Numerical investigation of Au-silane functionalised optical fibre sensor for volatile organic compounds biomarker (VOCs) detection

Metem, Prattakorn, Patchoo, Wisarn, Mohammed, Waleed, Viphavakit, Charusluk

Prattakorn Metem, Wisarn Patchoo, Waleed S. Mohammed, Charusluk Viphavakit, "Numerical investigation of Au-silane functionalised optical fibre sensor for volatile organic compounds biomarker (VOCs) detection," Proc. SPIE 11635, Optical Fibers and Sensors for Medical Diagnostics, Treatment and Environmental Applications XXI, 116350P (5 March 2021); doi: 10.1117/12.2578258

Event: SPIE BiOS, 2021, Online Only

Numerical Investigation of Au-silane Functionalised Optical Fibre Sensor for Volatile Organic Compounds Biomarker (VOCs) Detection

Prattakorn Metem[1], Wisarn Patchoo[2], Waleed S. Mohammed[2], and Charusluk Viphavakit[1,3*]

[1]International School of Engineering (ISE), Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand; [2]Center of Research in Optoelectronics, Communication and Control Systems (BU-CROCCS), School of Engineering, Bangkok University, Pathumthani 12120, Thailand; [3]Intelligent Control Automation of Process Systems Research Unit, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

ABSTRACT

A numerical modelling to theoretically investigate and analyse the characteristic of the surface functionalised optical fibre based sensor to detect volatile organic compounds (VOCs) biomarker is introduced in this paper. A 125-micron diameter of coreless silica fibre (CSF) connected to single-mode fibre (SMF) at both ends to achieve a structure of SMF-CSF-SMG is proposed to detect VOCs biomarkers for diabetes such as acetone and isopropanol. The coreless fibre region is considered to be a sensing region where the multimode interference (MMI) occurs having a higher light interaction at the interface between the fibre and sensing medium which leads to the enhancement of sensitivity. The sensing region undergoes surface functionalisation with Au-silane for the sensor to be selectively detect VOCs biomarker with electrostatic absorption. The length of the sensing region is numerically optimised to achieve a reimaging distance where the highest possible of coupling efficiency occurs and the maximum output signal can be obtained. Coupling efficiency spectra at different volume fractions of gold nanoparticles with various acetone and isopropanol concentrations are also presented. A sensitivity of the Au-silane functionalised optical fibre sensor is achieved by using the analysis of wavelength shift interrogation. The results show the spectra undergoes red-shift phenomenon in the near-infrared region (NIR) when concentrations of acetone and isopropanol are increased. The functionalisation of Au-silane on the optical fibre sensor provides a higher sensitivity compared to the unfunctionalised sensor as it shows more dramatic shifts of absorption spectra when there is a change in VOCs biomarker concentration.

Keywords: Optical fibre sensor, surface functionalisation, VOC biomarker

1. INTRODUCTION

As invasive diagnosis is deemed as unpleasant, painful, and traumatizing, an accurate, fast-processing diagnosis sensor have attracted researchers from various fields. Numerous non-invasive diagnosis methods have been developed throughout the years, including detection of volatile organic compounds (VOCs) in exhaled breath as they contain biomarkers of some chronic diseases.

Volatile organic compounds (VOCs) are organic compounds having low vapor pressure and, therefore, able to be vaporized easily at room temperature. These compounds, as a metabolic waste, are transported to the excretion organs via body fluids. One major method of excretion is exhaled breath; hence, exhaled breath contains VOCs profile corresponding to metabolism of the body[1]. Concentrations of VOCs in exhaled breath are reported to be associated with several chronic diseases and can be served as viable biomarkers. For instance, acetone has been widely supported as a biomarker for type 1 diabetes[2]; isopropanol has been also reported as a biomarker for lung cancer[3].

*corresponding author: charusluk.v@chula.ac.th

Optical Fibers and Sensors for Medical Diagnostics, Treatment and Environmental Applications XXI
edited by Israel Gannot, Katy Roodenko, Proc. of SPIE Vol. 11635, 116350P

· doi: 10.1117/12.2578258

Aimed to detect a ppb-level concentration of the interested VOCs among a plethora of other abundant organic compounds, such as, carbon dioxide, nitrogen, water, and even oxygen[4], exhaled breath VOCs sensors serve as a tall challenge in terms of selectivity and sensitivity. A variety of methods has been explored in order to achieve the necessities of sensitivity and selectivity, mostly divided into 2 major methods: electrical-based measurement and optical-based measurement. Electrical-based method revolves around measurements of resistances and potentials with a presence of the interested VOCs; for instance, chemiresistor and potentiometry sensor for detection of nitric oxide and hydrogen peroxide, respectively[5,6]. Optical-based sensors are mainly associated with absorption, transmission, and intensity measurements, which can be measured by a spectrometer[7,8].

Optical fiber sensors for VOCs sensing applications have attracted researcher due to its lightweightness, less prone to electrical noises, and possibility of multiplexing compared to its electronic counterpart[9]. Several architectures and designs have been applied for the sensing applications, in particular, singlemode-multimode-singlemode (SMS) fibre structure which has been recently explored for many biomedical applications. By using coreless silica fibre (CSF) for multimode segment of the structure, the propagating light is allowed to interact with surrounding environment. Hence, multimode segment is served as a sensing region for the structure. On top of that, the structure is relatively easy fabrication method, and it is selected as a method of interest in this research[10].

Surface functionalization on the sensing region of the optical fiber sensor has also been investigated in order to improve selectivity and sensitivity. Zinc oxide coated optical fiber sensor is reported to have high sensitivity and selectivity for ammonium gas and ethanol[11,12]. Gold deposited optical fiber sensor exhibits high sensitivity to methanol with a low-detection limit of 0.0001 refractive index unit[13].

The well-known effects of surface functionalization combined with advantages of SMS optical fiber structure have intrigued researchers to design a sensor involving with this structure. Although the functionalised SMS sensors have been studied, further research and proving theories to understand and predict the propagation behaviors and characteristics of electromagnetic radiation guided inside the sensor are extremely important. In this paper, a numerical investigation on gold-silane surface functionalized SMS optical fiber sensor is proposed. The propagation parameters of the light propagating inside the sensor will be studied, via the simulations of sensing isopropanol in air solution.

2. METHODOLOGY

The singlemode-multimode-singlemode (SMS) fibre structure is illustrated in Figure 1. It is composed of a multimode fibre (MMF) segment inserted in between two segments of singlemode (SMF) fibres. The theories necessary for the simulations, propagation mode calculation and multimode interference theory is covered, as well as calculation of medium's refractive index calculation.

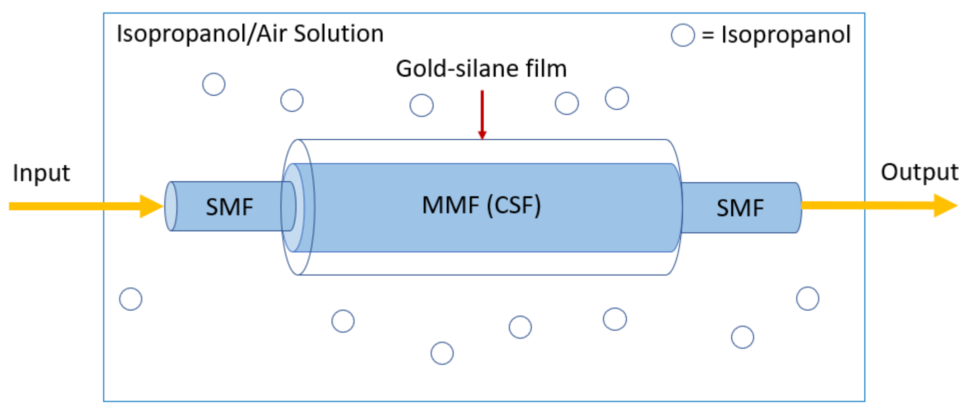

Figure 1 Singlemode-multimode-singlemode fibre structure.

2.1. Propagation mode calculation

In optical fibre, electric field at a specific position inside the fibre can be calculated from the equation (1) [14] assuming on-axis coupling,

$$R(r) = \begin{cases} AJ_l\left(\frac{ur}{a}\right) \; for \; r \leq a, \\ CK_l\left(\frac{wr}{a}\right) \; for \; r \geq a, \end{cases} \tag{1}$$

where r is radial position of an optical fibre. a is a radius of propagating region. J_l and K_l are lth order of Bessel function of the first kind and lth order modified Bessel function of the second kind, while A and C are fitting constants. Due to circular symmetry of light propagating through the singlemode fibre, it can be assumed that the modes in the SMS fibre structure is radially symmetrical, and that lth order Bessel functions are assumed to be 0^{th} order only. Therefore, (1) can be rewritten as

$$R(r) = \begin{cases} AJ_0\left(\frac{ur}{a}\right) \; for \; r \leq a, \\ CK_0\left(\frac{wr}{a}\right) \; for \; r \geq a. \end{cases} \tag{2}$$

where u and w can be defined as

$$u^2 = k_0^2 a^2 \left(n_{core}^2 - n_{eff}^2\right), \tag{3}$$

$$w^2 = k_0^2 a^2 \left(n_{eff}^2 - n_{cladding}^2\right). \tag{4}$$

Here, k_0 is a wavenumber of a light in a vacuum. n_{core} and $n_{cladding}$ are refractive indexes of core and cladding of the fibre, respectively. For the coreless silica fibre (CSF), n_{core} is the refractive index of the glass fibre region, and $n_{cladding}$ is substituted with effective index of the surrounding medium. n_{eff} is an effective index of the whole optical fibre system.

Since the electric field must be continuous for all of domain r, we obtain 2 boundary conditions from (2) which are,

$$R(a-0) = R(a+0), \tag{5}$$

$$\left.\frac{\partial R(r)}{\partial r}\right|_{r=a-0} = \left.\frac{\partial R(r)}{\partial r}\right|_{r=a+0}. \tag{6}$$

and thus,

$$AJ_0(u) - CK_0(w) = 0, \tag{7}$$

$$AuJ_0'(u) - CwK_0'(w) = 0. \tag{8}$$

Through (7) and (8), the effective indexes can be calculated. After substitution of effective indexes into (2), intensity of electric fields propagating through an optical fibre is obtained.

2.2. Multimode interference and reimaging distance

When the light is coupled from SMF into MMF, the multiple-mode light propagation is occurred in the MMF. These excited multimodes of propagation can interfere with each other, which is defined as multimode interference. The interference governs the intensity at the output of the SMS structure, which is defined by coupling efficiency, η [15]. The coupling efficiency determines the loss of the intensity at the output compared with the input and can be calculated from

$$\eta = \sum_{j=0}^{M-1}\sum_{h=0}^{M-1} \tilde{a}_j^2 \tilde{a}_h^{*2} exp\left[i\left(\beta_j - \beta_h\right)z\right], \tag{9}$$

where

$$\tilde{a}_j = a_j\sqrt{\frac{P_{j,h}}{P_s}}, \tag{10}$$

$$a_{j,h} = \frac{\int_{\theta=0}^{2\pi}\int_{r=0}^{\infty} E_s(r,\theta) \times R_{j,h}(r,\theta)^* \, rdrd\theta}{P_{j,h}}, \tag{11}$$

$$P_s = \int_{\theta=0}^{2\pi}\int_{r=0}^{\infty} |E_s(r,\theta)|^2 rdrd\theta, \tag{12}$$

$$P_{j,h} = \int_{\theta=0}^{2\pi}\int_{r=0}^{\infty} \left|R_{j,h}(r,\theta)\right|^2 rdrd\theta, \tag{13}$$

$$\beta_{j,h} = k_0 n_{eff}. \tag{14}$$

Denoted as j or h is a parameter of j^{th} or h^{th} propagation mode of the output. $\tilde{a}_j$ and a_j represent modified expansion coefficient and expansion coefficient of the j^{th} mode of propagation, respectively. The two parameters show how the power of the field expanded between input field (E_s) and output field (R_j) when there are two optical fibers connected. Representing wave number of the light in propagating z-direction, β is called propagating constant and is a product of the wave number in vacuum, k_0, and effective index, n_{eff}, of the j^{th} mode.

The equation (9) provides a relationship between coupling efficiency, η, and propagation length, z. The propagation length that yields the maximum coupling efficiency is defined as reimaging distance, which is used as the length of the no-core fibre for further calculation of the sensor.

2.3. Surrounding medium effective index

2.3.1. Isopropanol refractive index

Isopropanol is selected as volatile organic compound of choice for numerical investigation. From the data of its refractive index[16], a formulation for its best-fitted curve is obtained as

$$n_{IPA}^2 = 1 + \frac{(0.0107)(\lambda^2)}{\lambda^2 - 8.88} + \frac{(0.8702)(\lambda^2)}{\lambda^2 - 0.01036}. \tag{15}$$

Here n_{IPA} is the refractive index of isopropanol, which is a function of wavelength, λ, in µm. This can only be applied to wavelengths in between 0.185 to 2.800 µm.

2.3.2. Gold silane film refractive index

Gold is electric material which has complex refractive index values. The complex refractive index of gold in this work is obtained from Johnson et al. [17],which is varied with the wavelength. The thin gold layer with the thickness of 285 Å is considered in this case.

2.3.3. Medium effective index

Medium effective index can be roughly approximated from volume fraction, f, times with refractive index of each component in the medium. First, the effective index of isopropanol in air solution can be obtained from

$$n_{Sol} = (f_{IPA} \cdot n_{IPA}) + ((1 - f_{IPA}) \cdot n_{air}) \tag{16}$$

Here, f_{IPA} is the volume fraction of isopropanol in the solution, and n_{IPA} is its refractive index. While n_{air} is the air refractive index, which is approximated as 1.

Next, the gold film and the solution combined for the effective index of the medium. Calculated in the same manner, the effective index of the medium can be approximated as

$$n_{Med} = \left(f_{gold} \cdot n_{gold}\right) + \left((1 - f_{gold}) \cdot n_{Sol}\right), \tag{17}$$

where f_{gold} is the volume fraction of the gold film, n_{gold} is gold film's refractive index, and n_{Sol} is the effective index of isopropanol in air solution.

After obtaining effective index of the medium at each wavelength and volume fraction, coupling efficiency is calculated and the relationship between volume fraction and spectra of coupling efficiency is obtained.

3. RESULTS AND DISCUSSION

3.1. Sensor dimension from reimaging distance calculation

A graph of propagation distance, and coupling efficiency, can be obtained at the operating wavelength of 1550 nm, as shown in Figure 2. It can be seen that the calculated coupling efficiency is nearly 0 dB at the propagation distance of 5.85 cm. This means that at the length of 5.85 cm, the sensor can have the lowest loss leading to a high coupling efficiency at the output.

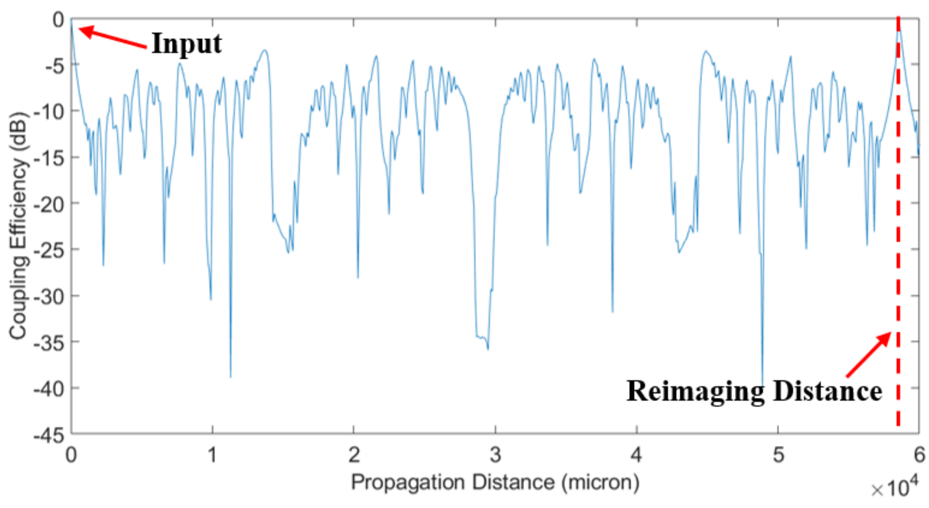

Figure 2 Coupling efficiency and propagation distance calculated at the wavelength of 1550 nm. Input and reimaging position is signified in figure. Reimaging distance is calculated to be 5.85 cm.

From the coupling efficiency result, the Au-silane functionalised optical fibre is numerically designed to have a length of 5.85 cm in order to achieve the maximum output signal due to the reimaging of the light propagation. The maximum possible output signal in order to achieve the optimum sensitivity of the sensor.

3.2. Sensor sensitivity

After the length of the proposed sensor is selected to be 5.85 cm, the sensor is then analysed for its sensitivity by calculating the shift in peak wavelength where there is a change in refractive index from the VOCs surrounding medium. In this work, the different volume fractions of isopropanol (IPA) varied from 0.00 to 0.10 is considered as the VOCs surrounding medium. With the different volume fractions, the refractive index of the medium is varied between 1 and 1.036748. The graph of coupling efficiency varied with operating wavelength for different refractive index is shown in Figure 3. In this Figure, the proposed sensor is designed to be coated with 0.003 volume fraction of Au-silane as it is the most optimum volume fraction to obtain the fundamental mode light interaction at the thin metal layer interface. For a larger gold volume fraction, the metal layer becomes thicker as starts to have multiple modes light interaction at the metal layer interface. However, only the fundamental mode light interaction is considered in this work to obtain the high linear relationship between the peak wavelength shift and the change in refractive index of the VOCs medium.

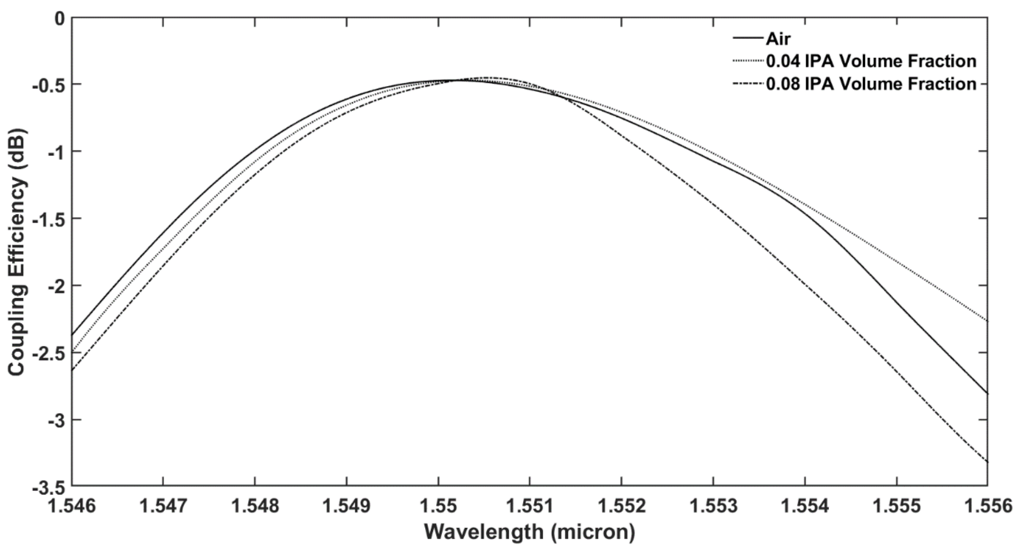

Figure 3 Coupling efficiency versus wavelength when using propagation distance at reimaging distance of 5.85 cm at fixed gold volume fraction of 0.003 and varies isopropanol volume fractions from 0.0 to 0.08.

The graph exhibits red-shift phenomenon as the volume fraction of isopropanol increases. An increase in isopropanol leads to a higher effective index of isopropanol mixed in air. The higher refractive index resulting in higher effective index values, and therefore, having the peaks occur at higher wavelength.

The sensitivity of this proposed sensor can be studied from the relationship between peak wavelength and the change in refractive index of VOCs medium which is isopropanol in this case as shown in Figure 4. In this graph, non Au-coated and Au-silane coated sensor with the volume fraction of gold at 0.001 to 0.003 are considered. At the 0.003 volume fraction gold-silane coated sensor, the wavelength shifts of coupling efficiency is more significant compared to those occur in the lower gold volume fraction. The sensitivity of the sensor with the volume fraction of gold at 0.003 is calculated to be 0.0132 micron per change in solution refractive index (RIU).

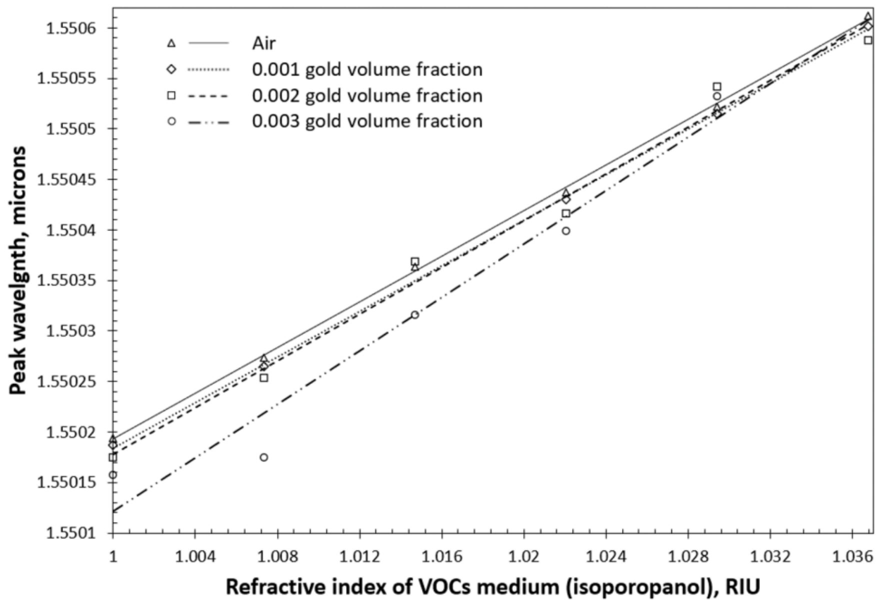

Figure 4 Peak wavelengths of the coupling efficiency spectra when varies volume fraction of both gold from 0.000 to 0.003 and isopropanol from 0.0 to 0.1.

4. CONCLUSION

Numerical analysis on gold-silane-coated SMS fibre sensor is studied. The Au-silane coated optical fibre sensor is designed to be 5.85 cm long in order to achieve the maximum possible coupling efficiency or the lowest loss. Coupling efficiency spectra are calculated for each different gold and isopropanol volume fraction. The graphs exhibit red-shift phenomena as volume fraction of isopropanol increases. Volume fraction of Au-silane at 0.003 is the most optimum volume fraction to obtain the fundamental mode of light interaction at the Au-silane film. In the operation range of 1 and 1.036748, at Au-silane film volume fraction of 0.003, the sensor also exhibits the highest sensitivity at 0.0132 micron per RIU.

5. ACKNOWLEDGEMENT

This research is supported in part by the ASAHI Glass foundation (RES-62-384-21-070) and Rachadapisek Sompote Fund for Development of New Faculty Staff, Chulalongkorn University (DNS 63_088_21_005_1).

REFERENCES

[1] Haick, Hossam, et al. "Assessment, origin, and implementation of breath volatile cancer markers." *Chemical Society Reviews* 43.5 (2014): 1423-1449.

[2] Wang, Zhennan, and Chuji Wang. "Is breath acetone a biomarker of diabetes? A historical review on breath acetone measurements." Journal of breath research 7.3 (2013): 037109.

[3] Rudnicka, Joanna, et al. "Determination of volatile organic compounds as biomarkers of lung cancer by SPME–GC–TOF/MS and chemometrics." Journal of Chromatography B 879.30 (2011): 3360-3366.

[4] Di Natale, Corrado, et al. "Solid-state gas sensors for breath analysis: A review." Analytica Chimica Acta 824 (2014): 1-17.

[5] Pantalei, Simone, et al. "Improving sensing features of a nanocomposite PEDOT: PSS sensor for NO breath monitoring." Sensors and Actuators B: Chemical 179 (2013): 87-94.

[6] Komkova, Maria A., et al. "Hydrogen peroxide detection in wet air with a prussian blue based solid salt bridged three electrode system." Analytical chemistry 85.5 (2013): 2574-2577.

[7] McCurdy, M. R., Y. A. Bakhirkin, and F. K. Tittel. "Quantum cascade laser-based integrated cavity output spectroscopy of exhaled nitric oxide." Applied Physics B 85.2-3 (2006): 445-452.
[8] Mitsubayashi, Kohji, et al. "Optical bio-sniffer for methyl mercaptan in halitosis." Analytica chimica acta 573 (2006): 75-80.
[9] Elosua, Cesar, et al. "Volatile organic compound optical fiber sensors: A review." Sensors 6.11 (2006): 1440-1465.
[10] Lan, Xinwei, et al. "Fiber ring laser interrogated zeolite-coated singlemode-multimode-singlemode structure for trace chemical detection." Optics letters 37.11 (2012): 1998-2000.
[11] Renganathan, B., et al. "Nanocrystalline ZnO coated fiber optic sensor for ammonia gas detection." optics & laser technology 43.8 (2011): 1398-1404.
[12] Wen, X. Y., et al. "ZnO-coated SMS structure interrogated by a fiber ring laser for chemical sensing." Measurement Science and Technology 25.11 (2014): 114002.
[13] Mitsushio, M., S. Higashi, and M. Higo. "Construction and evaluation of a gold-deposited optical fiber sensor system for measurements of refractive indices of alcohols." Sensors and Actuators A: Physical 111.2-3 (2004): 252-259.
[14] Kawano, Kenji, and Tsutomu Kitoh. Introduction to Optical Waveguide Analysis: Solving Maxwell's Equation and the Schrödinger Equation. John Wiley & Sons, 2004.
[15] Mohammed, Waleed S., Peter WE Smith, and Xijia Gu. "All-fiber multimode interference bandpass filter." Optics letters 31.17 (2006): 2547-2549.
[16] Sani, Elisa, and Aldo Dell'Oro. "Spectral optical constants of ethanol and isopropanol from ultraviolet to far infrared." Optical Materials 60 (2016): 137-141
[17] Johnson, Peter B., and R-WJPrB Christy. "Optical constants of the noble metals." Physical review B 6.12 (1972): 4370.