fig. 1(a, b & c) shows the cross-sectional area: the sections in (a) and (c) are flat, and (c) is smooth while (a) is heterogeneous. For section (b), the cross-sectional area was not smooth and non-flat. The three types of fibres were drawn using the same temperature and tension, and coated with the same conditions; the differences in the surfaces resulted from fluorine doping.

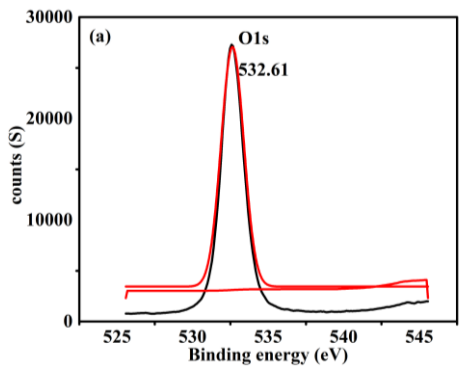

Fig. 2. Section (a): production parameter analysis of XPS for fibre A for O 1s spectra

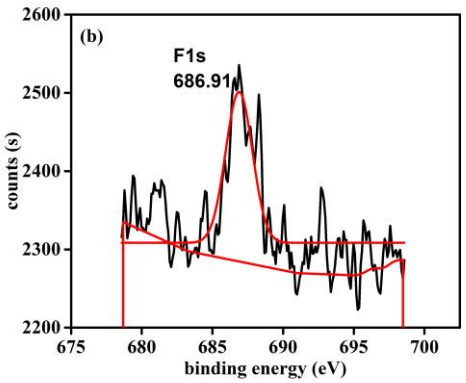

Fig. 2. Section (b): production parameter analysis of XPS for fibre A for F 1s spectra

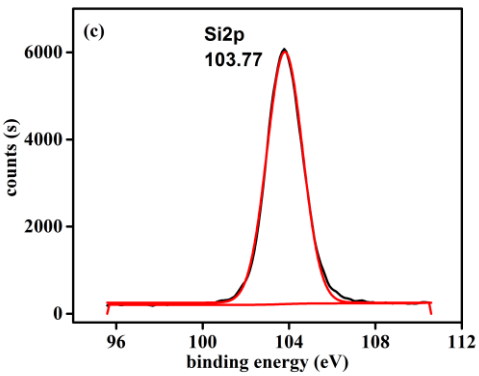

Fig. 2. Section (c): production parameter analysis of XPS for fibre A for Si 2p spectra

The doped fluorine content in the silica glass was determine by EDX to be 3.16 wt%, 2.16 wt%, and 1.85 wt% for fibres A, B, and C, respectively. The remaining

chemical components of the materials are shown in Figs. 2, 3, and 4. O 1s and Si 2p spectra were studied and analysed using XPS. Constraints were used to fit the XPS spectra by using the Origin Lab software program to fit all XPS spectra. A spectrum fitting was done by using Gauss's line shape. All spectra were calibrated to the standard energy. The O 1s and F 1s signals were composed of a single and a peak to fit these spectra with binding energies (BE). The Si 2p signals consisted of a peak. These peak areas were used as the measure of the intensity of all peaks.

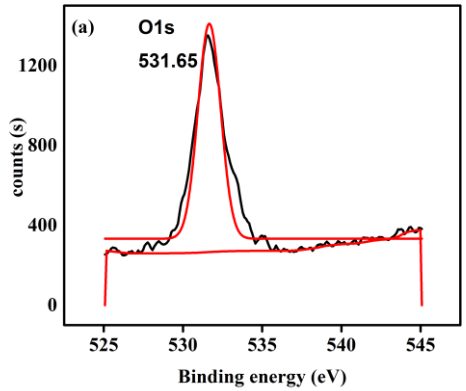

Fig. 3. Section (a): production parameter analysis of XPS for fibre B for O 1s spectra

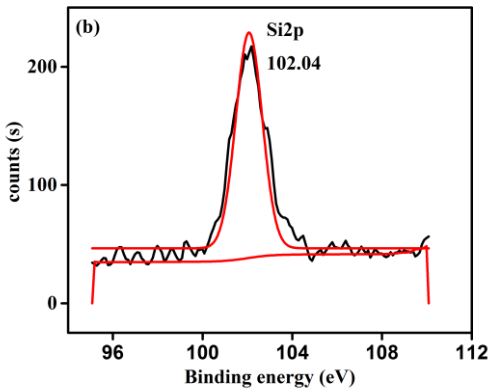

Fig. 3. Section (b): production parameter analysis of XPS for fibre B for Si 2p spectra

Fig. 2(a) shows the O 1s spectrum of the optical fibre A. The peak around 532.61eV corresponds to $Si-OH$ [24-26].Hydrogen is present within the silica glass because it diffuses from the surface of the coating to the inside of the optical fibre during the coating process. The F 1sXPS peak, shown in Fig. 2(b), corresponded to the peak obtained at 686.9eV and appears as an unresolved signal. Various conditions of F 1s cannot be independently part of the X-ray source [27], and the SiO_2 structure was disturbed by the abundant doping of fluorine in the sample. The spectrum of Si 2p at 103.77eV corresponding to a silica-based network, as shown in Fig. 2(c) [28].

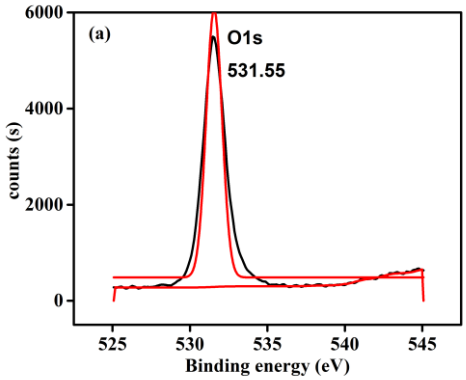

Fig. 4. Section (a): production parameter analysis of XPS for fibre C for O 1s spectra

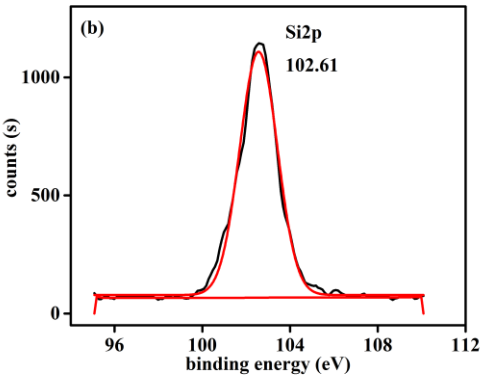

Fig. 4. Section (b): production parameter analysis of XPS for fibre C for Si 2p spectra

Fig. 3(a) shows the O 1s spectrum for fibre B with the peak around 531.65eV corresponding to the Si-O-Si bridging bond [26]. Fig. 3(b)shows the Si 2p spectrum for fibre B; The peak around 102.04eV corresponds to the structure$\equiv Si-O-Si \equiv$[26]. Fig. 4 gives the results for fibre C: Fig. 4(a) shows the O 1s spectrum. The peak around 531.55eV corresponds to the $Si-O-Si$ bridging bond, and this peak was found to be similar to that of fibre B (Fig. 3(b)). In section (b) of Fig. 4, the XPS spectra at 102.61eV demonstrate that the silica glass is a complete network structure with the form$\equiv Si-O-Si \equiv$ [26]. The symmetric shape of the Si 2p peak indicated a homogeneous chemical environment for silicon atoms. After the removal of the coating of the optical fibre, the main component of the remaining part is silicon dioxide.

On the other hand, the difference between fibres B and C was small (about $0.31wt\%$), and is corresponding to the same structure due to the difference between each of them on the fluorine content. A series of peaks produced in the transmission band of the optical fibres is shown in Fig. 5.

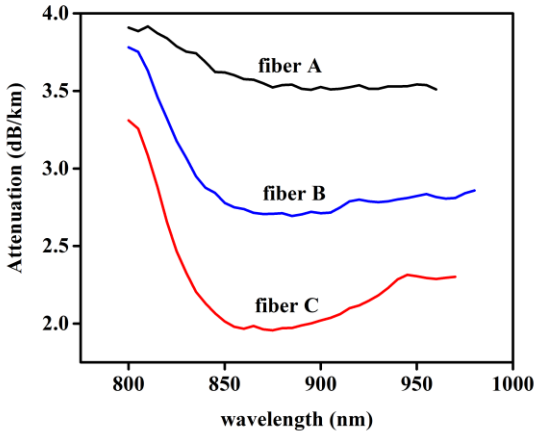

Fig. 5. Comparison of attenuation spectra of F doped SiO_2 for range of 800-980nm wavelength for the three samples

The attenuation spectrum of the first window at wavelength 850nm was found to be 3.6dB/km for fibre A, 2.830dB/km for fibre B, and 2dB/km for fibre C; thus, fibre C has the lowest attenuation. It was confirmed that fibre C has a wide low-loss window at the wavelength ranging from 855nm to 890 nm.

4. Conclusion

In conclusion, the compositions of fluorine-doped glass fibres were investigated using SEM and XPS. The fluorine content was found to be 3.16 wt%, 2.16 wt%, and 1.85 wt% for fibres A, B, and C, respectively. Moreover, the atomic percentages of all elements were referred to silicon, which is considered constant in all samples. The attenuation tests results showed that fibre A exhibited a higher loss than fibre C. The attenuation was found to be high at 800–840nm and above 900nm wavelength for the three samples, and the loss was induced at the fabrication method. Fibre C has a low loss at 855–890 nm wavelengths, while fibre A has a high loss. The optimal fluorine was found to be around 1.85wt%, and the addition of fluorine to the glass fibre inhibits the generation of defects that cause optical loss. Fluorine doping affects not only the microstructure of the optical glass fibres but also the transmission loss.

Acknowledgments

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