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Photoluminescence properties of Bi/Al-codoped silica optical fiber based on atomic layer deposition method

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ABSTRACT

The Bi/Al-codoped silica optical fibers are fabricated by atomic layer deposition (ALD) doping technique combing with conventional modified chemical vapor deposition (MCVD) process. Bi_2O_3 and Al_2O_3 are induced into silica optical fiber core layer by ALD technique, with Bis (2,2,6,6-tetra-methyl-3,5-heptanedionato) Bismuth(III) ($Bi(thd)_3$) and H_2O as Bi and O precursors, and with $Al(CH_3)_3$ (TMA) as Al precursor, respectively. The structure features and optical properties of Bi/Al-codoped silica optical fibers are investigated. Bi_2O_3 stoichiometry is confirmed by X-ray photoelectron spectroscopy (XPS). The valence state of Bi element is +3. Concentration distribution of Si, Ge and O elements is approximately 24–33, 9 and 66 mol%, respectively, in fiber preform core and cladding layer region. Bi and Al ions have been also slightly doped approximately 150–180 and 350–750 ppm in fiber preform core, respectively. Refractive index difference of the Bi/Al-codoped fiber is approximately 0.58% using optical fiber refractive index profiler analyzer. There are obvious Bi-type ions absorption peaks at 520, 700 and 800 nm. The fluorescence peaks are at 1130 and 1145 nm with 489 and 705 nm excitations, respectively. Their fluorescence lifetimes are 701 and 721 μs, respectively. And then there are obvious fluorescence bands in 600–850 and 900–1650 nm with 532 nm pump exciting. There is a maximum fluorescence intensity peak at 1120 nm, and its full wave at half maximum (FWHM) is approximately 180 nm. These may mainly result from the interaction between Bi and Al ions. The Bi/Al-codoped silica optical fibers would be used in high power or broadly tunable laser sources, and optical fiber amplifier in the optical communication fields.

1. Introduction

Bismuth oxide is an interesting material with many promising applications. In 2001, Fujimoto etc. discovered a new infrared luminescence in bismuth-doped silica glass [1]. In recent years, the luminescent materials were demonstrated that they were a promising candidate for optical amplifier in the second telecommunication window [2,3]. Since then the bismuth-doped materials have been studied widely. The broadband luminescence of Bi-doped glasses [4,5] and optical fibers [6,7] in the near-IR region covers from 1.1 μm to 1.8 μm, while these spectral region's fiber lasers and broadband sources are very promising for a number of important applications. In 2005, the first bismuth-doped fiber was fabricated by the modified chemical vapor deposition (MCVD) method [8]. In the following years, some bismuth-doped fiber lasers and amplifiers in the wavelength 1100–1550 nm were also reported [9–12].

Now, the fabrication technologies of Bi-doped fibers like rare-earth doped fibers, are mainly using MCVD, and combining with solution doping technique [13,14]. However, the combining technology lacks of uniformity, and doping materials are easily volatilize in high temperature, which have limited the excellent performance for the doped fibers' fabrication. Atomic layer deposition (ALD) is a chemical vapor deposition technique based on the sequential use of self-terminating gas–solid reactions, and that is a self-limiting surface reaction [15], whose advantages [16] include good uniformity, favorable dispersibility, and high doping concentration as a novel method. At present, there are only few reports

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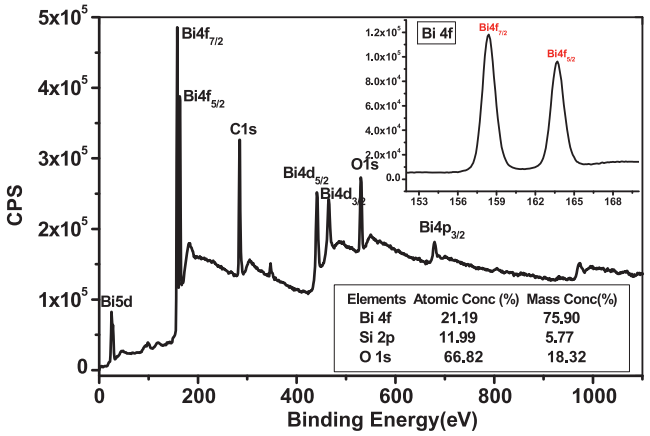

Fig. 1. XPS spectrum of the Bi/Al-codoped silica optical fiber material, (inset) atomic ratio of **Bi**, **Si** and **O** elements.

about the preparation of rare earth optical fiber by ALD [17–19]. However, the Bismuth oxide induced into silica optical fiber core by ALD technique and its optical properties was seldom reported.

In this paper, we present a new doping method for Bi/Al-codoped silica optical fibers combining ALD with MCVD technique, investigate their structure features and optical properties, and confirm its stoichiometry using XPS. For the Bi/Al-codoped silica optical fibers, there are typical absorption peaks at 520, 700 and 800 nm. Their fluorescence peaks are near 1130 and 1145 nm with 489 and 705 nm excitation, respectively. Fluorescence lifetimes are also 701 and 721 μs, respectively. These are good optical properties for its potential applications in the specialty optical fiber lasers and the growing demands of both existing and forthcoming optical communication systems.

2. Experiments

2.1. Formation process of Bi_2O_3

During the deposition process of Bi_2O_3 using ALD, a silica plate is placed in the silica substrate tube, which is used for XPS analysis with a monochromatic **Al** Kα (1486.6 eV) as X-ray source (Kratos AXIS Ultra DLD, England). It can confirm the stoichiometry of the bismuth oxide as shown in Fig. 1. The figure shows the presence elements including **Bi**, **O** and **Si** elements. The center of binding energy of **Bi** $4f_{7/2}$ is about 158.0 eV, The main peaks of Bi(4f) emission at 156.5 and 160.8 eV can be assigned to **Bi** $4f_{7/2}$ and **Bi** $4f_{5/2}$, these values correspond to Bi^{3+}, which is basically agreement with the bind energy of Bi_2O_3 (158.8 eV). These indicate that the valence state of **Bi** ion is +3. Therefore, there is main Bi_2O_3 existing on silica substrate using ALD doping technique. And then the doping concentrations of ions are [**Bi**] = 21.19 mol %, [**Si**] = 11.99 mol %, and [**O**] = 66.82 mol%, respectively, as shown in the down right corner of Fig. 1.

2.2. Fabrication of Bi/Al-codoped optical fiber

Bi/Al-codoped silica optical fiber is fabricated by ALD technique combining with MCVD technology [20]. The fabrication process can be divided into four steps: Firstly, a porous soot layer is deposited inside silica substrate tube using MCVD process; During the process, chemical reactions in the gas form a fine soot of silica, which coats the inner surface of the substrate tube and is sintered into a semi-clear soot layer; Secondly, **Bi** and **Al** ions are induced on the surface of the porous soot layer using ALD technique (TFS-200, Beneq, Finland), which is a self-limited chemical vapor deposition, and here is applied in the doping materials deposition for optical fiber; Thirdly, germanium ion is doped by MCVD, as optical fiber core layers, and then a Bi/Al-codoped optical fiber preform with a Ge-doped higher index core is formed by MCVD collapsing process; At last, The preform is finally drawn into fibers with typical dimensions of single mode fiber. Its diameters of cladding and core layers are about 124.0 and 9.0 μm, respectively.

For Bi_2O_3, the precursor is Bis(2,2,6,6-tetra-methyl-3,5-heptanedionato) Bismuth(III) ($Bi(thd)_3$) (supplied by Shanghai J&K Scientific Ltd.), and then participates in chemistry reaction with H_2O. $Al(CH_3)_3$ (TMA) is used as the precursor of Al_2O_3. It is noticed that O_3 originated from O_2. The temperature of $Bi(thd)_3$ precursor is controlled about 100–250 °C. In the deposition process, the substrate temperature is around 150–350 °C. And the high pure nitrogen is used as a carrier gas with a flow rate of 100 sccm (standard-state cubic centimeter per minute). Al_2O_3 is deposited with deposition rate approximating 0.94 Å/cycle [21].

The reaction mechanism [22] of $Bi(thd)_3$ and H_2O can be described with Eqs. (1)–(3): the whole reaction can be described in Eq. (1)

$$2Bi(thd)_3 + 3H_2O \rightarrow Bi_2O_3 + 6H\text{-}thd \quad (1)$$

A process is that hydroxyl on silicon reacts with Bi source to obtain $Si{-}O{-}Bi(thd)_2$, as shown in Eq. (2). B process is that $Si{-}O{-}Bi(OH)_2$ is obtained by the reaction with H_2O, and $Si{-}O{-}Bi(thd)_2$ terminated by hydryl groups, as described in Eq. (3). Repeat ABAB operations, the desired Bi-doped thickness is obtained. And Al_2O_3 formation mechanism is analogous to these.

$$A: Si{-}OH + Bi(thd)_3 \rightarrow Si{-}O{-}Bi(thd)_2 + H\text{-}thd \quad (2)$$

$$B: Si{-}O{-}Bi(thd)_2 + 2H_2O \rightarrow Si{-}O{-}Bi(OH)_2 + 2H\text{-}thd \quad (3)$$

2.3. Measurements section

The emission spectra, excitation spectra and fluorescence decay curves are measured with a high resolution spectrofluorometer (FLSP 920, Edinburgh Instruments Inc., English) equipped with a red sensitive single photon counting photomultiplier (Hamamatsu R928P) in Peltier air-cooled housing. A microsecond pulsed Xenon flash lamp μF900H with an average power of 60 W, which can measure decays from 1 μs to 10 s, is used to measure decay curves of Bi/Al-codoped fiber preform. The measurement is performed at room temperature.

Absorption spectra are measured by cut-back technique using a broadband optical spectrum analyzer (OSA, Yokogawa AQ-6315A) in the 400–1700 nm wavelength region, and resolution is 10 nm. Fluorescence spectra are measured by 532 nm backward pumping at room temperature. The optical fiber length of measuring absorption spectra is 20 cm, and that of testing luminescence spectra is 3.2 m with 532 nm pump.

3. Experimental results and discussion

The refractive index difference is measured by optical fiber analyzer (S14, Photon Kinetics Inc., USA), as shown in Fig. 2. The index difference between the core and the cladding is $\Delta n = 0.58\%$. The core and cladding diameter of fiber is approximately 9.09 and 123.67 μm, respectively. In addition, number aperture NA = 0.132. The cross-section of the optical fiber is also shown in Fig. 2.

The absorption spectrum of the Bi/Al-codoped optical fiber using cut-back technique is shown in Fig. 3. We can see that the fiber exhibits several absorption bands at 450, 520, 700, 800 and 1000 nm. These are the type-absorption peaks of Bi ions [1]. And the intensity of the absorption peaks at 520 and 700 nm are relatively stronger. The background attenuation at 1500 nm is approximately