High-sensitivity long-period fiber grating sensor with SAN/cryptophane A for coal mine gas detection

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Received February 23, 2013; accepted May 13, 2013; posted online July 18, 2013

A high-sensitivity long-period fiber grating (LPFG) methane sensor that contains a compact and uniform styrene-acrylonitrile (SAN)/cryptophane A nanofilm is presented. The sensor is prepared by using an automatic dip-coater in a solution of cryptophane A, SAN resin dissolved in ortho-dichlorobenzene, a low-volatile solvent. The effect of film thickness on the LPFG's resonant wavelength is thoroughly investigated. The optimum sensor among the three LPFGs with different film thicknesses is directly used to detect the methane concentration in a coal mine gas sample. The results indicate that the sensors with film thicknesses of 484 to 564 nm exhibit a redshifted resonant wavelength when the methane concentration is increased from 0% to 3.5% (vol). The data demonstrates that the sensor with a film thickness of 484 nm has remarkable sensitivity ($\sim$0.633 nm%$^{-1}$), and its detection limit can reach 0.2%. The methane concentrations determined by our sensor are consistent with those obtained by gas chromatography.

OCIS codes: 060.2370, 120.1880.

doi: 10.3788/COL201311.080601.

Methane is the main component of harsh gases in coal mines. Consequently, the detection of methane concentration is one of the most effective approaches to ensure the safe operation of industrial mines. Optical-fiber gas sensors possess superior advantages over conventional electricity-based gas sensors[1−4]. In particular, considerable attention has been given to the combination of optical fibers and sensitive materials such as cryptophane molecules because of its potential application in the fabrication of highly sensitive, fast-response methane gas sensors that can target methane gas in coal-mine production and in environmental applications[5−7]. Several techniques based on the interaction of cryptophane molecules and methane have been developed for methane detection, including the fabrication of an optical fiber sensing element via luminescence reflection[5], evanescent wave optical fiber sensor[6], and a mode-filtered light optical fiber sensor[7].

Long-period fiber grating (LPFG) has been extensively used as a fiber device with a photoinduced periodic modulation of the refractive index (RI) of the fiber core[8−11]. Previous studies demonstrated the relationship between the sensitivity of the fiber device and the RI of the surrounding material on the fiber grating[9,10,12]. RI-based gas sensors can be fabricated by coating a transparent polymeric cladding of chemosensitive material on the LPFG surface[13]. At present, various techniques have been used to develop polymer coatings on the optical fiber surface, including dip-coating[14,15] and Langmuir–Blodgett deposition[10]. The dip-coating technique is considered to be more convenient because it involves simple manual preparation or automatic operation. On the other hand, the thickness and uniformity of the coating are difficult to control precisely by the manual dip-coating method. In addition, the reproducibility of this method is not satisfactory. By contrast, an automatic dip-coater can be used to produce a significantly more compact and uniform coating deposition with controlled thickness.

In our previous studies, a styrene-acrylonitrile (SAN) nanofilm containing a cryptophane A LPFG sensor was fabricated by manual dip-coating in a solution of cryptophane A, SAN resin dissolved in dichloromethane, a highly volatile solvent. The RI of the nanofilm was approximately 1.57. The sensor, which has a film thickness of 500 nm and a grating period of 480 μm, can be used to detect methane at concentrations below 3.5 vol%. The detection with 0.375 nm%$^{-1}$ sensitivity was almost not interfered by dry air, O_2, CO, or CO_2[16]. Moreover, an optical-fiber methane sensor based on SAN film containing cryptophane-E-$(OEt)_6$ was also developed, exhibiting a sensitivity of 0.297 nm%$^{-1}$[17]. However, the abovementioned nanofilm produced by the manual dip-coating operation is often porous and non-uniform, which results in non-ideal sensitivity.

To address the aforementioned challenges, a LPFG methane sensor was fabricated in this letter by using an automatic dip-coater in a solution of cryptophane A, SAN resin dissolved in the low-volatile solvent ortho-dichlorobenzene. The effect of the thickness of the compact and uniform SAN/cryptophane A nanofilm on the resonant wavelength shift was investigated. The optimum sensor among the three LPFGs with different film thicknesses was used to detect the methane concentration in a coal mine gas sample.

The LPFG couples light from the forward propagating mode of the core to a discrete set of co-propagating cladding modes at wavelengths governed by the phase

matching condition, as follows

$$\lambda_{\rm res} = (n_{\rm co} - n_{{\rm cl}(\nu)})\Lambda, \quad \nu = 1, 2, 3, \cdots, \qquad (1)$$

where $\lambda_{\rm res}$ is the resonant wavelength, Λ is the grating period, and $n_{\rm co}$ and $n_{{\rm cl}(\nu)}$ are the effective indices of the fundamental core mode and the νth cladding mode of the fiber, respectively. Based on the model coupling theory, $n_{\rm co}$ and $n_{{\rm cl}(\nu)}$ can be obtained by solving the core mode eigenvalue equation and the cladding mode eigenvalue equation of the triple-clad LPFG, respectively[9,16,18–20].

From the cladding mode eigenvalue equation and phase-matching condition, $\lambda_{\rm res}$ is related to the sensing film RI n_3 and the film thickness h[9,10]. When the sensing film RI n_3 is stable (n_3=1.57), the resonant wavelength in the different film thicknesses can be calculated, and the relationship between the shift in the resonant wavelength ($\Delta\lambda_{\rm res} = \lambda_{\rm res} - \lambda_{\rm res0}$) and film thickness h is obtained. For the $HE_{1,14}$ mode, the shift curve is shown in Fig. 1. $\Delta\lambda_{\rm res}$ is significantly large when the film thickness is increased from 465 to 700 nm. A small change in the film thickness can cause a large shift in the resonant wavelength. However, the change rate of $\Delta\lambda_{\rm res}(|{\rm d}\lambda_{\rm res}/{\rm d}h|)$ is gradually reduced when the film thickness increases from 465 to 700 nm. An optimum overlay thickness (OOT) is observed when the resonant wavelength shift as a function of RI is highest. In this letter, the OOT is approximately 465 nm. In other words, the sensitivity of the sensor with a film thickness of 465 nm is higher than that of the sensor with a 700-nm film thickness. Meanwhile, for sensors with film thicknesses below 400 nm or greater than 700 nm, the change in film thickness has few effects on the shift in the resonant wavelength.

When the LPFG sensor coated with the SAN/ cryptophane A composite nanofilm is exposed to methane gas, the small variations in the sensing film RI results in a change in $n_{{\rm cl}(\nu)}$, which produces a shift in the resonant wavelength of the transmission spectrum. By measuring this shift ($\Delta\lambda_{\rm res}$), methane gas detection can be achieved[16]. This principle is conceptually illustrated in Fig. 2.

LPFG was fabricated using a writing method of high-frequency CO_2 laser pulses. In our work, the obtained grating period Λ is approximately 520 μm. Prior to dip-coating, the LPFG was thoroughly cleaned with acetone and ethanol. It was then ultrasonically treated in double-distilled water and subsequently dried at 60 °C. Cryptophane A (Fig. 2) was synthesized from vanillin

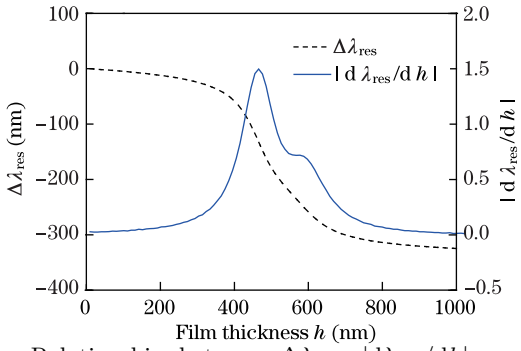

Fig. 1. Relationship between $\Delta\lambda_{\rm res}$, $|{\rm d}\lambda_{\rm res}/{\rm d}h|$, and film thickness h for the $HE_{1,14}$ mode.

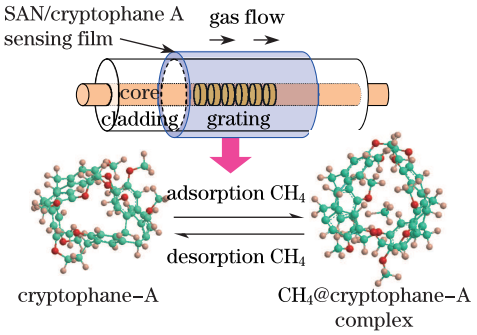

Fig. 2. Methane sensing principle of the sensor.

using a three-step method[5,6]. The optical material, the SAN resin, was purchased from Ashley Polymers, Inc. The dip-coating solution consisted of 0.5-g cryptophane A, 3-g SAN resin, and 25-ml ortho-dichlorobenzene. A SAN/cryptophane A composite nanofilm was coated on the cladding region of the LPFG using an automatic dip-coater (SYDC-100, Shanghai San-Yan Instrument Corp., China) at 60, 120, or 180-mm·min^{-1} dipping and withdrawing rates with 5-s residence time[14]. After withdrawing, the film was dried at 60 °C for 30 min. The corresponding film thicknesses, which vary from hundreds of nanometers to a few microns, were achieved by one or more dip-coatings. In this work, h were 484, 525, and 564 nm.

Figure 3 shows a schematic diagram of the automatic dip-coating technique and the typical scanning electron microscopy (SEM) images (JSM-6510LV, JEOL, Japan) of the fibers coated with the SAN/cryptophane A composite nanofilm. The results indicate that the coating on the cladding of the LPFGs is remarkably compact and uniform, with a film thickness of 484 nm. These results were prior to the SEM micrograph reported in Ref. [16].

The coated LPFG was immobilized in a stainless steel gas chamber, which was controlled by a gas-flow control system. The ends of the LPFG were connected to a broadband light source (2-mW SLD, Dense light Co., Ltd.) with a central wavelength of ~1 550 nm and to an optical spectrum analyzer (OSA, 86140B, Agilent, USA) with a resolution of 10 pm. The sensing setup is shown in Fig. 4.

LPFGs coated with three different thicknesses of SAN/cryptophane A nanofilm were prepared and exposed directly to various concentrations of methane gases to investigate the dependence of resonant wavelength shift on the nanofilm thickness of the sensor. Figure 5 shows the transmission spectra of the LPFG with a film thickness of 484 nm while sensing methane gas (concentration from 0% to 3.5%) and a coal mine gas sample in particular. All resonant bands of the LPFGs exhibit redshifted wavelengths as the methane concentrations increase.

Figure 6 shows the resonant wavelength shift of the sensors with different film thicknesses under a grating period of 520 μm. The resonant wavelengths of the sensor shift to longer wavelengths while sensing increasing concentrations of methane. The redshift is reduced when the film thickness increases from 484 to 564 nm. According to Fig. 6, the calibration curves for the methane sensors with three film thicknesses exhibit high linearity, with slopes of 0.633, 0.387, and 0.286 nm%$^{-1}$ (484, 525,

and 564 nm, respectively) and correlation coefficients (R^2) of 0.995, 0.995, and 0.994, respectively. The results indicate that the sensor with a film thickness of 484 nm exhibits the largest wavelength shift, which implies better reorganization ability for methane gas surpassing that previously reported in Ref. [16]. In addition, our experimental results consistently agree with the aforementioned theoretical analysis. The minimum detection limit for methane gas is confirmed as approximately 0.2%. Subsequently, the sensor with a film thickness of 484 nm was used to determine the response time. The inset in Fig. 6 shows that the relationship between the wavelength shift of the sensor and the response time alternates between 0% (nitrogen) and 0.5%(vol) CH_4. The signals all reached stable values when the sensor was exposed to nitrogen or 0.5% CH_4. The response time (t_{90}) of the sensor for the 0.5% CH_4 gas is 50 s, and the recovery time (t_{90}) is nearly 60 s.

The detection capability of the methane sensor to coal mine gas samples was also determined. The coal mine gas sample consisted mostly of CH_4, O_2, N_2, CO_2, and C_2H_6 (ethane), as determined by a gas chromatograph (GC-4085, East & West Analytical Instruments Co., Inc., Beijing, China), in which the CH_4 concentration was around 1.41%. According to the λ_{res} of the coal mine gas sample (Fig. 5), the central wavelength of the transmission spectrum shifts toward the longer wavelength by approximately 0.88 nm ($\Delta\lambda_{res}$), from 1 542.08 to 1 542.96 nm. By using the linearity regression equation in Fig. 6 ($\Delta\lambda_{res} = 0.633c + 0.0136$), a methane concentration c of approximately 1.37% was estimated for the LPFG film sensor. This value is in perfect agreement with that determined by gas chromatography (with a relative error of only ~2.83%). The results suggest that the LPFG film sensor exhibits a good response characteristic to the actual coal mine gas sample in the presence of common potential interferents such as O_2, N_2, CO_2, and C_2H_6[16].

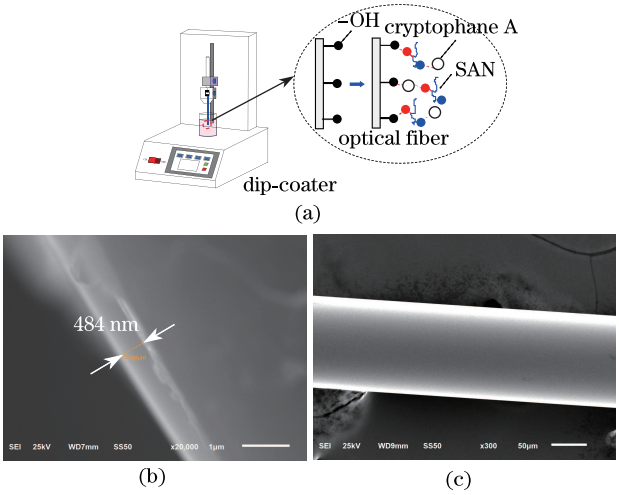

Fig. 3. (a) Schematic diagram of the automatic dip-coating technique and scanning electron microscopy (SEM) images of (b) the cross-section and (c) surface of the fiber coated with the 484-nm styrene-acrylonitrile (SAN)/cryptophane A nanofilm.

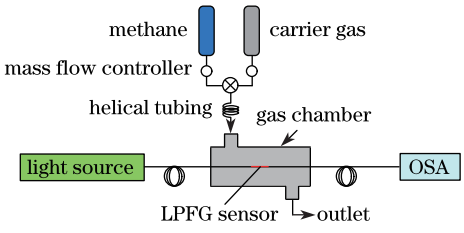

Fig. 4. Schematic diagram of the experimental setup.

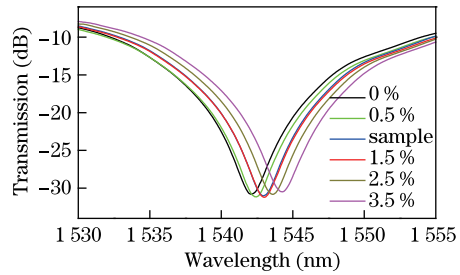

Fig. 5. Transmission spectra of the coated LPFG sensor with a film thickness of 484 nm in different concentrations of methane gas and coal mine gas sample.

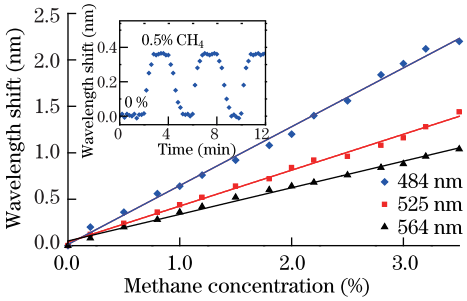

Fig. 6. Calibration curves between $\Delta\lambda_{res}$ and methane concentration for the LPFG sensors with different film thicknesses and reversibilities.

In conclusion, a high-sensitivity SAN/cryptophane A LPFG methane sensor is developed and implemented successfully. High-performance LPFG methane sensors are prepared by using an automatic dip-coater in a solution of cryptophane A, SAN resin dissolved in orthodichlorobenzene, a low-volatile solvent. The results show that all resonant bands of the LPFGs exhibit a wavelength redshift with increasing methane concentrations. The sensor with a film thickness of 484 nm and a grating period of 520 μm exhibits the largest resonant wavelength shifts and the highest response for methane gas, reaching a minimum detection limit of approximately 0.2%. The methane concentration in the coal mine gas sample detected by the sensor is reasonably consistent with that determined by gas chromatography. This work provides a promising approach for methane detection.

The author would like to thank Qibiao Ou for his/her help in the sensing principle. This work was supported by the National Natural Science Foundation of China (No. 61271059), the Natural Science Foundation Project of Chongqing (No. 2010BB4246), and the Science and Technology Development Project of Chongqing (No. CSTC2012gg-yyjs90007).

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