Enhanced Characteristics of Nondispersive Infrared CO₂ Gas Sensor by Deposition of Hydrophobic Thin Film †

Jinho Kim 1, Jayoung Lee 1, Keunheon Lee 2 and Seunghwan Yi 1,*

1 Department of Mechanical Engineering, Korea National University of Transportation (KNUT), 50 Daehakro, Chungjushi, Chungbuk 27469, Korea; wlsgh0614@naver.com (J.K.); lgc1812@naver.com (J.L.)
2 Humas Co., 59-6 Jang-Dong, YuSeong-Gu, Daejeon 34113, Korea; humas1@humas.co.kr
* Correspondence: isaac_yi@ut.ac.kr; Tel.: +82-43-841-5129
† Presented at the Eurosensors 2017 Conference, Paris, France, 3–6 September 2017.

Abstract: This paper presents the NDIR CO₂ gas sensor that has improved the sensitivity and also the accuracy by the deposition of thin hydrophobic film (Parylene-C film with 0.5 micrometer thick) onto the reflector surfaces of White-cell structure. After deposition of hydrophobic thin film, the sensitivity of sensor has been increased with averaged 10% and the estimated errors were reduced within 13 ppm to 143 ppm from 254 K to 324 K temperature ranges and from 0 ppm to 5000 ppm CO₂ concentrations.

Keywords: hydrophobic film; NDIR gas sensor; carbon dioxide gas sensor; White-cell structure; IR absorbance; temperature compensation

1. Introduction

The carbon dioxide gas sensor is using in indoor air quality (IAQ) and water quality control currently. For IAQ control and controlling CO₂ concentrations in greenhouse, electrochemical [1] and NDIR gas sensors [2] are used for their unique purposes: supplying fresh air without loss of internal energies in offices, controlling the concentrations of CO₂ in order to cultivate the plants. In case of water quality control, the measurement of total carbon (TC) and total organic carbon (TOC) are getting important in order to manage the rivers and supply high quality drinkable water [3]. The analysis of TOC is currently executed by two sensing methods: permeable CO₂ sensor system [4], NDIR CO₂ sensor [5]. The NDIR carbon dioxide gas sensor has some advantages like compact size, seamless analysis, and long-term stability without compensation. However, TOC system generates water vapor, toxic gases during the procedures of measurement of carbon dioxide concentrations. So the mixed gases can damage the surfaces of optical components, then this might deteriorate the performance of NDIR gas sensor.

This article tried to provide the method for protecting chemical reaction at the surface of optical components by deposition of hydrophobic thin film (0.5 micron thick Parylene-C film) and compare the performance of NDIR CO₂ gas sensors; one has a hydrophobic thin film on the reflectors, the other used a normal reflector (SiO₂/Au/Cr on fused-silica).

2. Theoretical Background and Fabrication

2.1. Theoretical Background

The output voltage of thermopile detector is proportional to the received infrared (IR) energy at the IR detector as described by Beer-Lambert law in Equation (1),
\[ I_r(T, x) = I_o(T) \cdot \exp[-\beta(T) \cdot x], \tag{1} \]

where, \( I_o(T) \) is the initial energy that is radiated from the source, \( \beta(T) \) is the product of the gas absorption coefficient and optical path length, \( x \) is the concentration of target gas [6]. Due to the non-absorbing wavelengths, the above equation could be rearranged as below [7],

\[ I_r = I_o(T) S + I_o(T)(1 - S) \cdot \exp[(-\beta(T) \cdot x)] \tag{2} \]

where, \( S \) is the contribution to the energy density caused by non-absorbing wavelengths irradiated from IR source.

In terms of absorbance of IR light at the detector [7], L. Jun et al.’s suggestion regarding on absorbance of IR light can be modified as Equation (3),

\[ F_a = 1 - \frac{V}{Z \times V_r} = 1 - \left( \frac{V_u}{V_{u0}} \right) \tag{3} \]

where, \( z \) is the ratio of the output of gas detector to the output of reference detector in the absence of target gas, \( V \) and \( V_r \) are the outputs of gas detector and of reference detector at a specific concentration of target gas.

The output of reference detector remains a constant value at certain ambient temperature because the wavelengths of bandpass filter in reference sensor does not overlap to the absorption wavelengths of gases in atmosphere, however, the output voltages of gas detector can be described in Equation (4) as presented in previous article [8],

\[ V_{CO_2}(T, x) = V_o(T) + \alpha(T) \cdot \exp[(-\beta(T) \cdot x)] \tag{4} \]

where, \( V_{CO_2}(T, x) \) is the measured value at certain ambient temperature and CO2 gas concentrations.

2.2. Fabrication

Figure 1 shows a top view of developed NDIR CO2 gas sensor for the application of TOC system. The simulation of optical waveguide structure is shown in Figure 1a, and it shows that the optical waveguide structure has two optical paths: for the output of gas detector with 4.26 µm center wavelength and the output of reference detector with 3.91 µm center wavelength. Two sensor modules were prepared for comparing the sensitivities and accuracies of sensors as photographed in Figure 1b; the one has normal reflectors (SiOx/Au/Cr on fused-silica), the other consists of the reflectors deposited with a hydrophobic film (Parylene-C) on the normal reflectors. The experimental setup and procedures are reported in previous article [8].

![Figure 1](image-url)

**Figure 1.** Developed NDIR CO2 gas sensor for the application of TOC system: (a) brief optical path and structure, (b) signal conditioning circuitry in sensor module.
3. Results and Discussion

After building two sensor modules, the amplified differential output voltages were acquired through RS485 and analyzed as a function of CO$_2$ concentrations and ambient temperatures from 254 K to 324 K. Their experimental results are shown as a function of ethanol concentrations and ambient temperatures from 253 K to 333 K in Figure 2, and the output voltages of developed sensor modules follow the equation as described in Equation (4). The amplified-differential output voltages of two sensor modules show large voltage decrements as a function of CO$_2$ concentration and ambient temperatures as shown in Figure 2. Even though the outputs follows similar tendency of decrement in both cases, however, the sensor module that has a hydrophobic film on the reflectors shows a distinctive ambient temperature dependency as can be seen in Figure 2. As the ambient temperature and concentration of CO$_2$ gas increase, the decrements of amplified differential output voltage also increase in case of the sensor module that has a hydrophobic film on the reflectors.

Figure 2. Amplified differential output voltages as a function of CO$_2$ concentration from 254 K to 324 K: (a) with normal reflectors, (b) with reflectors having a hydrophobic thin film.

Figure 3 shows the normalized absorbance of infrared light [7] as a function of CO$_2$ concentrations at 298 K. As presented in Figure 3, the sensor module that has the reflectors deposited with a hydrophobic film shows a larger absorbance (high sensitivity) than the one built with the normal reflectors. By depositing a hydrophobic Parylene-C film onto the surfaces of reflectors, the sensitivity of CO$_2$ sensor has been improved about 10% in this research.

Figure 3. Comparison of normalized absorbance of infrared light as a function of CO$_2$ concentrations (@ 298 K).

The concentrations of CO$_2$ gas can be calculated from the Equation (5),
\[ x = -\frac{1}{\beta(T)} \ln \left( \frac{V_{\text{CO}_2}(x,T) - V_0(T)}{\alpha(T)} \right) \]  

where, \( V_0(T) \), \( \alpha(T) \) and \( \beta(T) \) can be acquired from the regression analysis of experimental results as presented in Figure 2.

After implementing the algorithm of temperature compensation from 254 K to 324 K [8], the estimated \( \text{CO}_2 \) concentrations are shown in Figure 4. The estimated errors of normal structure were increased as the increment of ambient gas concentrations (20 ppm to 525 ppm in case of Figure 4a). However, when a hydrophobic film was deposited onto the normal reflectors, the errors of estimated \( \text{CO}_2 \) concentrations were reduced significantly from 13 ppm to 143 ppm within the entire temperatures and concentrations ranges in this research.

![Figure 4](image)

Figure 4. Estimated \( \text{CO}_2 \) concentrations after adopting temperature compensation algorithm: (a) with normal structure, (b) with reflectors deposited a hydrophobic thin film.

4. Conclusions

In this research, the effect of a hydrophobic thin film on the performance of NDIR \( \text{CO}_2 \) gas sensor has been studied. When the reflectors in optical waveguide structure are coated with a hydrophobic thin film (Parylene-C film), the absorbance of IR light is increased about 10% compared to the normal structure from 254 K to 324 K ambient temperatures. Furthermore, the accuracy of concentration estimation is also improved significantly. The optical waveguide structure coated with a hydrophobic thin film improves the sensitivity and also accuracy; it might also improve the chemical instability of conventional reflector against mixed toxic gases.

Acknowledgments: This research was supported by R & D Center for Green Patrol Technologies through the R & D for Global Top Environmental Technologies funded by Ministry of Environment, Republic of Korea (MOE) and the authors would like to thank SangHo Shin for 3-D modeling of optical structures.

Conflicts of Interest: The authors declare no conflict of interest and the founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. Kaneyasu, K.; Otsuka, K.; Setoguchi, Y.; Sonoda, S.; Nakahara, T.; Aso, I.; Nakagaichi, N. A carbon dioxide gas sensor based on solid electrolyte for air quality control. Sens. Actuators B Chem. 2000, 66, 56–58, doi:10.1016/S0925-4005(99)00411-6.
2. Yi, S.H.; Park, J.S.; Park, J.M. Temperature compensation of novel NDIR \( \text{CO}_2 \) gas sensor. In Proceedings of the IEEE 5th Conference on Sensors, Daegu, Korea, 22–25 October 2006.
3. Visco, G.; Campanella, L.; Nobili, V. Organic carbons and TOC in waters: An overview of the international norm for its measurements. Microchem. J. 2005, 79, 185–191, doi:10.1016/j.microc.2004.10.018.
4. Tian, K.; Dasgupta, P.K. A permeable membrane capacitance sensor for ionorganic gases: Application to the measurement of total organic carbon. *Anal. Chem. Acta* 2009, 652, 245–250, doi:10.1016/j.aca.2009.04.028

5. Kawasaki, N.; Matsushige, K.; Komatsu, K.; Kohzu, A.; Watanabe Nara, F.; Ogishi, F.; Mikami, H.; Goto, T.; Imai, A. Fast and precise method for HLPC-size exclusion chromatography with UV and TOC(NDIR) detection: Importance of multiple detectors to evaluate the characteristics of dissolved organic matter. *Water Res.* 2011, 45, 6240–6248, doi:10.1016/j.watres.2011.09.021.

6. Yi, S.H. Temperature dependency of non-dispersive infrared carbon dioxide gas sensor by using infrared sensor for compensation. *J. Sen. Sci. Technol.* 2016, 25, 124–130, doi:10.5369/jsst.2016.25.2.124. (In Korea)

7. Jun, L.; Qiulin, T.; Wendong, Z.; Chengyang, X.; Tao, G.; Jijun, X. Miniature low-power IR monitor for methane detection. *Measurement* 2011, 44, 823–831, doi:10.1016/j.measurement.2011.01.021.

8. Yi, S.H. Temperature compensation methods of nondispersive infrared CO2 sensor with dual elliptical waveguide. *Sens. Mater.* 2017, 29, 243–252, doi:10.18494/SAM.2017.1439.

© 2017 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 (CC BY) license (http://creativecommons.org/licenses/by/4.0/).