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Hydrogen sulfide gas sensor based on graphene-coated tapered photonic crystal fiber interferometer

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ABSTRACT

A hydrogen sulfide gas sensor based on graphene-coated tapered photonic crystal fiber (GTPCF) Mach-Zehnder interferometer (MZI) was proposed and experimentally demonstrated. The GTPCF-MZI is formed by fusion splicing a short length of tapered PCF between two single-mode fibers. The air holes of PCF in the splicing regions are fully collapsed and so that it is conducive to the mode coupling. The GTPCF-MZI was coated with a layer of graphene by using a dip-coating and sintering process. Experimental results show that with the increasing concentration of hydrogen sulfide, the interference spectra appear blue shift. In addition, a high sensitivity of 0.03143 nm/ppm and a good linear relationship are obtained within a measurement range from 0 to 45 ppm. The sensor has the advantages of simple structure, high sensitivity, easy manufacture and low cost, and can be used in indoor gas sensing fields such as factories and laboratories and so on.

1. Introduction

Hydrogen sulfide (H_2S), which is well known as a very poisonous, corrosive, flammable, and explosive gas, is produced from the prokaryotic breakdown of organic matter in the absence of oxygen gas, such as in sewers and swamps. It also occurs in volcanic gases, natural gas, and in some sources of well water. The toxicity of hydrogen sulfide is comparable with that of carbon monoxide. 320–530 ppm leads to pulmonary edema with the possibility of death [1]. Thus, those used by utility, sewage and petrochemical workers, are set to alarm at 10 ppm and to go into high alarm at 15 ppm for personal safety.

On one hand, graphene, which has many unusual properties, is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice in which one atom forms each vertex. Graphene has unique optical properties with an unexpectedly high opacity and huge specific surface area for an atomic monolayer, therefore, it is suitable for gas sensing material [2,3]. The improving gas sensing properties of graphene was investigated by the first-principle calculation [4]. Flexible and transparent gas molecule sensor integrated with sensing and heating graphene layers was proposed by C.G. Choi, and Y.J. Yu, et al. [5]. On the other hand, photonic crystal fibers (PCFs), also called microstructured optical fibers, which hold unique guiding mechanisms and modal properties that are impossible with traditional optical fibers, have a lot of applications in the fiber-based sensors [6–29]. However, to the best of our knowledge, the research reports of the gas sensing sensor combining graphene with photonic crystal fiber is not yet seen. Thus, a Mach-Zehnder interferometer (MZI) gas sensor based on graphene-coated tapered photonic crystal fiber (GTPCF) is presented in this work. This sensor is easy to manufacture and only needs to be spliced with the common single mode fiber (SMF) at the two ends of the tapered photonic crystal fiber (PCF), and then graphene was coated on the surface of PCF. The graphene-coated tapered photonic crystal fiber (GTPCF) can enhance the coupling between core mode and cladding mode. Therefore, the sensitivity of the sensor can be improved effectively. As an application, hydrogen sulfide gas was detected by using the GTPCF interferometer and some useful results were obtained.

2. Experimental

2.1. Principle of operation

The schematic diagram of the GTPCF-MZI is shown in Fig. 1(a). After tapering the PCF, a strong evanescent field is formed near the tapered region and makes the susceptible to the refractive index variations of the external coated membrane. As shown in Fig. 1(a),

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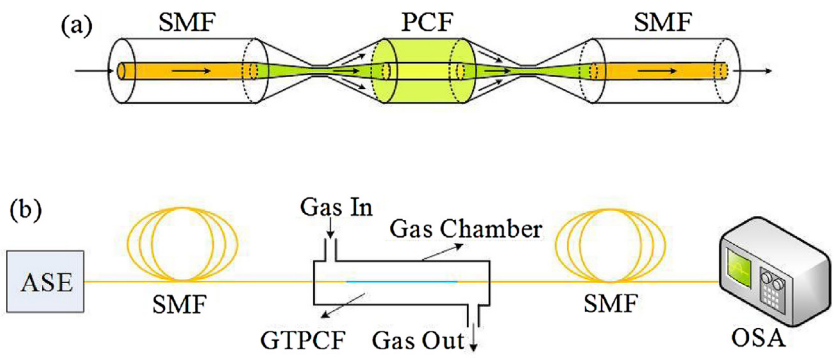

Fig. 1. (a). Schematic diagram of GTPCF-MZI structure; (b). Schematic diagram of the experimental setup.

when light travels from the SMF to the tapered PCF, the core mode of SMF begins to diffract, i.e., after the first splice, a part of the light is coupled to PCF in the transmission of core mode, and another part of light is coupled to the cladding with the transmission of cladding mode. In this process, the propagation constants between the core mode and cladding mode of GTPCF are different. After the transmission distance L, there will be a phase delay between the two modes. Finally, when the two parts of lights arrive at the second splice, the cladding mode of the sensing region and the core mode of the GTPCF will be interfered in the second input port of SMF, that is, Mach-Zehnder interference. Thus, the phase delay of the two modes of interference and the central wavelength of the interference are, respectively, expressed as [30–32]

$$\varphi = \frac{2\pi(n_{eff}^{co} - n_{eff}^{cl})L}{\lambda} = \frac{2\pi\Delta n_{eff}L}{\lambda} \quad (1)$$

$$\lambda_m = \frac{\Delta n_{eff}L}{m} \quad (2)$$

where n_{eff}^{co} and n_{eff}^{cl} are the effective refractive indices of core and cladding modes, respectively. L is the distance between the two coupling points corresponds to the physical length of the interferometer and λ is the wavelength of incident light. $\Delta n_{eff}(=n_{eff}^{co}-n_{eff}^{cl})$ is the difference between the effective refractive indices of core and cladding modes. λ_m is the m^{th}-order wavelength of interference. When the coated-graphene absorbs the target gas, the refractive index of the cladding in tapered PCF's evanescent field changes, and then n_{eff}^{cl} and Δn_{eff} will change together. The m^{th}-order shift $\Delta\lambda_m$ can be given as

$$\Delta\lambda_m = \frac{(\Delta n_{eff} + \Delta n)L}{m} - \frac{\Delta n_{eff}L}{m} = \frac{\Delta nL}{m} \quad (3)$$

in which $\Delta\lambda_m$ is the m^{th}-order wavelength shift of interference. Δn is the difference between the refractive indices of the target gases of different concentrations. From Eq. (3), the shift in the interference fringes is a function of Δn when L is a definite value.

As shown in Fig. 1(b), a broadband amplified spontaneous emission (ASE) source is launched into the structure of GTPCF. When two (core and cladding) modes of light arrive at the second collapsed region, the interfere is formed. Transmission spectra can be monitored by using an optical spectrum analyzer (OSA, Yokogawa, AQ6370D).

2.2. Fabrication of the GTPCF-MZI

For the fabrication of the GTPCF-MZI, the PCF was sandwiched between two SMFs and then tapered via a fiber fusion splicer (Furukawa Electric Co. Ltd., S178C). A 5-cm-long PCF (YOFC, TIR-PCF) and SMF (SMF-28) were employed for a lower fusion loss because they have the same diameter. The cross section of PCF used in the sensing experiment is shown in Fig. 2(a). As depicted in Fig. 2(b), two SMFs, are respectively, spliced two ends of PCF. The air holes of the PCF around the ends were fully collapsed during the fusion splicing. And then, the fusion splicer can accurately control the motor to draw the middle section between SMF and PCF, and forms a taper.

It should be pointed out that the automatic operation mode of the splicer is used for splicing and tapering the standard SMF and PCF. In the operation program of the splicer, the default parameters for the splicing of the SMF and PCF are as follows: the first and second arc-power setting at 100, the initial and second end arc-power setting at 40, the cleaning duration time of 200 ms, the prefusion time of 160 ms, the initial arc-duration time of 1 s, the second arc-duration time of 2 s, the Z-pull time of 1 s, and Z-pull distance of 400 μm. The arc-duration time, arc-power and Z-pull distance can influence the size of the waist and length of transition zone of the taper. Generally, the bigger Z-pull distance can obtain the smaller size of the waist and longer length of transition zone of the taper.

The GTPCF were prepared by a dip-coating and sintering process. Firstly, the isopropanol and the monolayer graphene nanopowders are fully mixed according to the stoichiometric ratio, and then the above prepared tapered PCF is put into the mixed solution for dipping coating. Secondly, put the graphene-coated tapered PCF into the vacuum drying box with drying at 80 °C for 6 h. Lastly, put it into the tubular furnace to sinter at 350 °C for 2 h under the protection of nitrogen, and then the GTPCF was obtained. The graphene-free and graphene-coated tapered PCF are shown in Fig. 2(b) and (c), respectively. Compared Fig. 2(b) with (c), the isopropanol dispersed graphene evenly distributed on the surface of the tapered PCF, and by calcining, has been formed on the surface of a film thickness of about 80 nm (see Fig. 2(d)). It should be noted that the thickness of the graphene film can be controlled by the concentration of graphene solution, dip-coating time, etc. In this experiment, the greater concentration of graphene can get the thicker graphene film.

3. Results and discussion

Based on successful fabrication of GTPCF-MZI, the gas sensing test was performed according to the sensor system of Fig. 1(b). The left and right ends of the gas chamber are respectively sealed by epoxy resin, and the upper and the lower two parts of the gas chamber are respectively the inlet and outlet of the measured gas. All the measurements were carried out at room temperature (about 20 °C).

Different concentrations of hydrogen sulfide can be prepared by mixing the nitrogen gas. Transmission spectra of the GTPCF-MZI before and after coating with graphene were recorded for comparison in Fig. 3. The results indicate that the contrast was slightly reduced but still enough high with an obvious wavelength shift.