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Integrated Chemical Vapor Sensor Based on Thin Wall Capillary Coupled Porous Glass Microsphere Optical Resonator

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Abstract

A miniaturized chemical vapor sensor probe was developed using a porous glass microsphere (PGM) as the alignment-free optical microresonator. The porous microsphere was placed inside a thin wall silica capillary tube that was fusion-spliced to an optical fiber. The whispering gallery modes (WGMs) of the microsphere were excited by the evanescent field of the light propagating inside the capillary thin wall. Adsorption of chemical vapor molecules into the pores led to a refractive index change of the PGM and thus the resonance wavelength shift of the WGMs. To facilitate the in-taking of chemical vapor molecules into the PGM, a micro window was opened at the backend of the capillary tube using femtosecond laser micromachining. Ethanol vapor was used to demonstrate the probe for chemical vapor sensing. With a miniaturized size, integrated structure and reflection mode of operation, the proposed probe may find useful in many practical applications such as environmental monitoring and biomedical sensing.

Keywords

chemical vapor sensor; Whispering Gallery Modes; optical resonator; thin wall capillary; microfabrication; porous structure

1. Introduction

Optical microresonators are miniature axially symmetric (polygonal, cylindrical, ring, toroid and spherical) structures made of optically transparent materials. Light trapped in these symmetric structures propagates circumferentially around the surfaces in the form of whispering gallery modes (WGMs). The interaction between the circulating light and the

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outside medium is amplified many times as the light circulates inside the resonator. As a result, optical resonators have been used for various sensing applications [1-5] including chemical detection [2, 5-10]. The microresonator based chemical sensors have the general advantages of high measurement resolution and small size.

However, most of the optical resonators are made of solid materials (e.g., silica and silicon). When used for chemical vapor detection, the light probes the vapor molecules located at the close vicinity of the outer surface of the solid resonator through the evanescent fields of the WGMs. As a result, the detection sensitivity is limited by the penetration depth of the evanescent field. To improve the detection sensitivity, porous materials have been used to make the WGMs resonators [5, 6]. The vapor molecules are adsorbed and concentrated in the pores, and the effective light-molecule interaction volume is significantly increased. For example, Lin [6] proposed a microresonator chemical sensor by coating a porous zeolite layer on the external surface of a solid glass microsphere. The simulations showed that such porous zeolite film can efficiently enhance the sensitivity. We also experimentally [5] and theoretically [11] proved that a porous microsphere resonator could enhance the sensitivity by at least ten times in chemical vapor detection, compared to that of a solid silica microsphere.

Various optical couplers have been investigated to excite the WGMs of an optical resonator, including the pedestal waveguide [2], prism [2, 12], and fiber taper [5]. Light can be coupled into and out of the resonator by phase-matching the evanescent waves of the coupler and the WGMs of the resonator. In general, optical prisms are bulky and pedestal waveguides require precision fabrication. Although fiber tapers are easy to fabricate and have been proven very efficient for WGM excitation, they are fragile and operate in the transmission mode. In addition, high-precision alignments are required to position these couplers with respect to the resonator. As such, these couplers are widely used in the laboratories but impractical for field applications.

Recently, we demonstrated a fiber pigtailed thin wall capillary coupler for exciting the WGMs of a microsphere resonator [13]. The microsphere resonator is dropped inside a thin wall silica capillary tube that is fusion-spliced to an optical fiber. The WGMs of the microsphere are excited by the evanescent field of the light propagating inside the capillary thin wall. In such a way, the microsphere resonator is integrated and the coupler is alignment-free. In addition, the microresonator operates in a reflection mode, making it a convenient sensor probe for practical applications.

In this paper, we report an integrated chemical vapor sensor probe made of a PGM optical resonator coupled by a fiber pigtailed thin wall capillary waveguide. Adsorption of chemical vapor molecules from the surrounding environment into the porous microsphere leads to a refractive index change that produces a shift of the resonance wavelength. Compared with a solid glass bead, the PGM allows the direct interaction between the adsorbed molecules and the WGMs circulating inside the resonator. As a result, the detection sensitivity is expected to be higher. The integrated PGM optical resonator might be used as a convenient, *in-situ*, highly sensitive chemical vapor sensor probe.

2. Sensor structure, fabrication and sensing mechanism

Fig. 1 (a) shows the schematic and microscopic image of the integrated chemical vapor sensor using the thin wall waveguide coupled PGM resonator. The sensor is made by fusion splicing a fused silica capillary tube to a multimode optical fiber (MMF). The capillary tube is made of fused silica (Polymicro Technologies, LLC) with the inner and outer diameters of 75 μm and 150 μm , respectively. The MMF is a graded-index fiber made by Corning Inc. with the core and cladding diameters of 62.5 μm and 125 μm , respectively. During fusion splicing, the arc power and duration of the fusion splicer (Sumitomo T-36) is adjusted to obtain a cone-shape joint between the MMF and the capillary. A PGM with suitable diameter is inserted into the capillary tube and pushed all the way to contact the wall of the capillary tube. After PGM insertion, the open end of the tube is sealed. The entire structure is then etched in a hydrofluoric (HF) acid solution (Acros Organics, 20% concentration) to reduce the wall thickness. The etching process is stopped when strong resonant peaks appear in the WGM spectrum. The actual wall thickness may vary depending on the size and the contact position of the PGM. Fig. 1 (b) shows the scanning electron microscope (SEM) images of an etched tube with the wall thickness of about 1 μm . After etching, the sealed end of the tube is cleaved open to allow access to the chemical vapor.

To facilitate flow of chemical vapor into the tube, a micro window (μwindow , 20 $\mu\text{m} \times 20 \mu\text{m}$) is fabricated on the capillary tube wall by drilling using a femtosecond (fs) laser micro machining system [14]. The fs laser is a regeneratively amplified Ti: Sapphire laser (RegA-9000, Coherent, Inc.). The repetition rate, center wavelength, and pulse width of the fs laser are 250 kHz, 800 nm, and 200 fs, respectively. The μwindow provides a flow-through path of the chemical vapor, resulting in an improved detection speed and repeatability. The vent introduces power loss, however, the circular multi-dimensional waveguide guarantees enough light to couple the resonator. The intensity loss from the μwindow is about 10% of total power.

To interrogate integrated sensor structure, the light propagating inside the MMF is first coupled into the capillary thin wall (depicted as the blue line). At the contact point between the capillary wall and PGM, the WGMs (depicted as the red circle) are excited by the evanescent waves. The WGMs are coupled back to the capillary wall at the contact point on the opposite side of the PGM. The light travels backwards along the capillary wall and the MMF (depicted as the red line). At the far end of the MMF, the light is detected and analyzed to study the WGMs.

The PGMs in the experiment was provided by MO-SCI Corporation. Fig. 1 (c) shows the scanning electron microscope (SEM) images of the PGM. The PGMs are composed of a chemically stable sodium borosilicate glass material constructed in the form of a tortuous network of nanometer-scale channels. The glass is heat treated and drawn by a leaching process to produce interconnected pores. The PGMs range from 50 μm to 75 μm in diameter. The pore diameter ranges from 20 nm to 200 nm. The size of the porous channels ensures the molecule adsorption and small optical scattering losses.

When exposed to the chemical vapor, molecules are adsorbed into the pores, resulting in an increase of the effective refractive index and correspondingly a shift in the WGM resonant wavelength. The chemical concentration in the environment can thus be monitored by measuring the amount of WGM resonant wavelength shift. In a solid microsphere resonator, the light interacts with the vapor molecules only at the sphere surface through its evanescent field which has a very shallow depth. The PGM resonator, however, adsorbs the vapor molecules into its body where the light-molecule interaction depth is significantly large. As a result, the PGM resonator is expected to have a better detection sensitivity compared with a solid microsphere resonator. In addition, the integrated sensor probe shown in Fig. 1 operates in the reflection mode that is convenient in practical applications.

3. Experiments

Fig. 2 shows the block diagram of the experimental setup to test the integrated PGM resonator sensor. The light from the tunable laser source (TLS, HP-8168F) transmits through the MMF and 50/50 fiber coupler to interrogate the integrated PGM sensor. The signal light propagates backward along the optical fiber, passes through the 50/50 fiber coupler and is received by the optical power meter (OPM, Agilent 8163A). The WGM resonance spectrum is obtained by scanning the wavelength of the TLS and synchronizing the OPM under the control of the computer.

The probe is placed inside the test chamber that is made of a stainless steel (SS) tube with a outer diameter of $\frac{1}{4}$ inch. Nitrogen is used as the carrier gas. As shown in Fig. 2, nitrogen gas from the cylinder splits into two paths. One path going through the ethanol (Sigma-Aldrich, 99.8%) saturator that is immersed in the ice-water bath. The other path is direct passing-through. The flow rates of these two paths are independently regulated by two flow controllers (Aalborg, GFC17) to vary the ethanol vapor concentration. The actual vapor concentration in the mixture can be calculated based on the flow rates of the two paths and the saturated ethanol vapor pressure at 0°C. In each test concentration, the vapor is first adjusted and let settled to reach equilibrium before it is switched into the test chamber. The readings are taken after the output spectrum becomes stable.

3. Results and discussions

Figure 3 shows the resonance spectrum of a PGM resonator with a diameter of 72 μm under room temperature. The wall thickness of this particular sensor was estimated to be about 2 μm based on the SEM image. The spectrum shows a clear pattern of periodic resonances. The Q-factor of the 72 μm PGM resonator was calculated to be 1.38×10^3 at the resonant wavelength of 1599.48 nm. The corresponding full width at half maximum (FWHM) was 1.16 nm and the free spectrum range (FSR) was 7.61 nm. The related mode order numbers (l) of the resonant peaks are also provided in Fig. 3.

The Q-factor is lower than the solid sphere resonator coupled by a fiber taper [15]. The low Q-factor can be attributed to several aspects. First, the porous structure of the PGM introduced a higher scattering loss compared to a solid microsphere. Second, the contact coupling approach was not the best option for high efficiency coupling, in which the

excitation waveguide should be at a certain distance (~300 nm) from the resonator [15]. There were multiple paths that light could be coupled into and out of the PGM due to the circular periphery of the microsphere in contact with the capillary inner wall. These multiple paths might see different PGM diameter due to the imperfect spherical structure, resulting in the broadening of the resonant peaks. As a fact, a number of sets of resonant peaks that can be clearly identified in the resonant spectrum shown in Fig. 3, which were caused by the multi-path excitations of the PGM resonator using the fiber pigtailed thin wall capillary coupler.

Fig. 4 plots the resonant wavelength shift as a function of ethanol vapor concentration using a thin wall capillary-coupled PGM optical resonator sensor probe. Experiments were performed using a PGM with 57 μm in diameter. The tests were performed at local atmospheric pressure and room temperature. The tested vapor concentration was set at 0 ppm, 128.7 ppm, 254.8 ppm, 378.3 ppm, 500.5 ppm and 618.8 ppm, respectively. The ethanol vapor concentration was calculated based on the vapor pressure at 0°C. The standard deviations of these measurements are shown in Fig. 4 as the error bars.

As the ethanol concentration increased, the resonance spectrum shifted towards longer wavelengths, indicating the increase of effective refractive index of the PGM as a result of adsorption of ethanol molecules into the pores. The chemical sensor probe responded monotonically to vapor concentration change and provided an obvious correlativity for quantitative measurement. The response curve is nonlinear, showing larger responses at lower concentrations. As the vapor concentration increased, the response approaches a plateau due to the saturation in adsorption. The nonlinear relationship between the wavelength shift and the concentration indicates that the adsorption agrees with the Langmuir adsorption model.

Theoretically, the porous glass sphere can absorb gas molecules with dimension less than the pore channel width. In the vapor test, the 57 μm PGM average pore size is about 50nm, which provides enough travelling space for majorities of molecules, such as ethanol (0.44nm), acetone (0.469nm), and water vapor (0.275nm). In other words, the sensor has limited vapor detection specificity of these molecules.

The detection limit at low concentration (<100 ppm) was estimated to be about 20ppm based on the standard deviation value at the concentration of 128.7 ppm. The sources of errors may include the vibration of the PGM inside the capillary tube, the uneven gas flow through the PGM, and the noises of the instrumentation. Comparing with a solid microsphere resonator, although the Q-factor of the PGM is degraded due to the porous structure induced scattering loss, the porous structure makes it advantageous for sensing chemical vapors that are adsorptive into the interconnected glass pores. As a result, we expect that the PGM resonator based sensors offer a better detection sensitivity towards adsorptive vapors than that of a solid microsphere resonator. The integrated PGM resonator sensor yields low detection limit due to the low Q-factor compared with a resonator excited using a fiber taper. However, the integrated structure and the reflection mode operation make the sensor robust and convenient to use in many practical applications such as environmental monitoring and biological sensing.

4. Conclusions

In summary, an integrated chemical vapor sensor based on the thin wall capillary coupled porous glass microsphere optical resonator was proposed and experimentally demonstrated. The fiber pigtailed thin wall capillary was proven to be an effective coupler for excitation of the WGMs in a porous glass microsphere. The relatively low Q-factor of 1.38×10^3 could be attributed to scattering loss of the porous beads, the contact loss between the bead and the capillary wall, and the multiple paths of WGM excitations. Ethanol vapor was used to test the sensing capability of the integrated sensor probe. The experiment results indicated that the adsorption of chemical vapors into the porous structure increased the effective index of the resonator and produced a shift of the resonance spectrum towards longer wavelength. There was a monotonic relation between the vapor concentration and resonance wavelength shift, which could be used for chemical vapor detection after proper calibration. The detection limit for ethanol vapor at lower concentrations (<100 ppm) was estimated to be about 20ppm based on the standard deviation. With a miniaturized size, integrated structure and reflection mode of operation, the proposed probe may find useful in many practical applications such as environmental monitoring and biomedical sensing.

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Biography

Hanzheng Wang received his PhD in Electrical Engineering Department at Clemson University in Aug 2014. He is now an Imaging & Measurement System engineer in Corning, Inc. His research interest mainly focuses on image processing, machine vision, fiber optics, optical sensors and optical microresonator for applications in chemical and biomedical sensing. He was awarded Newport Spectra-Physics Research Excellence Awards in 2012 and the SPIE Education and Travel Scholarships in 2014. Dr. Wang is a member of the Optical Society (OSA), the Institute of Electrical and Electronics Engineers (IEEE), the International Standard Association (ISA), and the International Society for Optical Engineers (SPIE).

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Fig. 1. Integrated porous glass microresonator (PGM) chemical vapor sensor probe: (a) schematic and microscopic image of the probe; (b) SEM images of the cross section of the etched capillary wall; (c) SEM images of the PGM and its porous structure.

Fig. 2. Block diagram of the experimental setup to test the integrated PGM resonator sensor for chemical vapor detection. TLS: tunable laser source, OPM: optical power meter, MMF: multimode optical fiber

Fig. 3.
Reflection resonance spectrum of the PGM resonator coupled by thin wall capillary.

Fig. 4. Sensor response to ethanol vapor concentration changes using N_2 as a carrier gas. Inset: resonance spectrum shift as a function of increasing ethanol concentrations.