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Metallic hollow waveguide based on GeO_2–NaOH precursor solution for transmission of CO_2 laser radiations

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Abstract
By using the GeO_2–NaOH precursor solution, the hexagonal structural GeO_2 reflective films with high flatness were grown on the inner wall of stainless steel (SUS) capillary tubes by liquid phase deposition method. XRD and SEM were measured to investigate the structure and surface roughness of GeO_2 films prepared with different precursor solution. Subsequently, the transmission losses were measured and calculated which revealed the transmission loss was only one third of previous value in the sample using the glass tube. Considering the processing technology limit of 1 mm-bore hollow waveguide, the output energy distribution of the 1.5 mm-bore sample approximates to Gaussian distribution which may excite the less high-order modes. Furthermore, the full divergence angles, bending loss and output power were further investigated. These results demonstrate that the transmission performance of the GeO_2 SUS tube-based hollow waveguide can meet the requirements for laser surgery and material processing.

Keywords GeO_2–NaOH precursor solution · Stainless steel tube · Hollow waveguide · Liquid phase deposition · Transmission performance

1 Introduction

Mid-infrared CO_2 laser is an attractive alternative to be widely applied for the infrared ray communication, device precision machining and laser surgery due to its high power and appropriate frequency (Lai et al. 2017; Yardi et al.2016). Nonetheless, the application of CO_2 laser has been limited to the lack of high-efficiency transmission waveguide. Although the processing technologies have been matured for preparing the silica glass core fiber, this sort of fiber is rarely used as the transmission medium of CO_2 laser radiation because of its high

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absorption loss in mid-infrared region. Fortunately, the hollow waveguide with air core can be used as mid-infrared transmission medium which benefits from its low coupling loss and scarce end reflection. There are two main types of hollow waveguides which reported in recent research (Melzer and Harrington 2015; Wang et al. 2017), including the leaky optical fiber and attenuated total reflective (ATR) hollow fiber. For manufacturing the ATR hollow waveguide, a key technique is to grow a reflective layer whose reflective index value less than the air core (refractive index is 1) at the wavelength of CO_2 laser (10.6 μm).

Some materials such as Al_2O_3, GeO_2 and SiC have been reported which their reflective index values are lower than 1 at 10.6 μm due to the anomalous dispersion (Kamynin et al. 2015; Ayas et al. 2014). Meanwhile, various procedures are proposed for preparation of the mid-infrared hollow waveguide, including single crystal growth (Harrington and Gregory 1990), chemical vapor deposition (Zhou et al. 2010; Zhang et al. 2003), sol-gel (Jing et al. 2008; Kozodoy and Harrington 1995) and liquid phase deposition (LPD) (Wang et al. 2016). Among of them, LPD method has widespread applications on the fabrication of optoelectronic materials and devices which may benefit from simple process and film forming homogeneously (Nagayama et al. 1988; Hwang et al. 2016; Ramana et al. 2012). In our group, this method has been developed for growing GeO_2 films at room temperature (Wang et al. 2016). The key point of the acid-induced LPD method is how to precipitate GeO_2 solutes gradually and uniformly from a precursor solution, and form GeO_2 films on the regular or irregular shaped substrates. What is a vital in this technology is to dissolve GeO_2 solid powders in an alkali solvent to obtain germanate ion solution, then the germanate ions could be controlled to decompose gradually with addition of acid and release GeO_2 solutes onto the substrates. Previously, the aqueous-ammonia precursor solution was used to prepare GeO_2 reflective layers in the metal capillary (Wang et al. 2016). Considering the strong active behavior of ammonia solution, the adverse reaction would likely occur between ammonia and metal capillary. When using the GeO_2–$NH_3{\cdot}H_2O$ precursor solution, the metal capillary tube is likely corroded to some degree. In addition, the growing rate of GeO_2 reflective layer may become slow relatively and the quality of final formed films needs to be further improved. Hence, research efforts are required to make on fabrication of metal tube-based hollow waveguide using other precursor solution.

It is worth noting that the reaction activity between NaOH solution and metal is lower than $NH_3{\cdot}H_2O$ and metal, and this NaOH solution has been used as the precursor to prepare glass tube based GeO_2 hollow waveguide (Li 2012). Therefore, it can be anticipated that the GeO_2–NaOH aqueous solution might be suitable for growing GeO_2 reflective layer inside a metal capillary tube.

In this work, we intend to prepare the metal tube based GeO_2 hollow waveguides by using GeO_2–NaOH precursor solution (see Fig. 1). The fabrication and transmission performances of hollow waveguides for transmitting CO_2 laser are measured and investigated systematically. It is found that when GeO_2–NaOH solution is used as the precursor, the growth speed of GeO_2 crystalline film is fast and the film quality is improved. The transmission performances of the as-obtained metal tube-based GeO_2 hollow waveguides are greatly improved compared with that of the GeO_2 glass tube-based hollow waveguides which fabricated using GeO_2–NaOH precursor solution.

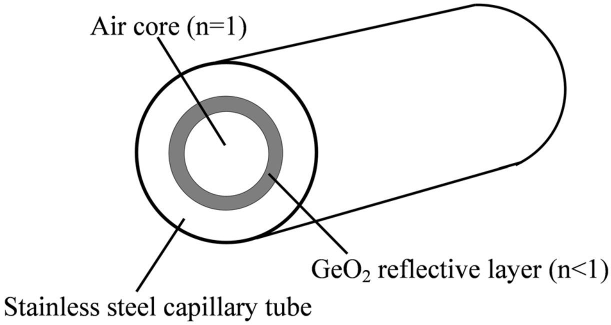

Fig. 1 The structural schematic of SUS tube-based GeO_2 hollow waveguide

2 Experiment

Initially, a certain amount of germanium dioxide powder was dissolved in sodium hydroxide solution to get a NaOH–GeO_2 aqueous precursor solution with mass concentration of 6%. Then sulfuric acid was added to the precursor solution for adjusting PH value to 2. Second, the solution was injected into two SUS capillary tubes with internal diameter of 1 mm and 1.5 mm, respectively. Two ends of SUS capillary tubes were sealed. Subsequently, these tubes were horizontally put on the support equipment and rolled slowly (0.2 r/min). After 7 days, the solution inside the tube was emptied. Two LPD cycles were used to build up a thick GeO_2 reflective film in the tube. Finally, the hollow waveguide samples were dried for several hours before serving for measurement.

In addition, the GeO_2 reflective layers were grown on the planar metal substrates by same LPD method. As comparison, we provided the GeO_2 layer on the planar metal substrate with GeO_2–$NH_3{\cdot}H_2O$ precursor solution at same condition. The crystal phase structure and surface morphology of the as-obtained planar film samples were determined by XRD and SEM, respectively. The transmission losses of GeO_2 hollow waveguides were measured by a Coherent C30A laser device and an optical fiber power detector (LP-3C). The input laser beam power is set as 6 W. The laser beam was focused through a ZnSe lens with a focal length of 10 cm and coupled into the hollow waveguide sample. At the output end, the output beam power was measured by the optical fiber power detector. The transmission losses of hollow waveguides were calculated by cut-off method. The output laser beam profiles and full divergence angles (FDA) of as-obtained hollow waveguides for transmitting CO_2 laser radiations were measured and analyzed by LaserDec CL200. The bending transmission losses of hollow waveguides were measured by displacement method.

3 Results and discussion

Figure 2 gives the XRD pattern of the GeO_2 films grown on planar SUS substrates with GeO_2–NaOH precursor solution. As can be seen, the peak positions and intensities are in good agreement with the hexagonal phase GeO_2 (Wei et al. 2017; Sun et al. 2017). It indicates that the hexagonal structural GeO_2 with excellent crystal quality can be fabricated by LPD process in GeO_2–NaOH precursor solution at room temperature. Considering that the hexagonal structural GeO_2 has abnormal dispersion at the wavelength of CO_2 laser,

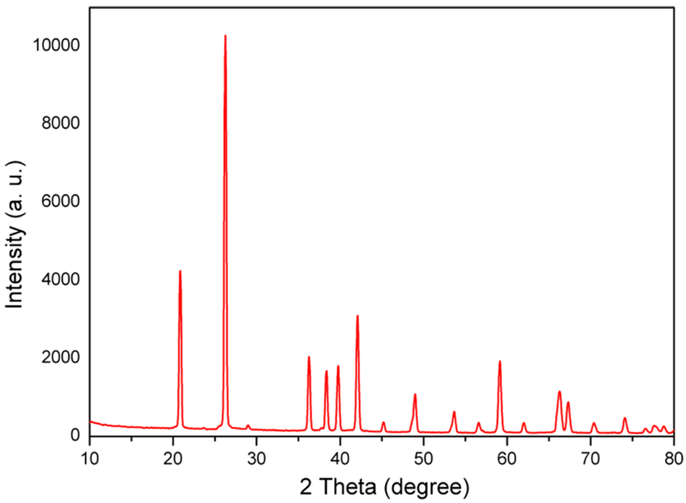

Fig. 2 XRD pattern of the GeO_2 film grown on planar SUS substrate with NaOH solution

thus the refractive index and extinction coefficient of as-obtained GeO_2 film are lower than glassy and tetragonal structural GeO_2. It is the basic requirement for preparing and forming ATR GeO_2 hollow waveguides.

The SEM topographies of the GeO_2 reflective films are shown in Fig. 3 which correspond to the GeO_2–$NH_3{\cdot}H_2O$ (a) and GeO_2–NaOH (b) precursor solution, respectively. From Fig. 3a, there are some large island-shaped particles on the surface of GeO_2 film which lead to increase surface roughness, even though the particles of film are small. By using GeO_2–NaOH precursor solution as shown in Fig. 3b, the particles of film become larger slightly. Nevertheless, these particles are evenly distributed on the surface. NaOH is a strong alkali that the number of OH^- are more than $NH_3{\cdot}H_2O$ solution at the same concentration. Herein, the deposition rate of GeO_2 with $NH_3{\cdot}H_2O$ solution proceeds slowly. With $NH_3{\cdot}H_2O$ solution, the preferential growth caused by local heterogeneous nucleation could easily create island-shaped particles on the surface of film which may contribute to the increase of surface roughness. In contrast, the LPD process with GeO_2–NaOH

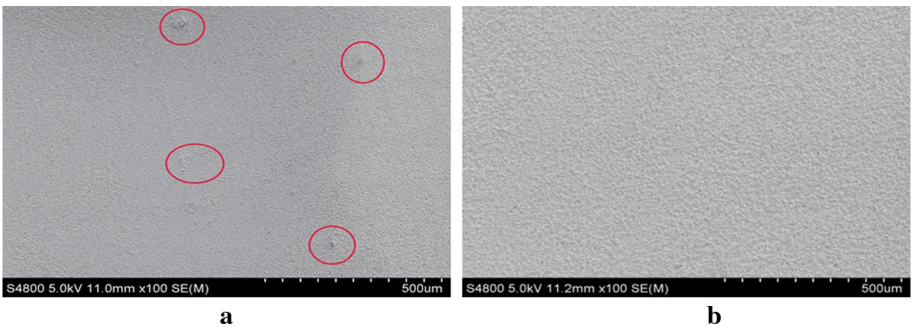

Fig. 3 SEM images of the GeO_2 films grown on planar SUS substrates by two LPD cycles. **a** With GeO_2-$NH_3{\cdot}H_2O$ precursor solution **b** with GeO_2–NaOH precursor solution. Note: the red circles show the island-shaped particles on the film surface. (Color figure online)

precursor solution reacts more quickly and intensely which may inhibit the preferred orientation growth. Consequently, GeO_2 layer tends to grow on the substrate uniformly. The laser transmission performance of hollow waveguide is affected by surface roughness of reflective film, for the reason that the island-shaped particles of surface may increase light scattering and absorption. In addition, the fluctuation of the waveguide core size can excite more high-order modes and lead to the increase of transmission loss. The results reveal that GeO_2 reflective film with using NaOH solution has higher flatness than using $NH_3 \cdot H_2O$ solution. Therefore, it can be suggested that the LPD process with GeO_2–NaOH precursor solution is more convenient for metal tube-based GeO_2 hollow waveguides.

In order to investigate the transmission losses of hollow waveguides, we present the theoretical calculation and experimental measurement. The classic MS equation is given by (1) (Wang et al. 2016; Kozodoy and Harrington 1995).

$$\alpha_{nm}(a) = \left(\frac{U_{nm}}{2\pi}\right)^2 \cdot \frac{\lambda^2}{a_0^3} \cdot Re\left[\frac{N^2+1}{2\left(N^2-1\right)^{1/2}}\right] \tag{1}$$

where α_{nm} is the attenuation coefficient, a_0 is the waveguide bore radius, U_{nm} is a mode-dependent parameter, and N is the complex index of refraction. As for the HE_{11} mode, U_{nm} equals 2.405 for the lowest-order HE_{11} mode. At the wavelength of 10.6 μm, N of the GeO_2 film is 0.48–0.66j. According to this formula, the calculated transmission losses of the 1.5 mm-bore and 1 mm-bore hollow waveguides are 0.0135 dB/m and 0.0455 dB/m, respectively. The measured transmission losses of them are 0.49 dB/m and 2.39 dB/m (Table 1).

In the related researches, the 1.5 mm-bore silica glass tube based GeO_2 hollow fiber presents a calculated transmission loss of 0.0127 dB/m and a measured loss of 1.65 dB/m (Li 2012; Li et al. 2011). From the report results by Wang et al. (2016), a 1.4 mm-bore SUS GeO_2 hollow fiber also shows a difference between calculation loss (0.033 dB/m) and measured loss (0.27 dB/m). Compared with the simulation/measurement results present in this work (1.5 mm-bore fiber sample: calculated 0.0135 dB/m, measured 0.49 dB/m; 1 mm-bore fiber sample: calculated 0.0455 dB/m, measured 2.39 dB/m), one can see that the simulation/measurement results in current work show similar tendency to those reported results. There exist differences between the measured and calculated results. It is worth noting that a mid-infrared ATR hollow fiber with a transmission loss below 3 dB/m may find possible practical application (Li 2012). The as-fabricated fibers may be potentially used in practice, especially as for the 0.49 dB/m loss fiber sample although the measured loss is much higher than the calculated loss (0.0135 dB/m).

Equation (1) has been widely used to evaluate the transmission loss of a mid-infrared ATR hollow waveguide (Harrington and Gregory 1990; Jing et al. 2008; Kozodoy and

Table 1 The transmission losses of GeO_2 hollow waveguides with different diameters and tube substrates

Optical fiber number	Type of tube-based	Inner diameter of hollow waveguide (mm)	Measured loss dB/m	Calculated loss dB/m
1#	SUS tube	1	2.39	0.0455
2#	SUS tube	1.5	0.49	0.0135
3#(Li et al. 2011,2012)	Glass capillary tube	1.5	1.65	0.0127

Harrington 1995; Harrington 2004). Simulations based on Eq. (1) assume transmission of fundamental HE_{11} modes. However, higher-order modes may be excited and transmitted in a hollow waveguide, especially in a hollow fiber with a relative large core size (Wang et al. 2016). The higher-order modes exhibit higher transmission loss than the HE_{11} modes. This arouses difference between the calculated and measured loss (Harrington 2004). In present work, the core size of the fiber goes up to 1–1.5 mm, higher-order modes inevitably exist in the hollow waveguide. The output beam profile analysis also confirms the existence of higher-order modes (see Fig. 4 and related discussions). In addition, Eq. (1) supposes the hollow fiber has a perfect circular hollow waveguide structure. However, the core size of the as-fabricated hollow fiber sample fluctuates more or less along the fiber length direction. We designed and manufactured the SUS structural tubing materials in a company and the 1 mm and 1.5 mm-bore SUS structural tubes exhibit ± 2.4% and ± 1.5% variations in nominal core size, respectively. This is believed to cause additional transmission loss for hollow fiber samples (Kozodoy and Harrington 1995; Wang et al. 2016; Harrington 2004). Therefore, existence of higher-order modes and geometry deviation from a perfect circular hollow waveguide structure are considered to be responsible for the as-observed difference between the theoretical and experimental loss results.

From the calculation and measurement, we can observe that the value of transmission loss decreases when the diameter increases, though there is a large difference between the calculation and measurement. For the changing trend of transmission losses with two

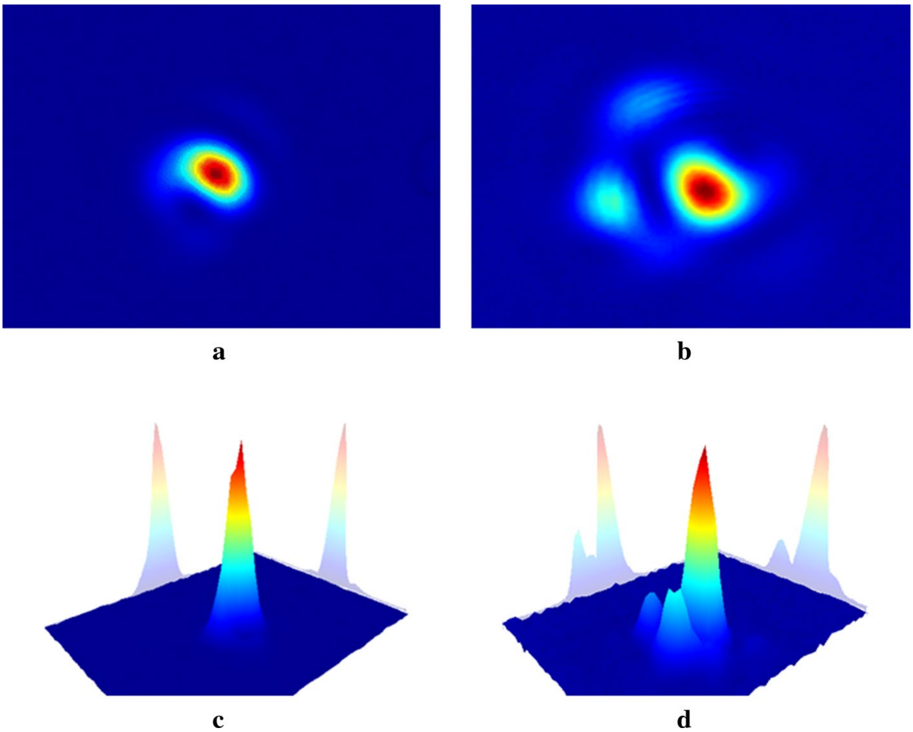

Fig. 4 The output laser beam profiles of a 6 W 10.6 μm CO_2 laser beam transmitted through GeO_2 SUS tube-based hollow waveguides. The 2D and 3D profiles of 1.5 mm-bore sample are in **(a)** and **(c)**. The 2D and 3D profiles of 1 mm-bore sample are in **(b)** and **(d)**

different inner diameters, there is also the distinction between calculation and measurement. The difference of the 1.5 mm-bore hollow waveguide (Δ = 0.49 dB/m–0.0135 dB/m = 0.4765 dB/m) is smaller than which of the 1 mm-bore hollow waveguide (Δ = 2.39 dB/m–0.0455 dB/m = 2.3445 dB/m). For the processing technology of SUS capillary tube, it is difficult to control the fabricating precisely when the diameter of tube is quite small such as 1 mm. Thus, it might explain the large difference of transmission loss between calculation and measurement when the inner diameter of hollow waveguide becomes tiny particularly. Compared with the silica glass hollow fiber sample reported by Li et al. (see table1–3# Li et al. 2011, 2012) using same LPD process, the measured transmission loss of 1.5 mm-bore SUS fiber sample is only one third of the measured loss of the silica glass hollow fiber. It indicates that the LPD process using the NaOH–GeO_2 precursor solution is suitable for the preparation of ATR SUS tube-based hollow waveguides.

The two dimensional (2D) and three dimensional (3D) output laser beam profiles of GeO_2 SUS tube-based hollow waveguides with 1 mm-bore and 1.5 mm-bore are presented at Fig. 4. As shown in Fig. 4a, the 2D profile of the 1.5 mm-bore fiber sample is close to a circle shape, and the corresponding 3D profile (see Fig. 4c) intimates that the power distribution of output beam mainly approximates to the Gaussian energy distribution. From the 2D and 3D profiles of 1 mm-bore sample in Fig. 4b, d, besides a strong circular center, several weak pattern areas are observed which may be ascribed to the scattered light. It should be noted that the hollow waveguide tends to exhibit a high-mode transmission, when the inner diameter is 20 times higher than the wavelength of operation (Jing et al. 2016). Exactly, the inner diameters of the fiber samples (1 mm, 1.5 mm) are much 20 times higher than the wavelength of CO_2 laser (10.6 µm). Therefore, these hollow waveguide samples would support high-order mode transmission, which may explain the difference between the output laser beams profiles (Fig. 4) and standard Gaussian energy distribution. In general, the hollow waveguide with smaller diameter should have stronger capacity for filtering high-order modes. Related research reported of Matsuura et al. (1995) prepared the hollow waveguides with inner diameter of 200–300 µm to realize the lowest-order HE_{11} mode for transmitting the mid-infrared laser. As mentioned above, the sample with inner diameter of 1 mm should possess better ability to filter high-order modes than which with inner diameter of 1.5 mm, hence it obtains better transmission performance. It is obviously inconsistent with the experimental results in Fig. 4. As mentioned earlier, the structure of hollow waveguide with inner diameter of 1 mm has a larger dimension variation from ideal structure, due to the processing technology limit. Besides the HE_{11} modes, more high-order modes are excited in the hollow waveguide containing imperfections. It can be inferred that the profile of the 1 mm-bore fiber is less concentrated owning to the more high-order modes. And this characteristic and behavior can elucidate the large difference between measured loss and calculated loss of 1 mm-bore fiber sample.

The FDA and power density of output laser beam are crucial parameters for the practical applications of CO_2 laser surgery and material processing (Xiao 2004). For a laser beam with an enough small FDA, it could directly be used as flexible scalpel and manipulator without an additional focal convex for secondary focusing. Moreover, the FDA is also a vital parameter for selecting the suitable focal convex (Hou et al. 2008). The FDA of hollow waveguide has a significant effect on the size of output beam, energy density and the effective distance. By measuring 10 spot sizes of output beam along the light path (see Fig. 5), the FDA of 1.5 mm-bore hollow waveguide is 28.4 mrad when transmitting 6 W CO_2 laser. In general, the output laser beam of the hollow waveguide with long length and small taper angle has a small FDA. In this work, although the inner diameter of 1.5 mm-is not quite small, the FDA of output beam still maintains at a small value (28.4 mrad) with

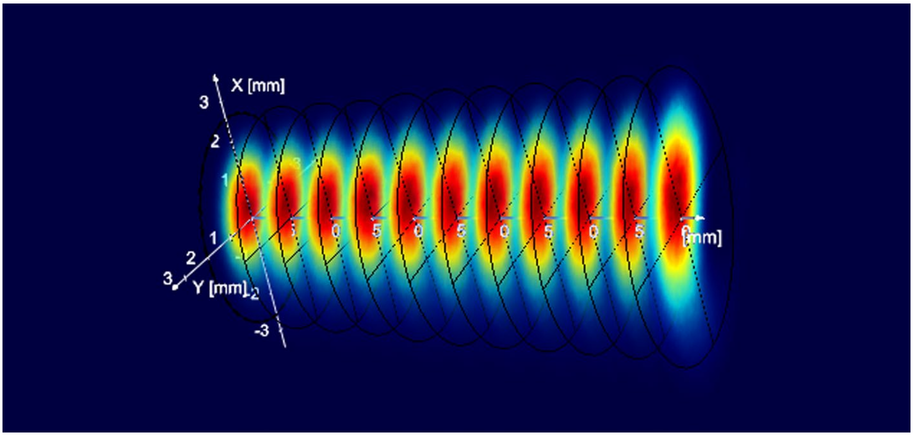

Fig. 5 Distribution of output laser beam spots along the light propagation direction of the 1.5 mm-bore hollow waveguide

the short fiber length of 75 cm. It is related to the pure transmission modes (HE_{11} modes) within the fiber. Actually, this excellent value at 28.4 mrad represents the superiority of GeO_2 ATR SUS tube-based hollow waveguide in the practical application.

In practical applications, it is necessary to apply the hollow waveguides in the condition of bending. In an attempt to investigate the transmission performance of hollow waveguide affected by bending degree, the bending loss of 1.5 mm-bore sample was measured by offsetting the output end (Nubling and Harrington 1996) as shown in Fig. 6. The bending loss increases from 0.76 to 3.77 dB/m, and meanwhile the output power decreases from 4.56

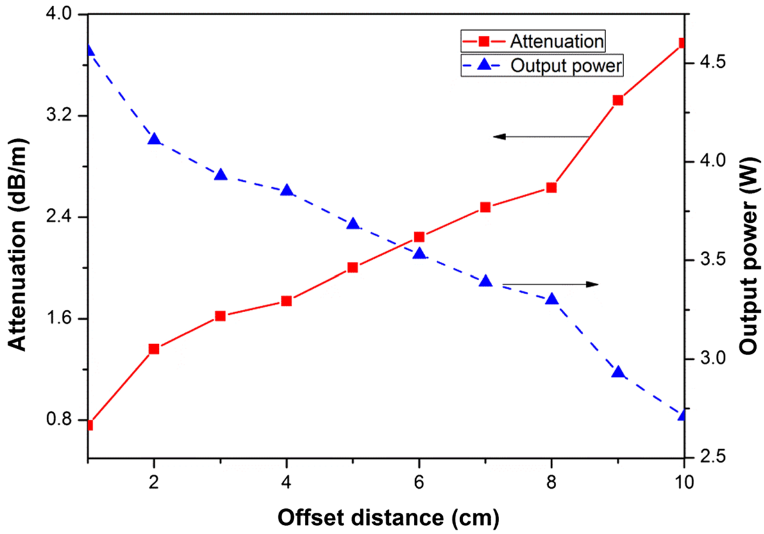

Fig. 6 The bending loss (marked as square-solid line) and output power (marked as triangle-dashed line) of the GeO_2 SUS tube-based hollow waveguide transmitting a 6 W CO_2 laser

to 2.67 W, as the displacement goes up from 1 to 10 cm. The transmission mode is sensitive to the curvature radius of fiber which depends on the displacement. With the increase of displacement, more and more high-order modes are excited. Comparing with the low-order modes, the higher-order modes could increase transmission loss when the laser beam transmits in the hollow waveguide (Matsuura et al. 1994). In fact, the high bending loss is the drawback of the hollow-core fiber. Considering that the laser beam transmission is limited to the wavelength (mid-infrared region) and power for the solid core fiber, the GeO_2 SUS tube-based hollow waveguides still have a great advantage for practical applications. It is measured that the bending loss of hollow waveguide is 3.77 dB/m and the output power decreases to 2.67 W when the displacement reaches to 10 cm. However, a relatively high output power at 2.67 W is still able to meet the needs for laser surgery and material processing.

4 Conclusion

In conclusion, the hexagonal structural GeO_2 reflective films with high flatness were prepared on the inner wall of SUS tube substrates by using the GeO_2–NaOH precursor solution. The transmission losses were measured and calculated which exhibit the transmission performance of the GeO_2 SUS tube-based waveguides improves 3.36 times comparing with the sample using the glass tube. The 2D and 3D output laser beam profiles reveal that the energy distribution of the 1.5 mm-bore hollow waveguide is close to Gaussian distribution which brings benefit to beam energy aggregation. Compared with 1.5 mm-bore hollow waveguide, more imperfections may occur in the 1 mm-bore sample during the preparation process. The FDA of 1.5 mm-bore sample shows a small value at 28.4 mrad with the short fiber length of 75 cm. By offsetting the output end, the measured bending loss increases to 3.77 dB/m and the output power decreases to 2.67 W, which can still meet the needs for laser surgery and material processing. These results confirm that the GeO_2 SUS tube-based hollow waveguide is potential candidate for the transmission medium of mid-infrared laser radiation.

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