Notched Long-Period Fiber Grating with an Amine-Modified Surface Nanostructure for Carbon Dioxide Gas Sensing

Janw-Wei Wu and Chia-Chin Chiang *

Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan; E-Mail: cafa95011@gmail.com

* Author to whom correspondence should be addressed; E-Mail: ccchiang@kuas.edu.tw; Tel.: +886-07-381-4526 (ext. 5340).

Academic Editor: Teen-Hang Meen

Received: 29 May 2015 / Accepted: 16 July 2015 / Published: 21 July 2015

Abstract: This paper presents the fabrication and application of a notched long-period fiber grating (NLPFG) with an amine-modified surface nanostructure for carbon dioxide (CO₂) gas sensing. The NLPFG with the modified surface nanostructure was fabricated by using inductively coupled plasma (ICP) etching with an Ag nanoparticle etching barrier. The experimental results show that the spectra were changed with the CO₂ gas flow within 12 min. Thereafter, the spectra of the NLPFG remained steady and unchanged. During the absorption process, the transmission loss was decreased by approximately 2.019 dB, and the decreased rate of transmission loss was 0.163 dB/min. The sensitivity was about −0.089 dB/%. These results demonstrate that the NLPFG CO₂ gas sensor has the advantages of steady performance, repeatability, and low cost. Therefore, the NLPFG can be utilized as a reliable CO₂ gas sensor.

Keywords: optical fiber sensor; notched long-period fiber grating; carbon dioxide

1. Introduction

Optical fiber sensors have many advantages, such as immunity to electromagnetic interference, low power consumption, corrosion resistance, high temperature resistance, and being lightweight. As a result, optical fiber sensors are widely used in various applications [1]. Long-period fiber grating (LPFG) couples a core mode to a cladding mode. This coupling phenomenon causes a resonant dip in
the spectrum, which is very sensitive to external environmental conditions. Thus, LPFG is suitable for use as a sensor. The manufacturing methods for LPFG include excimer laser writing [2], CO₂ laser writing [3], arc discharged fabrication [4], the mechanical pressure method [5], and fabrication by MEMS technology with etching [6] and photoresist [7]. In this paper, the proposed notched long-period fiber grating (NLPFG) sensor was manufactured by the inductively coupled plasma (ICP) etching method, which was used to create corrugated surface structures on the optical fiber [8].

Various techniques for detecting gas have been developed for applications such as environment monitoring [9], medical diagnosis [10], chemical and mining safety [11], and modern gas laser designs [12]. Among these techniques are several effective optical methods for detecting the gas, including interferometry [13], absorption spectroscopy [14], surface plasmon resonance [15], fluorescence spectroscopy [16], and grating-based refractive index transmission [17].

Around the world in recent years, CO₂ emissions have been increasing, causing global weather anomalies and the greenhouse phenomenon. Therefore, the production of a CO₂ gas-monitoring sensor is very important. In 2010, X. Wei et al. [18] proposed the perovskite-type metal oxide BSCF (Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃−δ) as a gas-sensing layer for coating an LPFG sensor. The perovskite structure of the metal oxide allows CO₂ to be detected at high temperatures. The absorption effect is best demonstrated in the high temperature range of 600–700 °C and under higher CO₂ partial pressure. The perovskite structure of the metal oxide after CO₂ adsorption can be recovered at temperatures higher than 680 °C. At a temperature of 600 °C, the sensor was exposed to a gas mixture containing 10% CO₂ and 90% air. The resonance wavelength of the LPFG started to decrease, taking approximately 24 min to reach a stable value. At 700 °C, the sensor demonstrated a faster response time and a larger wavelength shift. In 2013, B.N. Shivananju et al. [19] proposed clad etched fiber Bragg grating (FBG) with polyallylamine-amino-carbon-nanotube film coated on the surface of the core for detecting CO₂ gas concentrations. This core FBG sensor for CO₂ sensing had a response time of 3.07 min. A Bragg wavelength shift of ~6 pm was observed when the CO₂ gas concentration reached 1000 ppm, and the sensitivity was 1.954 pm/min. The limit of detection calculated was approximately 75 ppm. In 2014, Luis Melo et al. [20] proposed a CO₂ gas concentration sensor comprising a long period grating coated with polystyrene, with coating thicknesses of 204 nm, 249nm, and 365 nm. The sensor had a grating period of 450 µm and a length of 10 mm. The results showed the coating thickness of 365 nm indicated the highest grating sensitivity at approximately 1.23 ± 0.08 pm/% CO₂. The approaches used by the aforementioned research teams mostly used a sensitive coating layer on the optical fiber sensor, which was suitable for sensing under high temperatures.

This study proposes the use of amine-modified adsorbents as a coating for an NLPFG sensor with a surface nanostructure for CO₂ gas sensing. The environmental refractive index changes in the sensor are caused by amine-modified adsorbents with CO₂ capture. Therefore, we can evaluate the spectra change as the test chamber is loaded with the CO₂ gas. The proposed NLPFG sensor utilizes its nanostructure to improve the function of the amine-modified adsorbents for improved sensitivity.

2. Working Principle of the NLPFG Gas Sensor

The NLPFG bears periodic surface-corrugated gratings. As an external load is applied to it, the strain field in the longitudinal direction of the NLPFG is modulated as a square wave because of
the periodic surface grating structure of the optical fiber. Based on the elastic-optic effect [21], the refractive index of the NLPFG will also be modulated as a periodic square wave distribution along the optical fiber.

When light is transmitted in the NLPFG, the periodic refractive index grating structure generates a resonant attenuation dip in the spectrum based on the coupled mode theory [7,21]. The resonant attenuation dip (transmission loss) is calculated as

\[ T = \cos^2(\kappa_{ac}^{co-cl} L) \]

where \( L \) indicates the length of the LPFG and \( \kappa_{ac}^{co-cl} \) is the AC component of the coupling coefficient between the core and cladding modes. The transmission loss of an LPFG can be deduced from the AC component of the coupling coefficient between the core and the cladding. Transmission loss is a function of \( \kappa_{ac}^{co-cl} \), which is proportional to the amplitude of changes in the refractive index. From the above formula, it can be seen that the transmission loss of an LPFG is related to the coupling coefficient and grating length. Therefore, the loss can be altered by the external refractive index.

In this study, the tetraethylenepentamine (TEPA)-modified adsorbents coat the optical fiber for CO\(_2\) gas sensing. As the CO\(_2\) reacts with the sensing layer, the coupling coefficient and effective refractive index are changed. Therefore, the spectra of the NLPFG sensor are deformed and the dips of the spectra are changed. We can measure the CO\(_2\) by monitoring the transmission loss of the NLPFG.

3. Experiment

3.1. Production Process and Fabrication of the NLPFG

In this study, single-mode optical fibers (Corning SMF-28e) were used for fabricating the NLPFG through the ICP dry etching process. First, a buffered oxide etching chemical was employed for etching the fibers in order to reduce the thickness of the fibers from 62.5 to 20 \( \mu \)m. The fibers were attached to a period-structured metal-plated gratings mask (amplitude mask), and, utilizing electrospinning technology, nano-sized silver particles were sprayed onto the fibers as a barrier layer. The gap region between the Ag nano particles was then etched to form the surface nano-needle structure. The nano-needle structured and notched long-period gratings were produced by ICP etching. The nano-needle structure was used mainly to increase the effective area of the sensing layer. The production process is illustrated in Figure 1. The metal-plated gratings mask was designed with periods of 600 \( \mu \)m to achieve a wavelength with a resonant dip close to 1550 nm. The surface-notched period structure was etched on the etched fiber at an ICP etching rate of approximately 2.5 \( \mu \)m/min. Finally, the etched device was released via acid pickling with sulfuric acid (H\(_2\)SO\(_4\)) to remove the high temperature–resistant adhesive on the fiber. The NLPFG with the surface needle nanostructure was thus obtained after it was released from the metal-plated mask. Figure 2 shows a scanning electron microscopy (SEM) image of the NLPFG sensor with the surface nanostructure.
3.2. Preparation of the NLPFG Gas Sensor Chip

First, we applied an axial pre-load (0.1 N) on the NLPFG sensor to form a periodic refractive index change for producing a long-period grating effect. Then, ultraviolet adhesive was used to fix the sensor onto a glass plate and thereby prevent any strain from influencing the NLPFG sensor.

3.3. Coating the Sensing Layer with Amine-Modified (TEPA-Coated) Adsorbents

A surface modification method was used to coat the NLPFG sensor with amine-modified (TEPA-coated) adsorbents. In order to ensure that the TEPA-modified adsorbent sensing layer was tightly adsorbed on the NLPFG sensor, we used a portable corona treater at a high voltage of 10,000–48,000 V to change the hydrophobic material into hydrophilic material, which ensured that the
powder would be strongly attached to the NLPFG sensor. When carbon dioxide was adsorbed by the NLPFG gas sensor, the effective refractive index of the sensor’s cladding was changed. These changes subsequently result in variations in transmission loss. We can measure the carbon dioxide by monitoring the transmission loss of the NLPFG.

3.4. The Experimental Setup for the CO₂ Gas Sensing

Figure 3 shows the experimental setup for the CO₂ gas sensing. First, we put a prepackaged gas-sensing chip into a gas-sensing tube with amine-modified (TEPA-coated) surfaces. The light source was a super luminescent diode, and the light signal was observed by using an optical spectrum analyzer. The gas used was 15% mixed CO₂ gas (CO₂ 15% + N₂ 85%), which was injected at a flow rate of 0.2 L/min into the gas-sensing tube. The experimental temperature was controlled at room temperature (25 °C). When the CO₂ reacted with the TEPA-modified adsorbent sensing layer, the refractive index changed. The optical signal change caused by the CO₂ capture was then observed. The chemical formula for CO₂ adsorption is indicated below:

$$\text{CO}_2 + 2\text{R–NH}_2 \rightarrow \text{RNH}_3^+ + \text{R–NHCOO}^-$$

The mechanism of chemical adsorption between the amine active sites and the CO₂ in anhydrous conditions was the formation of ammonium carbamate [22].

4. Results and Discussion

4.1. CO₂ Gas-Sensing Experimental Results

The CO₂ gas-sensing experiments were conducted by using TEPA-modified adsorbents for CO₂ capture. The experimental results are shown in Figure 4. The resonant wavelengths of the NLPFG (with a period of 600 μm and with a fiber diameter of 40 μm) were 1548.102 nm, and the transmission loss was −18.827 dB. After the addition of the TEPA-modified adsorbent coating to the NLPFG using the dip-coating method, the refractive index changed. This resulted in a drop in the transmission loss to −7.718 dB, so the transmission loss was reduced by −10.109 dB, and the wavelength was shifted by 0.25 nm. This demonstrates that coating with TEPA-modified adsorbents can change the refractive index to influence the magnitude and wavelength position of the attenuated dip. The experimental
monitoring was conducted at 1-min intervals. The resonant wavelength shifted slightly, while the transmission loss decreased by approximately 2.019 dB (from $-7.718$ to $-9.737$ dB), and the decreased rate of transmission loss was 0.163 dB/min. The CO$_2$ sensors reached saturation within 12 min. The spectra of the NLPFG were steady. Therefore, the proposed NLPFG gas sensor can successfully monitor CO$_2$ adsorption.

![The spectra of CO$_2$ gas sensing. (a) First cycle spectra of CO$_2$ gas sensing; (b) Second cycle spectra of CO$_2$ gas sensing; (c) Third cycle spectra of CO$_2$ gas sensing. The insets represent magnified images of the spectra.](image)

4.2. CO$_2$ Gas-Sensing Cyclic Adsorption/Desorption Test

The desorption process consisted of heating the NLPFG sensors to 100 °C by using a furnace. This temperature was held steady for 20 min before the chamber was cooled to room temperature to allow for the renewal of the gas sensor through desorption of the carbon dioxide. Once the desorption process was complete, the NLPFG gas sensor transmission loss returned to its original value. Figure 4b shows the spectra of the second CO$_2$ gas-sensing experiment. The original value of the transmission loss was $-6.859$ dB. The experimental monitoring was conducted at 1-min intervals. The resonant wavelength shifted slightly, while the transmission loss increased by approximately 1.067 dB (from $-6.859$ to $-7.926$ dB). The decreased rate of transmission loss was 0.069 dB/min, and the CO$_2$ sensors reached saturation within 21 min. The spectra of the NLPFG remained steady.
We used the same method for the third experiment. The results of the gas sensing are shown in Figure 4c. The original value of the transmission loss of the gas sensor, $-7.417$ dB, was restored. The experimental monitoring time was unchanged. The resonant wavelength shifted slightly, the transmission loss increased by approximately 0.688 dB (from $-7.410$ to $-8.098$ dB), and the decreased rate of transmission loss was 0.036 dB/min. The results of a cyclic adsorption/desorption comparison are shown in Figure 5. The NLPFG CO$_2$ gas sensor has the capacity for repeated use, and the required recovery time was short. From the above results, it can be concluded that the NLPFG gas sensor has potential for sensing CO$_2$ gas.

![Figure 5. Repeatability of the CO$_2$ gas sensor.](image)

**4.3. CO$_2$ Gas Concentrations Sensing Test**

The NLPFG sensor was subjected to a CO$_2$ gas-sensing experiment with four different concentrations of CO$_2$ (6%, 9%, 12%, 15%). The experimental results are shown in Figure 6. The sensitivity of the NLPFG sensor was about $-0.089$ dB/\%. 

![Figure 6. The curve of CO$_2$ gas sensing with four different concentrations.](image)
5. Conclusions

This paper presents a nanostructured amino-modified NLPFG for gas sensing. The results showed that the spectra changed within 12 min and then reached a steady state. This phenomenon indicates the saturation adsorption of the TEPA-modified adsorbents. The transmission loss variation was approximately 2.019 dB (from $–7.718$ to $–9.737$ dB), and the decreasing rate of transmission loss was 0.163 dB/min. The sensitivity was about $–0.089$ dB/%. The cyclic adsorption/desorption experimental results showed that the required recovery time was short. Therefore, the proposed NLPFG gas sensor has potential as a gas sensor for monitoring the CO$_2$ adsorption process.

Acknowledgments

This work was supported by the Ministry of Science and Technology, Taiwan (grant number MOST 103-2221-E-151-009-MY3).

Author Contributions

Chia-Chin Chiang designed the study methods and experiments, analyzed the data, and wrote the paper. Janw-Wei Wu conducted the experiments and analyzed the experimental data.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Akki, J.F.; Lalasangi, A.S.; Raikar, P.U.; Srinivas, T.; Laxmeshwar, L.S.; Raikar, U. Core-cladding mode resonances of long period fiber grating in concentration sensor. *IOSR J. Appl. Phys.* 2013, 4, 41–46.
2. Liu, Y.; Liu, Q.; Chiang, K.S. Optical coupling between a long-period fiber grating and a parallel tilted fiber Bragg grating. *Opt. Lett.* 2009, 34, 1726–1728.
3. Wang, Y.P.; Wang, D.N.; Jin, W. CO$_2$ laser-grooved long period fiber grating temperature sensor system based on intensity modulation. *Appl. Opt.* 2006, 45, 7966–7970.
4. Abrishamian, F.; Dragomir, N.; Morishita, K. Refractive index profile changes caused by arc discharge in long-period fiber gratings fabricated by a point-by-point method. *Appl. Opt.* 2012, 51, 8271–8276.
5. Tsutsumi, Y.; Ohashi, M.; Miyoshi, Y. Temperature-sensitive mechanical LPFG using contractive force of heat-shrinkable tube. *Opt. Fiber Tech.* 2013, 19, 55–59.
6. Li, Q.S.; Zhang, X.L.; He, H.; Meng, Q.; Shi, J.; Wang, J.N.; Dong, W.F. Improved detecting sensitivity of long period fiber gratings by polyelectrolyte multilayers: The effect of film structures. *Opt. Commun.* 2014, 331, 39–44.
7. Chiang, C.C.; Cheng, T.C.; Chang, H.J.; Tsai, L. Sandwiched long-period fiber grating filter based on periodic SU8-thick photoresist technique. *Opt. Lett.* 2009, 34, 3677–3679.
8. Chiang C.C.; Tseng, C.C. Characterization of notched long-period fiber gratings: The effects of periods, cladding thicknesses, and etching depths. *Appl. Opt.* **2014**, *53*, 4398–4404.

9. Risk, D.; Kellman, L.; Beltrami, H. A new method for in situ soil gas diffusivity measurement and applications in the monitoring of subsurface CO2 production. *JGR Biogeosci.* **2008**, *113*, doi:10.1029/2007JG000445.

10. Ryabtsev, S.; Shaposhnick, A.; Lukin, A.; Domashevskaia, E. Application of semi-conductor gas sensors for medical diagnostics. *Sens. Actuators B* **1999**, *59*, 26–29.

11. Hower, J.C.; Henke, K.; O’Keefe, J.M.; Engle, M.A.; Blake, D.R.; Stracher, G.B. The Tiptop coal-mine fire, Kentucky: Preliminary investigation of the measurement of mercury and other hazardous gases from coal-fire gas vents. *Int. J. Coal Geol.* **2009**, *80*, 63–67.

12. Börzsönyi, Á.; Heiner, Z.; Kovács, A.; Kalashnikov, M.; Osvay, K. Measurement of pressure dependent nonlinear refractive index of inert gases. *Opt. Express* **2010**, *18*, 25847–25854.

13. Liu, J.; Sun, Y.; Fan, X. Highly versatile fiber-based optical Fabry-Pérot gas sensor. *Opt. Express* **2009**, *17*, 2731–2738.

14. Liu, D.; Fu, S.; Tang, M.; Shum P.; Liu, D. Comb filter-based fiber-optic methane sensor system with mitigation of cross gas sensitivity. *J. Lightwave Technol.* **2012**, *30*, 3103–3109.

15. Ohodnicki, P.R.; Buric, M.P.; Brown, T.D.; Matranga, C.; Wang, C.; Baltrus, J.; Mark, A. Plasmonic nanocomposite thin film enabled fiber optic sensors for simultaneous gas and temperature sensing at extreme temperatures. *Nanoscale* **2013**, *5*, 9030–9039.

16. Ong P.L.; Levitsky, I.A. Fluorescent gas sensors based on nanoporous optical resonators (microcavities) infiltrated with sensory emissive polymers. *IEEE Sens. J.* **2011**, *11*, 2947–2951.

17. Kanka, J. Design of turn-around-point long-period gratings in a photonic crystal fiber for refractometry of gases. *Sens. Actuators B* **2013**, *182*, 16–24.

18. Wei, X.; Wei, T.; Li, J.; Lan, X.; Xiao, H.; Lin, Y. Strontium cobaltite coated optical sensors for high temperature carbon dioxide detection. *Sens. Actuators B* **2010**, *144*, 260–266.

19. Shivananju, B.N.; Yamdagni, S.; Fazuldeen, R.; Kumar, A.S.; Hegde, G.; Varma, M.M.; Asokan, S. CO2 sensing at room temperature using carbon nanotubes coated core fiber Bragg grating. *Rev. Sci. Instrum.* **2013**, *84*, doi:10.1063/1.4810016.

20. Melo, L.; Burton, G.; Davies, B.; Risk, D.; Wild, P. Highly sensitive coated long period grating sensor for CO2 detection at atmospheric pressure. *Sens. Actuators B* **2014**, *202*, 294–300.

21. Lin, C.Y.; Wang, L.A.; Chern, G.W. Corrugated long-period fiber gratings as strain, torsion, and bending sensors. *J. Lightwave Technol.* **2001**, *19*, 1159–1168.

22. Liu, S.H.; Lin, Y.C.; Chien, Y.C.; Hyu, H.R. Adsorption of CO2 from flue gas streams by a highly efficient and stable amino silica adsorbent. *J. Air Waste Manag. Assoc.* **2011**, *61*, 226–233.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).