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Fabrication of fluorescent oxygen gas-sensor probe module based on asymmetric 1×2 optical waveguides using UV imprint lithography

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Abstract. We proposed and developed an integrated fluorescent oxygen gas-sensor probe module based on asymmetric 1×2 optical waveguides that can transmit power from an optical source and the fluorescence signal with high efficiency simultaneously. The fluorescent oxygen gas-sensor comprises an optical source part, optical detector part, and optical sensing probe part. The optical sensing probe comprises asymmetric 1×2 optical waveguides coated with an oxygen-sensitive fluorescent film on the end face of the optical waveguide. This optical probe module can transmit the optical power and fluorescence signal with high efficiency because of the same optical path for transmission of the optical source and the fluorescence signal. In addition, this structure facilitates an integrated miniature oxygen-sensor module. We optimally designed the asymmetric 1×2 optical waveguides with an asymmetric structure and different two core size. Then, we fabricated the polymeric asymmetric optical waveguides using the UV imprint lithography process suitable for cost-effective mass production. The optical oxygen-sensor probe transmitted the optical source power and the fluorescence signal with 80% and 82% efficiency, respectively. An oxygen-sensitive fluorescent film was coated on the end face of the optical waveguide by using the spray coating method. The oxygen-gas detection sensor constructed using this optical probe module with 1×2 asymmetric optical waveguides could measure the concentration with 0.3% resolution for a gas concentration range of 0% to 25%. This optical oxygen-sensor probe module facilitates a compact, simple, and cheap measurement system. © The Authors. Published by SPIE under a Creative Commons Attribution 4.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.OE.58.9.097104](https://doi.org/10.1117/1.OE.58.9.097104)]

Keywords: oxygen gas-sensor probe; asymmetric 1×2 optical waveguides; fluorescence; UV imprint lithography.

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1 Introduction

Almost all living organisms use oxygen for breathing and energy generation. Therefore, monitoring oxygen is a very important factor applied in a wide range of areas, such as biology, environment, medicine, and maritime affairs.¹

The methods of measuring oxygen concentration, such as the classic Winkler titration, electrical analysis, pressure-based measurement, and optical method based on the fluorescence technique, are still being studied.²

The classic Winkler titration has been employed for the measurement of oxygen for many years and is considered, to some extent, the standard method. However, the time-consuming and cumbersome nature of the titration has hindered its application to process monitoring. Furthermore, the electrical analysis method has the problem of specificity since it reacts with other gases such as chlorine, ozone, and nitrogen oxides.³ On the other hand, fluorescence-based oxygen measurement has high detection resolution; the concentration can be measured in real-time, and it enables optical-fiber-based monitoring. As such, it is widely used in chemistry,⁴ medicine,⁵ and areas that monitor atmospheric or water quality.⁶

A typical fluorescence-based optical oxygen sensor usually measures the luminescence intensity or the lifetime of an organic dye immobilized in a polymer film, which varies according to the concentration of oxygen.^{7,8} Therefore, in the

optical oxygen sensor, the choice of organic dye and matrix material and the film preparation method are crucial factors. Moreover, research on optical probe modules in oxygen sensors to transmit the optical power and fluorescent signal efficiently is important.^{9,10}

In general, the optical probe module for fluorescent oxygen sensors uses two large-diameter optical fibers that transmit the optical source and fluorescent signal. However, since the excitation optical source and fluorescence emission have different optical paths, this structure for the optical probe module in the oxygen sensor cannot efficiently receive the fluorescence emitted by the fluorescent membrane. To solve this problem, an optical probe structure that can have one optical path with excitation and emission using a dichroic mirror was proposed. However, this method requires the accurate optical alignment of optical components such as mirror and lens in free space. Therefore, the optical probe structure using a dichroic mirror is susceptible to external shock and vibration. Further, several researchers have proposed bidirectional optical probe schemes using bifurcated fiber.^{11,12} The fiber is bifurcated with excitation along one fiber and emission monitoring through a second fiber.

We propose an oxygen gas-sensor probe module based on asymmetric 1×2 optical waveguides with different sizes. The proposed optical probe module structure has the same optical path for the power of the optical source and fluorescence signal. Therefore, this structure can transmit the power of the optical source and the fluorescence signal emitted from the fluorescent sensing layer simultaneously with high efficiency. The proposed and designed asymmetric 1×2

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optical waveguide is fabricated via the UV imprint process suitable for cost-effective mass production.¹³ We developed the oxygen-sensor probe module by coating a sol-gel solution mixed with optimum ruthenium concentration on the end face of the output channel in the asymmetric 1×2 optical waveguides. Further, we evaluated the sensor module based on the fabricated asymmetric 1×2 optical waveguide to confirm its effectiveness as an oxygen gas sensor.

2 Development of Fluorescent Oxygen Gas Sensor Probe Module Based on Asymmetric 1×2 Optical Waveguide

2.1 Design of Asymmetric 1×2 Optical Waveguide for Optical Oxygen Gas-Sensor Probe

Figure 1 shows the overall structure of the proposed optical oxygen sensor including the asymmetric 1×2 optical waveguide probe module consisting of two waveguides with different sizes. The optical oxygen gas sensor comprises an optical source, photodetector, oxygen-sensing probe module including the oxygen-sensitive fluorescent layer, an electronic driver circuit, and data signal-processing unit. The optical source is the energy source to excite the fluorescent dye at a specific wavelength. When the fluorescent sensing layer absorbs excitation light of a specific wavelength from the optical source, it emits the fluorescence. The emitted fluorescent intensity is dependent on the concentration of oxygen present in the measurement environment. Therefore, the oxygen sensor can detect the oxygen concentration by measuring the variation of emitted fluorescence intensity according to the gas concentration. The photodetector is a device that detects the fluorescence signal discharged by the reaction with oxygen. The photodetector is configured to detect only the fluorescence signal by the bandpass filter.

In order to transmit both the power of the optical source and the fluorescence signal at the same time efficiently, the probe module for the optical oxygen sensor comprises an asymmetric 1×2 optical waveguide that branches into channel 1 and channel 2 with different core sizes, as shown in

Fig. 2(a). The optical source enters through input channel 1 and passes through channel 2. The oxygen-sensitive fluorescent layer is coated on the end face of channel 2. The fluorescence emitted by the fluorescent sensing layer passes through channel 3.

We conducted an optic simulation based on beam propagation method using the design parameters listed in Table 1. We designed the asymmetric 1×2 optical waveguide structure for efficiently transmitting the power of the optical source (port 1 \rightarrow port 2) and fluorescence signal (port 2 \rightarrow port 3) simultaneously. The core size of channel 2 and channel 3 in the asymmetric 1×2 optical waveguide is $2000 \mu\text{m} \times 2000 \mu\text{m}$ and the core size of channel 1 for optical source transmission is $200 \mu\text{m}$. The refractive indices of the core and cladding were 1.49 and 1.42, respectively. Because the transmission efficiency of the optical source and fluorescence signal depends on the branch angle of channel 1 and channel 2, we respectively simulated the transmission efficiency of the optical source and the fluorescence signal according to the branch angle.

Figure 2(b) shows the transmission efficiency of the optical source and fluorescence signal with the branch angle varied from 1 deg to 5 deg at intervals of 0.2 deg. The transmission efficiency of the optical source decreased significantly at a branch angle of ~ 3 deg, with the fluorescence signal efficiency increasing relatively slightly as the branch angle increased.

We designed the optimum branch angle of 3 deg considering the transmission efficiency and manufacturing tolerance. The optical source and fluorescence signal efficiency on the waveguide at a branch angle of 3 deg was $\sim 89\%$ and 92% for the optical source and fluorescence signal transmission, respectively.

2.2 Fabrication of Asymmetric 1×2 Optical Waveguide Device

Figure 3 shows the fabrication process of the asymmetric 1×2 optical waveguide for the optical oxygen sensor probe. The

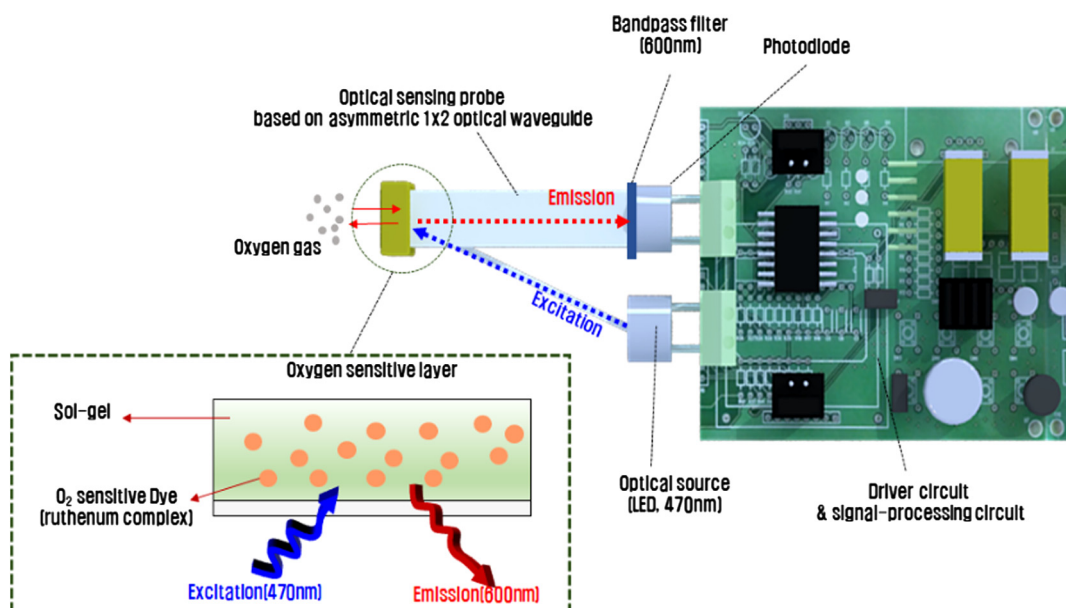


Fig. 1 Structure of optical oxygen sensor with asymmetric 1×2 beam optical waveguide.

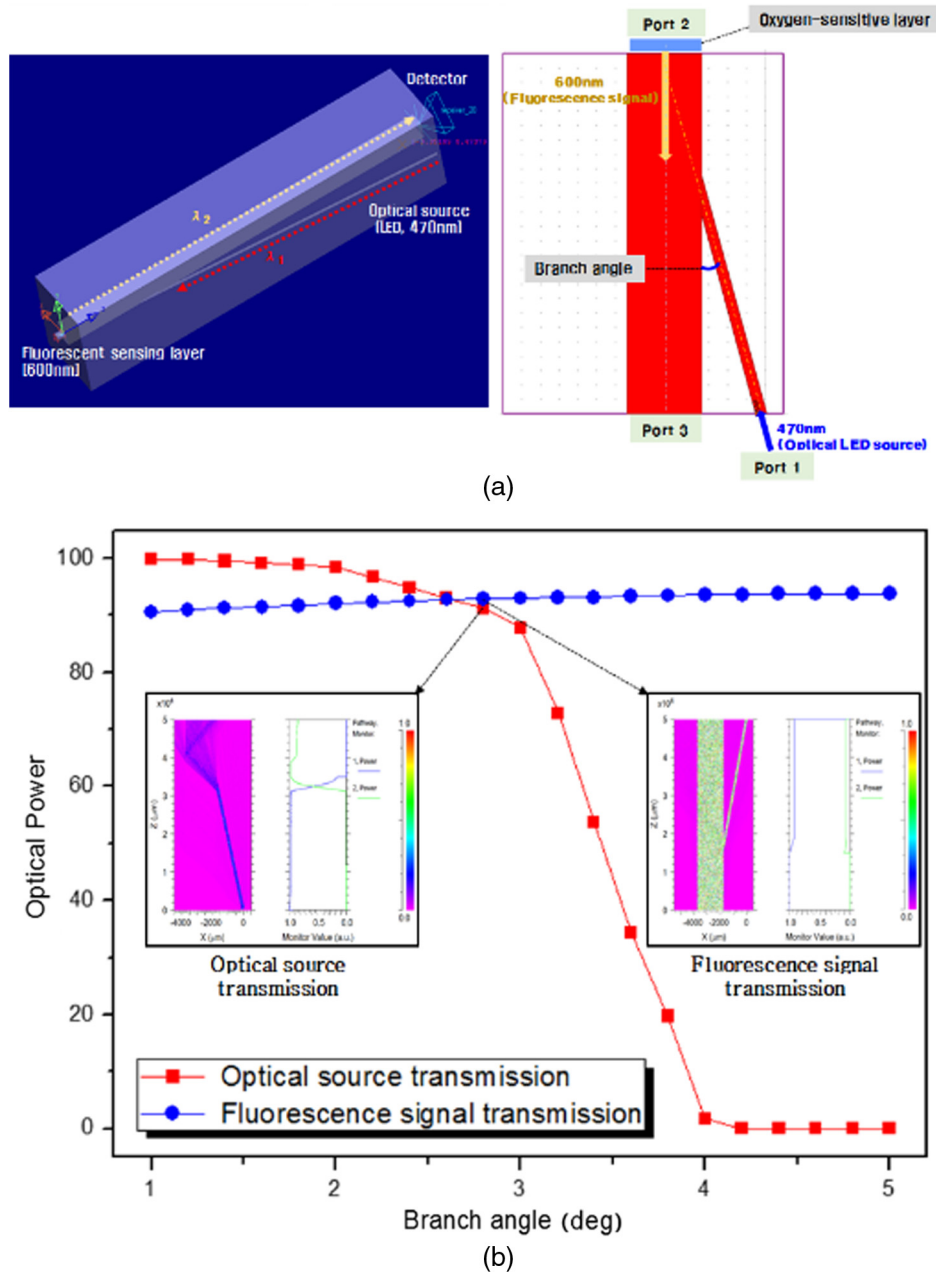


Fig. 2 Design of asymmetric 1 × 2 optical waveguide with different core sizes waveguides: (a) structure of asymmetric 1 × 2 optical waveguide and (b) optical transmission efficiency according to branching angle.

fabrication process includes four steps: (1) original metallic mold fabrication, (2) fabrication of a polydimethyl siloxane (PDMS) stamp using double-casting technology, (3) formation of the core layer using UV imprint lithography, and (4) lamination process.

The original metallic mold with the asymmetric 1 × 2 optical waveguide pattern was fabricated with an ultraprecision machine to reduce the optical propagation loss caused by the surface roughness. Then, we fabricated the PDMS stamp using PDMS double-casting technology to retain the same shape as the original mold. PDMS double-casting consists of two replication steps, where a structure obtained in the first replica molding becomes a master for the second replica molding step. However, PDMS double-casting may

be problematic, because the first replicated PDMS structure strongly adheres to the second PDMS structure. Therefore, the surface modification of the first PDMS master is required. We modified the surface of PDMS by using thermal aging of the PDMS surface.

First, we precisely replicated the first PDMS master by using the original fabricated metallic mold. The PDMS solution was made by mixing the precursor and curing agent (Sylgard™ 184, Dow Corning Co.) in a weight ratio of 10:1 followed by sufficient stabilization time. The mixed PDMS solution was carefully poured onto the original mold and cured at 70°C for 30 min. We could fabricate the first PDMS master with positive type by peeling off from the original mold. The surface of the first PDMS master was

Table 1 Optical design parameters for asymmetric 1 × 2 optical waveguide.

Elements	Unit	Value
Wavelength	μm	0.470
		0.600
Clad refractive index	—	1.506
Core refractive index	—	1.547
Width at port 1	μm	2000
Width at port 2	μm	200
Waveguide length	μm	40,000

modified by thermal aging at 120°C for 24 h. Then, we poured the PDMS solution on the first PDMS master and cured it at room temperature and 70°C for 1 h each. Through the PDMS double-casting process, the PDMS stamp in the same shape as the initial original master could be obtained, as shown in Fig. 4(a).

Afterward, the core resin (Chem Optics Co., FOWG 116) was filled in the patterns of asymmetric 1 × 2 optical waveguides on a PMMA sheet to be coated with the underclad resin (Chem Optics Co., FOWG 506). The core UV resin was cured by UV exposure of 110 mJ/cm² in a nitrogen atmosphere for 15 min. Figure 4(b) shows the fabricated core pattern of asymmetric 1 × 2 optical waveguides. We also formed the upper cladding layer in the lamination process to fabricate the optical waveguides, as shown in Fig. 4(c). Then, we cut the cross-section of the end of the channels and polished the end face to measure the characteristics of the

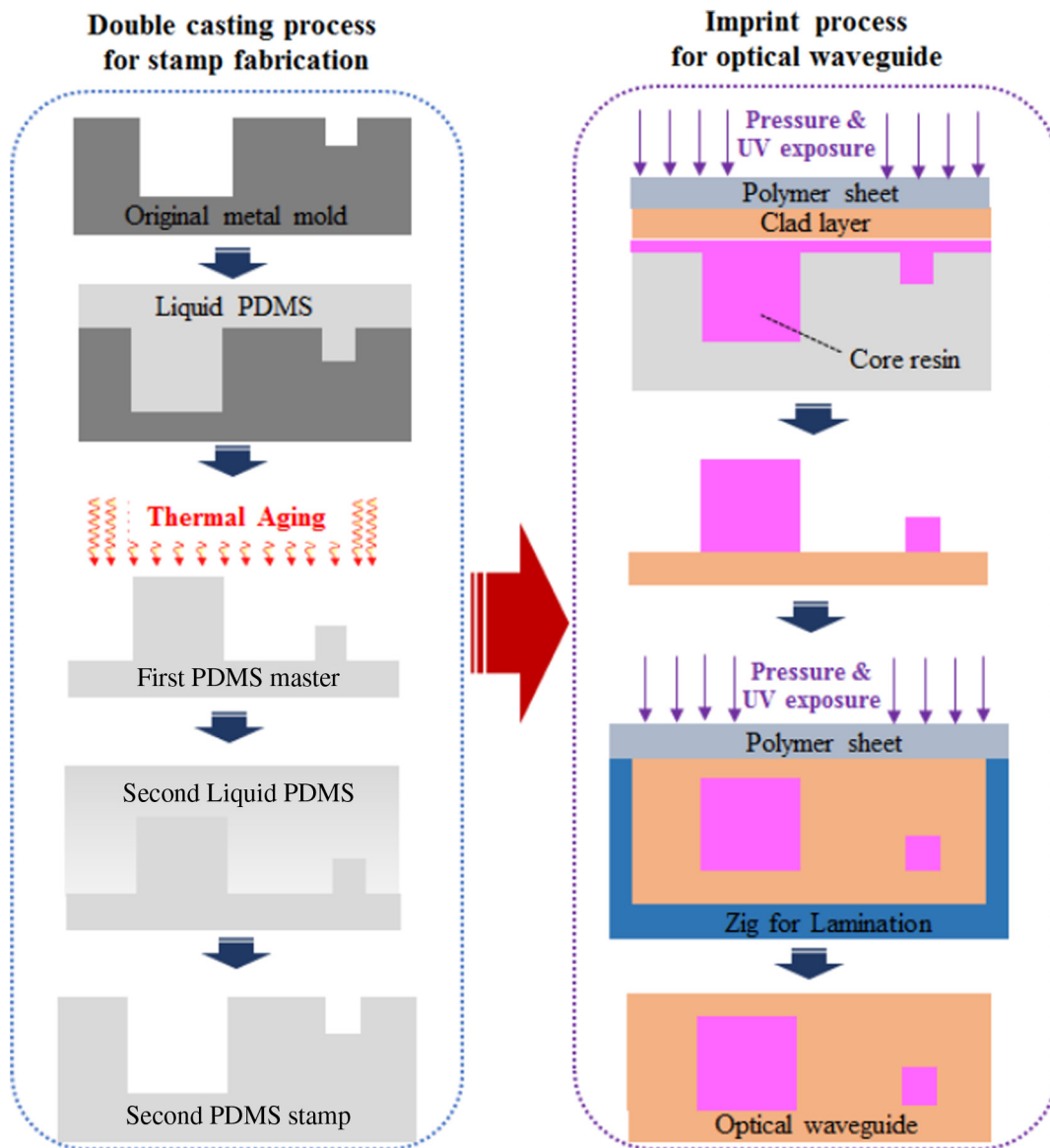


Fig. 3 Schematic view of fabrication process of asymmetric 1 × 2 optical waveguide for oxygen sensor probe.

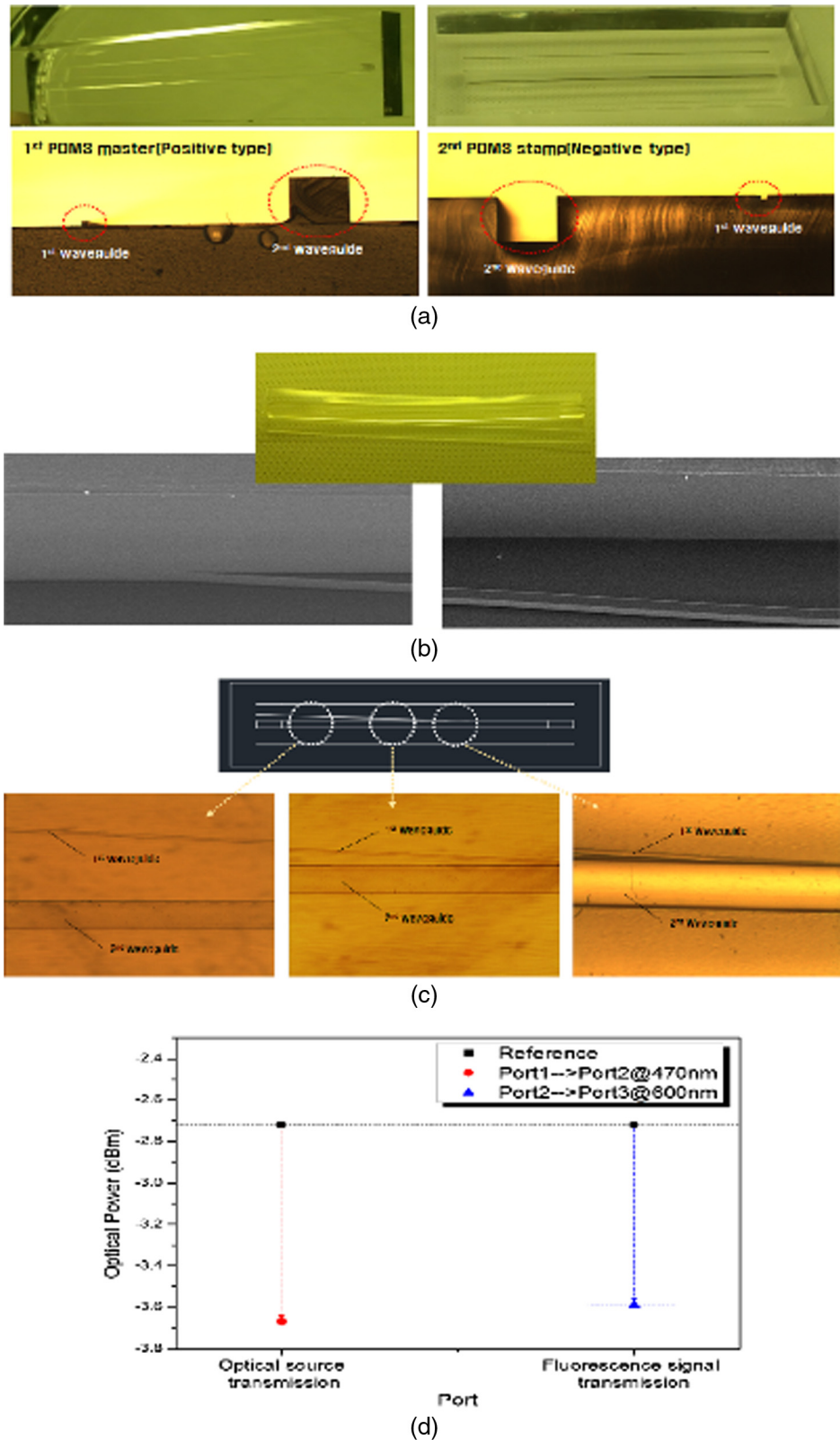


Fig. 4 Fabricated 1 × 2 optical waveguide with asymmetric structure and different core sizes: (a) SEM image of PDMS stamp patterns, (b) SEM image of core layer, (c) image of asymmetric 1 × 2 optical waveguide with different sizes, and (d) optical insertion loss of fabricated asymmetric 1 × 2 optical waveguide.

asymmetric 1 × 2 optical waveguide. We measured the insertion loss of the fabricated asymmetric 1 × 2 optical waveguide. Figure 4(d) shows the insertion losses of the optical source unit and fluorescence signal unit. The

insertion loss of each channel was measured as 0.97 and 0.86 dB. The optical oxygen-sensor probe transmitted the optical source power and the fluorescence signal with 80% and 82% efficiency, respectively.

2.3 Fabrication of Fluorescent Oxygen Gas Sensor Probe Module

In this work, the fluorescent ruthenium complex ((tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II), RuDpp₃²⁺) was synthesized as the oxygen-sensing dye because of its long lifetime and strong absorption in the blue-green region of the spectrum, which is compatible with recently available high-brightness blue light-emitting diodes (LEDs). The RuDpp₃²⁺ was purchased from GFS Chemicals, Inc. and purified as described in the literature.¹⁴ The RuDpp₃²⁺ displays fluorescence quenching effects to differing levels of oxygen concentration.^{15,16}

We analyzed the luminescence intensity at the fluorescent layer according to RuDpp₃²⁺ concentration in the sol-gel solution. For the analysis, the sol-gel solution was prepared with a composition ratio of 3.79 g: 1.45 g: 0.72 g: 21.24 mg for MTMS (Methyltrimethoxysilane, Sigma-Aldrich Chemical Co.), EtOH, H₂O, and HCl (35%), respectively. The mixture solution was left under stirring at room temperature for 2 h for forming sol-gel. We mixed the RuDpp₃²⁺ to be attached on the silica particles with a diameter of 4 μm in the sol-gel solution with concentrations of 3, 5, 10, and 20 mg/ml. Each sol-gel solution mixed with RuDpp₃²⁺ was coated on the UV-curable layer using the spray coating method and was dried at room temperature for 24 h and finally heated at 60°C for 24 h.

The excitation source is a high-brightness blue LED whose spectral output peaks at 470 nm. The emission spectrum of the LED has good overlap with the absorption

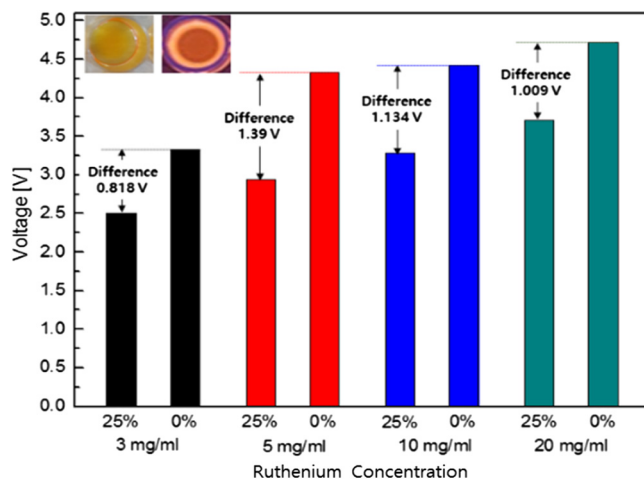


Fig. 5 Fluorescence intensity variation according to ruthenium concentration at 0% and 25% standard oxygen gas.

spectrum of the ruthenium complex. A silicon photodiode with built-in OP-AMP as the photodetector was used as the photodetector for sensing the fluorescence signal. The band-pass filter (bandwidth 20 nm, centered at 600 nm) at the front of the photodetector was packaged.

Figure 5 shows the fluorescence intensity at 0% and 25% standard oxygen gas according to RuDpp₃²⁺ concentrations. The difference in fluorescence intensity decreased at a specific concentration or higher. The UV-curable layer to be coated with a concentration of 5 mg/ml showed the highest fluorescence intensity variation between 0% and 25% standard oxygen. We coated the sol-gel solution with an optimized concentration of 5 mg/ml on the end of the 2000-μm channel in the asymmetric 1 × 2 optical waveguide using the spray coating method. The thickness to be coated with sol-gel solution is about 10 μm. The 200-μm channel was bonded to the 100-μm optical fiber connected to the 470-nm LED optical source.

Figure 6 shows the channel image of the fabricated asymmetric 1 × 2 optical waveguide and 600-nm fluorescence emitted when the 450-nm optical source is inputted.

3 Experimental Results

We performed the evaluation by injecting the standard oxygen gas and standard nitrogen gas for each concentration to examine the performance of the optical oxygen-sensor module based on the fabricated asymmetric 1 × 2 optical waveguide. We injected standard gases into the gas flow cells through the mass flow controller, which can control the gas flow. The output voltage signal according to the gas concentration is shown through the differential amplifier in comparison with the reference voltage. This output value is converted by a 16-bit A/D converter to indicate oxygen concentration. We fixed the oxygen-detecting optical probe module to the gas flow cell and injected standard oxygen gas at 0.3065%, 0.5061%, 0.54%, 0.70%, 1.0155%, 5.0574%, 20.0890%, and 25.016% sequentially. Figure 7 shows the fluorescence intensity variation of the sensor according to oxygen gas concentration. Gas detection in the range of 0% to 25% was confirmed with the fabricated oxygen sensor based on asymmetric 1 × 2 optical waveguides. Moreover, it could detect the oxygen concentration with a resolution of 0.3%. Figure 8 shows the measured response time of the sensor through each standard oxygen gas injection. The response time to reach 99% of the total response of the signal is measured within 2 s. Through these results, we confirm that our oxygen sensor is comparable with existing oxygen-sensor technology in terms of performance, size, and durability.

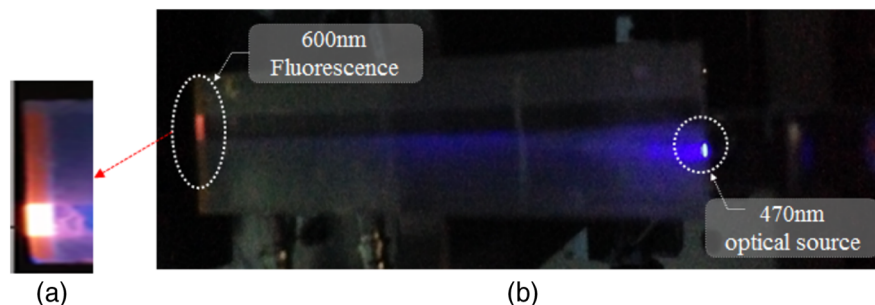


Fig. 6 Oxygen optical sensor probe module: (a) image of coated fluorescence layer on end face of optical waveguide and (b) beam propagation image and 600-nm fluorescence image.

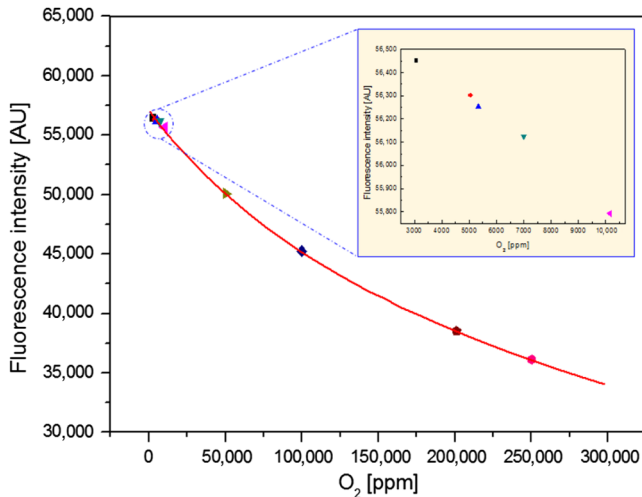


Fig. 7 Fluorescence intensity variation of the sensor according to oxygen gas concentration.

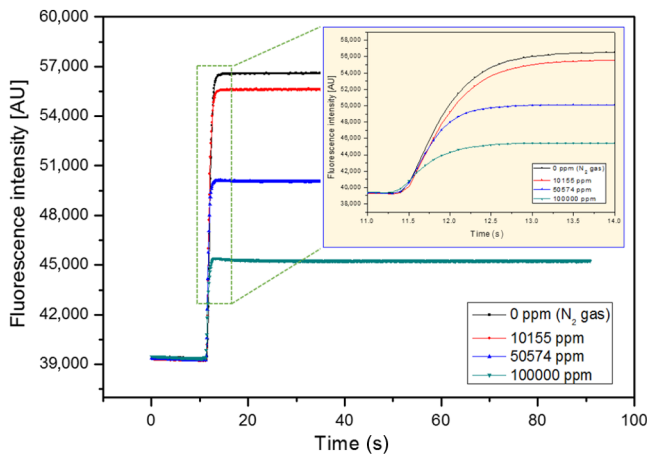


Fig. 8 Response times of the sensor module through each gas injection.

4 Conclusion

We proposed and developed an integrated fluorescent oxygen gas-sensor probe module based on asymmetric 1×2 optical waveguides, which can simultaneously transmit the power of the optical source and the fluorescence signal with high efficiency, using UV imprint lithography. The fabricated polymeric 1×2 beam splitter for the optical oxygen-gas sensor probe measured the transmission efficiency of the optical source and fluorescence signal to be 80% and 82%, respectively. The optical probe module for the oxygen sensor was implemented by coating a fluorescent sol-gel solution mixed with optimum ruthenium concentration on the end face of the output channel in the asymmetric 1×2 optical waveguides. The fabricated oxygen gas sensor using the optical probe module based on 1×2 asymmetric optical waveguides can measure the concentration with 0.3% resolution for an oxygen concentration range of 0% to 25%.

The optical probe module based on 1×2 asymmetric optical waveguides can simultaneously transmit the power of the optical source and the fluorescence signal emitted from the fluorescent sensing layer with high efficiency. It

is more suitable as an oxygen-gas sensor probe module than existing optical probe structures using a dichroic mirror and bifurcated fiber. Furthermore, by coating the fluorescent sensing layer integrally on the end face of the output channel in the asymmetric 1×2 optical waveguides, the emitted fluorescence can be received without optical loss. The application of our sensor to a wide range of uses could be expected. In particular, this sensor will be useful in biomedical applications, as miniaturized optical oxygen-sensor probe modules.

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