A Polarimetric Interferometer Based on Composite Optical Waveguide for Refractive Index Detection

Bin Du1, Xihui Mu1, Shuai Liu1, Zhiwei Liu1, Bing Liu1, Zhaoyang Tong1, Jianjie Xu1* and Zhimei Qi2

1State Key Laboratory of NBC Protection for Civilian, Beijing 102205, China
2State Key Laboratory of Transducer Technology, Institute of Electronics, Chinese Academy of Sciences, Beijing 100190, China
*Corresponding author’s e-mail: xujianjie@sklnbpc.com

Abstract. A sensitive interference refractive index sensor based on composite optical waveguide (COWG) was developed. Sol-gel technique was used to prepare TiO$_2$ sol, and the TiO$_2$ film was fixed on the surface of single-mode potassium ion-exchange (PIE) optical waveguide (OWG) by dip-coating and annealing treatment to fabricate an interference refractive index sensor device. The interference between the zeroth-order transverse electric (TE$_0$) and magnetic (TM$_0$) modes of the laser beam which transport in the COWG caused phase-difference change ($\Delta \phi$) of output light signals. Refractive index sensitivity of TiO$_2$/PIE COWG chip was examined by injecting aqueous NaCl solutions and distilled water in turn to detect its $\Delta \phi$. Experimental results show that, for the TiO$_2$/PIE COWG its refractive index sensitivity is $S_{RI} = (573.09 \times 2\pi)/RIU$ in the refractive index ranges of 1.3386~1.36. The sensor sees the advantages of high sensitivity, compact size, simple fabrication, as well as low cost.

1. Introduction
Refractive index is an inherent property of solid, liquid and gas materials, and it is usually regarded as an important parameter in the field of optical material detection. By measuring Refractive index, physical properties and optical properties such as concentration and purity of materials can be analyzed. Therefore, the research of refractive index detection has attracted more attention. Currently, types of optical sensors for refractive index detection involving surface plasmon resonance [1], optical fibers [2-3] and planar optical waveguides including gratings [5,6], slits [7,8], micro-disk resonators [9], and the like, have been developed. These optical sensors possess the benefits of high sensitivity and small size. However, they are also given the disadvantages of costly and hard to fabricate.

Composite optical waveguide (COWG) is a novel optical structure produced by coating a high-index film which has two tapered ends on the surface of a single mode optical waveguide (OWG) [10]. Moreover, the high refractive index contrast between the high-index film and the OWG leads to the spatial separation of zeroth-order transverse electric (TE$_0$) and zeroth-order transverse magnetic (TM$_0$) in the film-covered region. Compared with sensors which utilize evanescent wave as the nearfield probe [11], the COWG based polarimetric interferometer on the basis of the phase difference between TE$_0$ and TM$_0$ [12] possesses higher sensitivity.

Conventional high refractive index film, such as TiO$_2$ and Ta$_2$O$_5$ is usually prepared by methods such as sputtering [13,14] and chemical vapor deposition [15], laser deposition [16], etc. These methods are costly due to the complicated equipment and operation. Compared with other methods, the sol-gel
method [17] possesses the advantages of low cost, uniformity, and no need for vacuum equipment, and it has particularly extensive application prospect in the field of optical film preparation.

This paper demonstrated a polarimetric interferometer based on composite optical waveguide for liquid refractive index detection. As a classical optical material, TiO₂ was chosen to serve as film owing to its advantages of high refractive index. Sol-gel method was used to prepare TiO₂ sol for its inexpensive manufacturing costs, widely used and low-temperature fabrication capability. The TiO₂ film is fixed on the surface of potassium ion-exchanged (PIE) OWG by dip-coating method and annealing treatment in turn. The surface morphology of TiO₂ film was unveiled, either. Ultimately, response of TiO₂/PIE COWG for refractive index was investigated by using aqueous NaCl solution with different concentrations.

2. Materials and methods

2.1. Instruments and reagents
Technology Co., Ltd. (Beijing, China). Diiodomethane (CH₂I₂, refractive index is 1.74) was received from J&K Scientific Ltd. (Beijing, China). All the other reagents were of analytical grade and purchased from Beijing Chemical Works (Beijing, China).

Micro slide glass (S1111, 76 mm × 26 mm in area and 1.0 mm in depth, Matsunami Glass Ind., Ltd., Japan) with a refractive index of 1.52 was adopted as soda-lime glass substrate to prepare single mode planar waveguide. The particle size of TiO₂ sol was measured by Zetasizer Nano-ZS system (Malvern Panalytical Ltd., UK). PIE OWGs were fabricated in a ceramic fiber muffle furnace (MF-0610F, Huagangtong Technology (Beijing) Co., Ltd., Beijing, China). The thin film was coated onto the surface of PIE OWG using dip coater (SYDC-100, Shanghai SAN-YAN Technology Co., Ltd., Shanghai, China). The topographies were characterized by a scanning probe microscope (SPM) (SOLVER NEXT, NT-MDT Co., Moscow, Russia). The refractive index and thickness of TiO₂ film was measured by a spectroscopic ellipsometer (SE 850 DUV, SENTECH Instruments GmbH, Berlin, Germany).

2.2. Synthesis of TiO₂ sol
The mechanism of TiO₂ sol preparation is that the alcohol solution of titanate would be hydrolyzed under certain conditions, and then polymerized by hydroxyl group to further produce a polymer. In order to prevent the titanium alkoxide from reacting with water violently, acetylacetone (AcAc), triethanolamine, etc. are used as inhibitors of titanium alkoxides hydrolysis.

The process of TiO₂ sol preparation, briefly, 10 mL of TNBT and 1 mL of AcAc were added to 60 mL of ethanol, and the mixture was stirred for half an hour to obtain a mixed solution A. 1 mL of nitric acid as a catalyst and 1.2 mL of distilled water were dissolved into 10 mL of ethanol to obtain solution B. Then, the solution B was added dropwise to solution A, and the as-obtained mixture was stirred at room temperature for 2 h, followed by aging for 24 h to obtain a pale yellow stable TiO₂ sol. The typical particle size distribution curve of the obtained TiO₂ sol was measured by Zetasizer Nano-ZS system. As shown in figure 1, the diameter of the particles has a narrow particle size distribution with an average of 2.328 nm.
2.3. PIE OWG preparation
Single mode planar waveguides were prepared on soda-lime glass substrates by K⁺-Na⁺ ion-exchange method. In brief, dry glass substrates were immersed in the molten KNO₃ at 400 °C for 40 min. After the ion-exchange process, the glass OWGs were taken out of the molten KNO₃, cooled at room temperature, washed and dried, then the PIE OWGs were obtained.

2.4. Coating
The dip-coating method was chosen to fabricate high refractive index film. The cleaned PIE OWG which was selected as the substrate was immersed into the TiO₂ sol obtained via sol-gel method for 1 min to make the sol fully adhere to the surface of the substrate. Then the substrate was withdrawn upward and vertically at a speed of 2 mm/s, then the TiO₂ sol coated substrate was dipped into isopropanol to remove surplus film. The annealing treatment was carried out in ceramic fiber muffle furnace. First the film was dried at 100 °C for 1 h, then heated at a rate of 15 °C/min up to 400 °C and held at this temperature for 3 h in air. Ultimately, TiO₂/PIE COWG was obtained gave the thin film of TiO₂ pattern of 1 cm wide striping. The refractive index of the TiO₂ film was 1.927 and the value of thickness was 52.21 nm, as determined by ellipsometry measurements.

2.5. Measurement procedures for refractive index testing
As shown in scheme 2, the liquid refractive index testing system was consisted of a peristaltic pump, TiO₂/PIE COWG, sample chamber, 633nm linearly polarized He-Ne laser source, photodetector and computer. To carry out testing performance, the sample chamber was placed at the middle of the TiO₂/PIE COWG tightly to cover the entire TiO₂ film. Laser beam was introduced into the waveguide layer of COWG device via prism coupling method to excite evanescent wave, in brief, two glass prisms coupler (n = 1.75) were mounted at each end of the COWG device for laser beam irradiating and emerging from the waveguide layer at a given incident angle respectively, CH₂I₂ was introduced between the prism couplers and the waveguide layer as index-matching liquid to increase the coupling efficiency. The 633nm linearly polarized laser beam was used to excite TE₀ and magnetic TM₀ modes simultaneously in the waveguide layer. Meanwhile, the TE₀ and TM₀ modes with similar field profiles in the waveguide layer can be spatial separated from each other in region covered with TiO₂ film for the high refractive index contrast between the TiO₂ film and the PIE OWG [18], and the evanescent field with the TE₀ mode was much stronger than that with the TM₀ mode. Afterwards, the light beam emerged from another prism coupler passed through an analyzer with 45° polarization orientation, causing interference between the TE₀ and TM₀ components of the beam. The phase-difference change (Δφ) between the TE₀ and TM₀ components which caused by the interaction of the evanescent field with the analyte during measurement was monitored and converted into electric signals by a photodetector and recorded by the computer.
The aqueous NaCl solution with the mass fraction of 3 wt%, 5 wt%, 7.5 wt%, 10 wt%, 12.5 wt%, 15 wt% and 20 wt%, were prepared, and the corresponding refractive index of each solutions were 1.3386, 1.3423, 1.3465, 1.3511, 1.36 and 1.3685 respectively, which measured by an Abbe refractometer. The mass fractions of aqueous NaCl solutions (C_{NaCl}) configured in this paper fit the refractive indices of aqueous NaCl solution ($n_{NaCl}$) well, and the relationship is shown below:

$$n_{NaCl} = 0.177C_{NaCl} + 1.3332, R^2 = 0.9997$$

3. Results and discussion

3.1. Topographical of the TiO$_2$ film
In this paper, microstructure of TiO$_2$ film was observed by using a SOLVER NEXT scanning probe microscope. Any 10 μm × 10 μm region of the TiO$_2$ film was scanned using tapping mode at a resonant frequency of 380 kHz. An AFM scan was performed on a glass substrate not covered with TiO$_2$ film as a contrast. As can be observed in Fig. 3, the original PIE OWG substrate was rough and uneven, with irregular undulations and a surface root mean square roughness (RMS) roughness of 2.382 nm. When the TiO$_2$ film was dip coated on the surface of the PIE OWG substrate, its microscopic morphology was changed significantly. The surface became smooth and flat, with a small burr shape, and the surface RMS roughness was about 1.181 nm. All these morphologic changes indicated that an excellent optical film with smooth morphology was obtained by dip-coating.

3.2. Measurements of refractive index sensitivity of the COWG device
Refractive index sensitivity ($S_{RI}$) for the TiO$_2$/PIE COWG was investigated using aqueous NaCl solutions. First, the sample chamber was filled with distilled water using a peristaltic pump. When the
output light signal was stabilized, the aqueous NaCl solutions having different concentrations and distilled water were sequentially injected into the chamber by turns at a small rate to change the refractive index ($n$) of the liquid slowly. During this process, the refractive index of the solution near the surface of TiO$_2$/PIE COWG continuously changed, affected the evanescent wave which generated at the interface between the waveguide layer and the cladding, thereby causing the output optical signal changed. The temporal interference patterns were observed. As can be seen from the figure 3, after the 10 wt% aqueous NaCl solution injected into the sample chamber, the output light signal oscillated violently, and after about 40 s, the output light signal tended to be stable, the change of refractive index ($\Delta n$) was 0.0181 and $\Delta \phi$ was 7.5.

Figure 3 shows the curve based on $\Delta \phi$ of TiO$_2$/PIE COWG and the $\Delta n$ of cladding which caused by injection of aqueous NaCl solution ($\Delta n = n_{NaCl} - n_{water}$, where refractive index of distilled water $n_{water}$ is 1.333). The ordinate $\Delta \phi$ is the phase-difference change of output light when the sample chamber was filled with an aqueous NaCl solution from the injection until the output light signal tended to be stable. As can be seen from the figure 4, when the concentration of aqueous NaCl solution was 3~15 wt%, the $\Delta \phi$ of TiO$_2$/PIE COWG was determined as a function of $\Delta n$, and the following relation was obtained:

$$\Delta \phi = 573.09 \Delta n - 2.1563 \quad (R^2 = 0.9888)$$

Refractive index sensitivity was determined as $S_{RI} = (573.09 \times 2\pi)/RIU$ for the TiO$_2$/PIE COWG.

![Figure 3. Interference pattern induced by refractive index change between 10 wt% NaCl solution and distilled water of cladding on the TiO$_2$ film.](image_url)

![Figure 4. Relationship between the $\Delta \phi$ of the sensor and the refractive index increment $\Delta n$ of cladding.](image_url)

### 4. Conclusion

In this paper, the uniform TiO$_2$ sol was prepared by sol-gel method, and the transparent sol was fixed on the surface of the PIE OWG by dip-coating method. After annealing treatment, the TiO$_2$/PIE COWG device was prepared and its refractive index detection performance on aqueous NaCl solutions was examined by using the liquid refractive index testing system. The refractive index of the TiO$_2$ film was 1.927 and its thickness was 52.21 nm. AFM scan demonstrated the surface of TiO$_2$ film was smooth and flat, and its RMS roughness was about 1.181 nm, indicating that the sensor device possessed an excellent optical film with smooth morphology. The interference between the TE$_0$ and TM$_0$ modes of the laser beam which transport in the COWG caused $\Delta \phi$ of output light signals, and the $\Delta \phi$ linearly increased with $\Delta n$ when corresponding refractive index of aqueous NaCl solution $n_{NaCl}$ in a range from 1.3386 to 1.36, and its $S_{RI}$ was $(573.09 \times 2\pi)/RIU$. These results demonstrated that the sensing element had the advantages of low cost, fast response, reversible and so on, yielding application prospect in liquid refractive index detection. Meanwhile, due to the enhancement of evanescent wave in the COWG structure, the sensor could also be extended to the detection of other biochemical analyte. Next, our work will target the detection of biochemical poisons, and related research is underway.
Acknowledgments
This work was supported by the National Key R&D Program of China (2016YFF0103103).

References
[1] Rifat A A, Mahdiraji G A, Sua Y M, Ahmed R, Shee Y G and Adikan F R M. (2016) Highly sensitive multi-core flat fiber surface plasmon resonance refractive index sensor. Opt. Express, 24: 2485-2495.
[2] Coelho L, Viegas D, Santos JL and Almeida JMMM de. (2014) Enhanced refractive index sensing characteristics of optical fibre long period grating coated with titanium dioxide thin films. Sens. Actuators, B, 202: 929-934.
[3] Wu D K C, Kuhlme B T and Eggleton B J. (2009) Ultrasensitive photonic crystal fiber refractive index sensor. Opt. Lett., 34: 3219-3221.
[4] Zhou J, Wang Y, Liao C, Sun B, He J, Yin G, Liu S, Li Z, Wang G, Zhong X and Zhao J. (2015) Intensity modulated refractive index sensor based on optical fiber Michelson interferometer. Sens. Actuators, B, 208: 315-319.
[5] Liu A, Hofmann W H E and Bimberg D H. (2014) Integrated High-Contrast-Grating Optical Sensor Using Guided Mode. IEEE J. Quantum Electron., 51: 1-8.
[6] Beneitez N T, Missinne J, Shi Y, Chiesura G, Luyckx G, Degrieck J and Steenberge G V. (2016) Highly Sensitive Waveguide Bragg Grating Temperature Sensor Using Hybrid Polymers. IEEE Photonics Technol. Lett., 28: 799-802.
[7] Almeida V R, Xu Q, Barrios C A and Lipson M. (2004) Guiding and confining light in void nanostructure. Opt. Lett., 31: 1209-1211.
[8] Li K, Feng X, Cui K, Zhang W, Liu F and Huang Y. (2017) Integrated refractive index sensor using silicon slot waveguides. Opt. Express, 25(2): 1077-1086.
[9] Grist S M, Schmidt S A, Flueckiger J, Donzella V, Shi W, Fard S T, Kirk J T, Ratner D M, Cheung K C and Chrostowski L. (2013) Silicon photonic micro-disk resonators for label-free biosensing. Opt. Express, 21: 7994-8006.
[10] Lu D-f, Li J and Qi Z-m. (2013) Nonspecific detection of lead ions in water using a simple integrated optical polarimetric interferometer. J. Appl. Phys., 113: 213109.
[11] Bradshaw J T, Mendes S B and Saavedra S S. (2005) Planar integrated optical waveguide spectroscopy. Anal. Chem., 77: 28A.
[12] Qi Z-m, Itoh K, Murabayashi M and Yanagi H. (2000) A composite optical waveguide-based polarimetric interferometer for chemical and biological sensing applications. J. Lightwave Technol., 18(8): 1106-1110.
[13] Lu D F and Qi Z M. (2012) Characterization and chemical/biosensing application of a high-sensitivity integrated optical polarimetric interferometer. Acta Phys. Sin., 61: 114212.
[14] Lu D-f and Qi Z-m. (2011) Determination of surface protein coverage by composite waveguide based polarimetric interferometry. Analyst, 136: 5277-5282.
[15] Baryshnikova M V, Filatov L A, Petrov A S and Alexandrov S E. (2015) CVD Deposited Titania Thin Films for Gas Sensors with Improved Operating Characteristics. Chem. Vap. Deposition, 21: 327-333.
[16] Wang G-B, Fu M-G, Lu B, Du G-P, Li L and Shi W-Z. (2010) Growth of nanocrystalline TiO2 films by pulsed laser-induced liquid deposition method and preliminary applications for dye-sensitized solar cells. Appl. Phys. A: Mater. Sci. Process., 100: 1169-1176.
[17] Jung H S, Lee J-K, Lee J, Kang B S, Jia Q, Nastasi M, Noh J H, Cho C-M and Yoon S H. (2008) Mobility Enhanced Photoactivity in Sol-Gel Grown Epitaxial Anatase TiO2 Films. Langmuir, 24: 2695-2698.
[18] Lu D-f, Qi Z-m and Liu R-p. (2011) An interferometric biosensor composed of a prism-chamber assembly and a composite waveguide with a Ta2O5 nanometric layer. Sens. Actuators, B, 157: 575-580.