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Chapter

Optical Gas Sensors

Vivekanand Mishra, Rashmi and Sukriti

Abstract

Miniature and highly efficient optical-based gas sensors have gained enormous consideration over the last few years. Materials based on the group-IV elements, namely silicon, germanium and their compounds, are deemed to be the potential candidates for the optical gas sensors. Optical gas sensors based on these materials offer appreciable sensitivity and high-density integration. Basically, these sensors paved the path for the flexible applications areas, namely internet of things (IoT), point-of-care testing, information and communication technology, etc. because of their potential candidature for being integrated with the several other photonic or electronic devices for on-chip signal processing and communication. Herein, we review optical gas sensors and discuss their basic principles, applications, recent advancement in the devices, etc. Gas concentrations can be easily detected and measured utilizing the characteristic optical absorption of gas species. This detection is crucial both for interpretation and observing of a wider range of phenomena extended from industrial practices to overall environmental change. Based on the findings, this review extends over a comprehensive overview of plethora of individual gas detection techniques, namely non-dispersive infrared, spectro-photometry, tunable diode laser spectroscopy and photo acoustic spectroscopy. This article focalizes over the discussion of the basic principle of the techniques introduced, their latest advancements and performance constraints, etc.

Keywords: sensors, optical gas sensors, spectrometers, infrared spectrometers, ultra-violet/visible spectrometers, fiber optic instruments, laser spectroscopy, optical and dielectric properties of gases

1. Introduction

The detection of gases is webbed across a plethora of application fields. Primary application extended over sector of petrochemical, where sensors were incorporated to safeguard (namely by detecting the leakage of highly toxic or flammable gases). The monitoring of feed stocks, as well as the key species parameters utilized in products as well as processes, keeps on revising depending upon the requirements with passage of time and day-to-day advancement in the field of science and technology [1, 2]. Several fields of science, namely atmospheric science, encourage the application of extremely sensitive gas detectors in order to detect, measure and develop the understanding of properties and trajectories of numerous gases, namely the greenhouse gases [3]. In the field of medical, investigation is made over several gases (namely nitric oxide (NO), ethane, ammonia (NH₃), etc.) having potential candidature for

Materials	Advantage	Disadvantage	Target Gases and Application Fields
Metal Oxide Semiconductor	Lower Cost	Relatively lower sensitivity and selectivity	Industrial applications and civil use
	Shorter response time	Sensitive to environmental factors	
	Wider range of target gases	Higher energy consumption	
	Longer Lifetime		
Polymer	Highly sensitive	Long-time instability	Indoor air monitoring
	Shorter response time		Storage place of synthetic products as paints, wax or fuels
	Lower fabrication cost	Irreversibility	Industries namely, chemical industries
	Easy and portable structure	Poor selectivity	
	Lower consumption of energy		
Carbon Nanotubes	Ultra-sensitive	Complications in fabrication and repeatability	Partial discharge detection
	Great absorptive capacity	High cost	
	Large surface-area-to-volume ratio		
	Faster response time		
	Less weight		
Moisture Absorbing material	Lower cost	Vulnerable to friction	Humidity monitoring
	Less weight	Potential irreversibility in high humidity	
	Higher selectivity towards water vapor		
Optical Methods	High selectivity and stability, sensitivity	Difficulty in miniaturization	Remotely air quality monitoring
	Longer lifetime	Higher Cost	Gas leakage detection systems with excellent accuracy and safety
	Insensitive to environment change		High-end market applications
Calorimetric Methods	Stability at the ambient temperature	Danger of catalyst poisoning and explosion	Highly combustible gases under industrial environment
	Low cost	Intrinsic deficiencies in selectivity	Petrochemical plants
	Adequate sensitivity for industrial detection		Mine tunnels Kitchens
Gas Chromatograph	Outstanding separation performance	Higher cost	Laboratory analysis
	High sensitivity and selectivity	Difficulty in miniaturization for portable applications	

Materials	Advantage	Disadvantage	Target Gases and Application Fields
Acoustic Methods	Longer Life-time	Lower sensitivity	Components of the wireless sensor Networks
	Avoiding the secondary pollution	Sensitive to the environmental change	

Table 1.

Summary of the advantages, disadvantages and the myriad of applications for the listed methods of gas sensing.

biomarker gases application in fields of different for diagnostics, namely respiratory, etc. Chromatographs, analytical laboratory equipment has traditionally being utilized on larger scale for quantitative gas detection, but the equipment lacks the real-time data sampling [4]. Other than this sensor, semiconductor gas sensors or electrochemical devices were utilized. Other devices, namely Pellistor being, a potential sensor device (for the detection of the flammable gases closer to the lower range of the explosive limit but zero parts per million) for combustion on catalyst beads [5], semiconductor gas sensors can be very sensitive down to ppm [6], but they lack and suffer from the drift and erratic response to other gases as well as changing humidity levels. Other than this, electrochemical gas sensor being highly sensitive (ppm or ppb levels) and relatively specific to an individual gases suffers limited lifetimes and cross-response issues [7]. In comparative to this (**Table 1**), carefully designed optical absorption-based gas sensors are enriched with highly sensitivity, responsivity (approximately, 1 s), negligible drift, high-level gas specificity and seize to any cross response to other gases. They are blessed with highly controlled processes since the measurement corresponding to the detection can be made in real time and in situ devoid of any disturbance to sample under investigation [8].

Optical gas sensors act as a bridge among the sensors available at cheaper rates (with substandard performance) and costlier laboratory equipments. Optical gas sensors involve the transduction method which through direct measurement of molecules physical properties (e.g. the absorption of molecule at a particular wavelength) causes reduction in the drift. Since the intensity of the incident beam can be determined, the measurements are self-referenced and are compelled to be inherently reliable. Gas detection applications are webbed over the broader range of gas concentrations (proportion present in the air (or the other matrix) by the total volume). At standard temperature and pressure, gases mostly behave as an ideal gas and are approximately equal to molar concentration present in the given matrix. The study of widely used gas sensing methods based on the optical absorption measurements at particular wavelengths is the main focus of this article. Being non-dispersive gas sensing methods utilizing spectro-photometry, non-dispersive infrared, tunable diode laser spectroscopy and photo-acoustic spectroscopy [9–11].

Optical gas sensing proved to be the uncomplicated method and accomplish superior sensitivity, stability and selectivity over all other non-optical methods with much longer lifetime. Optical-based gas sensing has relatively shorter response time, enabling the detection on-line in real time. The performance of these sensors is immune to the any environment changes or catalyst poisoning triggered by the presence of specific gasses, etc. Optical gas sensing is spectroscopic investigation, but their applications on gas sensors are hampered because of miniaturization as well as comparatively high cost. That is the reason why only limited commercially available gas sensors based on the optical principle are available. Present review focusses over the general overview of optical-based gas sensors.

2. Classification of gas sensors

Factors affecting gas sensing mechanism:

Several factors should be taken into account when assessing the effectiveness of gas sensing techniques (**Figure 1** depicts the classification of gas sensor):

1. Sensitivity is a measure of the lowest volume concentration of a specific gas at which it can be detected.
2. Selectivity refers to the characteristic that analyses the capacity of a gas sensor to isolate a particular gas from a mixture of gases.
3. Response time is the amount of time taken by a gas sensor when the concentration of a gas reached to a certain value with respect to the time that it compels the sensor to generates an alarming signal.
4. Stability is the characteristic that tells whether the given sensing material can reconcile to its initial state once the detection is over. This includes retaining the response time, recovery time, sensitivity and selectivity.
5. Repeatability is the property of the sensor to exhibit certain response value when exposed to a certain value of gas concentration.
6. Fabrication cost, adsorptive capacity and energy consumption.

The operating stability of gas sensors that are intended for the market must also be guaranteed; or they must display a highly stable as well as repeatable signal over time.

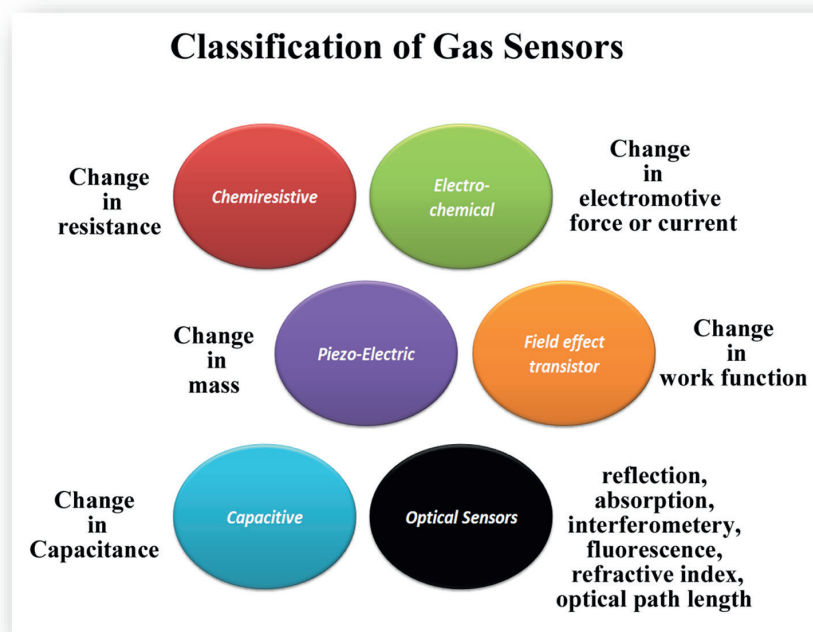


Figure 1.
Chart representing the classification of gas sensors.

But, the instability of the gas sensor is caused by a number of reasons such as design mistakes, structural modifications (such as changes in grain size or grain network), phase transitions (which typically refers to separation of the additives doped with sensing materials), poisoning brought on by the chemical processes as well as change in the environment.

The use of optical techniques for gas sensing is typically simple and can produce results with more sensitivity, stability as well as selectivity in respect to other non-optical techniques while having a significantly longer lifetime. Their quick response time makes on-line real-time detection possible. The changes in the atmosphere or poisoning of the catalyst brought on by particular gases, etc. will not affect performance. The majority of optical techniques utilized for sensing gas are based on spectroscopy.

2.1 Basic principles

There has been an extensive discussion about the principles of molecular absorption spectroscopy [12, 13]. Optical gas sensing techniques have been commercialized and while the majority are absorption-based, several other methods also play a significant role. Myriad of chemical substances show high absorption mainly in the region dominated over ultraviolet–visible range, near-infrared (NIR) as well as mid-infrared range of electromagnetic spectrum. Each substance has its unique set of absorption lines or bands that serve as the foundation for its detection and quantification. The parameters of the absorption spectra show variation in the various spectral bands displayed in **Table 2**.

Optical gas sensors work on the principle of the Beer and Lambert law and relation for the same is [14].

$$I(\lambda) = I_o(\lambda)e^{-\alpha cl} \quad (1)$$

were, $I(\lambda)$ and I_o are the detected as well as emitted optical intensity at a particular wavelength (λ), (respectively)

$\alpha(\lambda)[L/g]$ = Absorption coefficient of the gas.

$c[g/L]$ = Concentration of gas.

$l[m]$ = beam-gas interaction path length.

Figure 2 depicts a sensor comprised of different parts, namely

- i. Emitter (in order to generate the beam ($I_o(\lambda)$))
- ii. Optical Path (path length of gas cell (l) for guiding the beam interaction with gas.)
- iii. Optical filter (for the selection of the characteristic wavelength range of the gas being target)
- iv. Detector (for detecting the absorbed beam ($I(\lambda)$))

The spectroscopic investigation relied mainly on the spectrometry absorption as well as emission. Absorption analysis is completely based on the Beer and Lambert

Spectral Range	Reason for the absorption
Ultraviolet (200–400 nm)	Electronic transitions
Near Infrared (700 nm to 2.5 μm)	Molecular vibrations and rotation, first harmonic
Mid Infrared (2.5–14 μm)	Molecular vibrations and rotation, fundamental

Table 2.
Origin of absorption spectra in the various regions of the electromagnetic spectrum.

law and is basically concentration-dependent absorption of the photons at a particular wavelength of the gas. Other than this plethora of improvised techniques of absorption spectrometry, namely Differential Optical Absorption Spectroscopy, Raman Light Detection, Tunable Diode Laser Absorption Spectroscopy, Differential Absorption LIDAR and Intra-Cavity Absorption Spectrometry (ICAS), etc. [15–17]. Spectrometry based on emission is observed when the atoms sitting in the excited levels on their transition to the ground state emits photons. Emission-based techniques are namely Laser-Induced Breakdown Spectroscopy, Fourier Transform Infrared Analysis (FT-IR) can be utilized for both the spectroscopy, namely absorption and emission. Furthermore, the photo-acoustic and correlation spectroscopy techniques also come in the category of spectroscopic analysis. These spectroscopic techniques are generally employed to gas detectors. This can contribute to the designing of the more complicated system at a higher cost level and can incorporate exceptional sensitivity, selectivity and reliability as compared to the other available gas sensors. Extensively utilized optical-based sensors utilize infrared source. The infrared source-based gas sensors work on the principle of absorption spectrometry. That implies that each and every gas is having a specific absorption property to infrared radiation of varying wavelength and results in unique fingerprint of infrared absorption. This implies that each and every gas has some unique property of absorption to infrared radiation range with varying wavelengths and thus shows a rare fingerprint of infrared absorption. Gas sensors based on infrared source consist of mainly three major parts, namely (depicted in **Figure 2**),

- i. Infrared Source
- ii. Gas chamber
- iii. Infrared Detector

At the primary state, the infrared source emits broad-band of radiation wavelength containing the wavelength range corresponding to the absorption of target gas. After that the gas sample present in the gas cell absorbs the incoming radiation beam of their specific wavelength. Later on the optical filters are utilized to screen out the entire wavelength of the radiation except the radiation wavelength absorbed by the target gas. Thus, the gas of interest can be easily detected as well as measured just by employing infrared detector. The entire setup is named as Non-Dispersive Infrared gas sensor.

Non-dispersive sensing technique is utilized, wherein the beam (unfiltered) is utilized for the interaction with the gas. This sensing technique encourages the selective detection of beam (λ), just by filtering the beam detected by characteristic absorption spectra of the molecular species. Non-dispersive infrared (NDIR) sensors conventionally configured with infrared emitters and infrared detectors [18]. Sensors

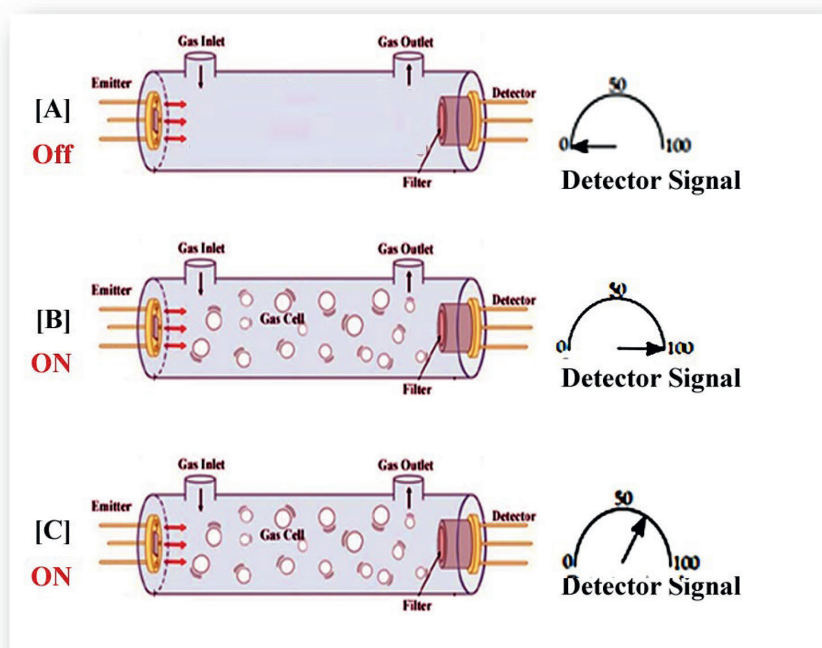


Figure 2.

Beer and Lambert law–based optical gas sensor; (A) off state (no any signal being detected), (B) on state maximum detected signal, (C) decreased detection with gas concentration.

work on the same principle of Beer–Lambert’s Law, if utilized for different spectral regions or configured for acoustic detectors.

A different gas cell consisting of the reference gas other than the single detector mode can be incorporated to uplift the overall accuracy of the infrared sensing method just by truncating the ambient environmental factors without inducing much more complexity. **Figure 2** depicts the layout of two detectors. Just to keep the radiation parameters of infrared source identical, gas cell utilizes the reflected infrared beams from the single source just utilizing the mirror property. The assortment of the range of wavelength of the infrared beam utilized as source impacts a lot on the concluding detection result. Spectral region of the mid-infrared gains more attention as it encourages stronger molecular absorption as compared to spectral region of near-infrared. The conventional mid-infrared laser sources suffer major drawbacks, namely wavelength tunability, lower power of output, complexity, requirement of coolants. Plethora of lasers have been developed and investigated in order to overrule the above mentioned disadvantages, e.g. Quantum-Cascade Lasers blessed with tunability, highly narrow line-width as well as lower average power for the operation at the room temperature.

Myriad of topologies have been employed for the fabrication of optical gas sensors. The commonly utilized sensors are based on gas cells formed between face-to-face configured emitters and optical detectors. Several approaches followed for the miniaturization of the gas cell include utilization of enhancement layers namely, Utilization of photonic crystals [19], optical cavities [20], multi-pass cells [21], gas enrichment layers [22–24], in order to enhance beam-gas interaction, the planar configurations of the emitters as well as detectors, utilization of waveguides for the interaction of evanescent field. Optical detectors, namely photodiode, thermopile or pyroelectric, acoustic detector are mainly implemented in order to detect the beam being absorbed ($I(\lambda)$) [25–28]. The mechanism of lock-in detection is employed to

extract the sensor response signal ($I(\lambda)$) and further known frequency is utilized to modulate the emitter. The reference detector is frequently utilized in order to compensate for the variation in emitted beam. Further, additional sensors can be utilized in order to compensate for the several parameters of environment, namely temperature, pressure, etc.

Types of Optical Gas Sensors

- Optical sensors' operation mainly includes controlling, then detection of the beam propagating through the target area where the photons which got detected generate the electrical signals. Frequently utilized optical sensors are, namely fiber-optic gas sensors and photonic-crystal gas sensors; these sensors are based on the principle of the detection of the beam propagation through utilization of devices. Fiber-optic-based sensor measures the modification in optical property (namely, wavelength) and detects the analytes introduced on the sensing polymeric layer by employing optical fiber. These sensors are enriched with excellent sensitivity, stability with respect to the environmental factor as well as longer lifetime. Implementation of optical fiber in the structure causes complications in the miniaturization. Structure of the photonic crystal sensor utilizes the periodic arrangements of dielectric materials with numerous refractive indexes.
- In order to detect the carbon monoxide, mid-infrared photonic crystals are commonly utilized. By the utilization of the advanced micro-machining technology, we can precisely control or tune the dimension as well as the shape of the pattern of the sensing device. But the implementation of this advance technique can lead to the enhancement in the overall fabrication price of the device. Optical gas sensors enriched with the detection level ranging over then ppm range have been successfully developed.
- Spectroscopy-based methods have traditionally included infrared absorption spectroscopy, gas chromatography (GC) and Raman scattering spectroscopy as the standard gas detection methods. Despite their sturdiness, the aforementioned spectroscopic sensing approaches typically need expensive and large apparatus, making them difficult to access and unsuitable for applications that call for in situ monitoring and on-site analysis. Therefore, alternate gas sensing methods are being developed concurrently for lower cost and greater portability.
- Electrical gas sensors such as chemiresistors, electrochemical sensors, Schottky diodes, field-effect transistors, chemiresistive sensors and impedance sensors are among these types of gas sensors.
- Optical gas sensors such as fiber-optic gas sensors and photonic crystal gas sensors are also available. Despite having been developed and commercialized gas sensors for a long time, traditional materials of gas sensing such as oxides of metals, conducting polymers and carbon nano tubes (CNTs) still face issues including low selectivity, high operating temperatures and poor repeatability. As a result, ongoing efforts are needed to explore and develop new gas sensing materials.
- Among the most used type of optical gas sensors are fiber gas sensors, as shown in the figure.

A waveguide with a fiber core and surrounding cladding makes up its primary part. The core allows a small amount of light to transmit in form of evanescent waves perpendicular to the axis of fiber with exponentially diminished intensity in the cladding. On the other hand, majority of the light travels along with the fiber core via total internal reflection because core has a greater refractive index than the cladding. The alteration in the refractive index of the cladding is caused by the adsorption of the molecules of gas on its surface, which in turn affects the wavelength and intensity of the output light signals. Due to the limited selectivity of the gas adsorption-induced variation in the overall refractive index of the material, the cladding is typically modified with molecules or nano-materials that have a particular affinity for the target gas.

3. Applications

A side-polished fiber (SPF) coated with cholesteric liquid crystal film (CLCF) has been employed for Volatile Organic compound (VOC) sensing, where a rise in the concentration of VOC on CLCF causes a rise in the pitch of the resulting light. As a result, the resonant dips exhibit a blue shift that can be linked to the exposure to VOCs. For acetone, tetrahydrofuran and methanol gas, the sensitivities of CLCF-SPF have been observed to be 3.46, 7.08 and 0.52 nm-L/mmol, respectively. It can be observed that the overall sensitivity of the CLCF-SPF rises with the VOCs' molar mass.

- ZnO nanoparticle-coated fiber-optic sensors have demonstrated the relation between concentration and selectivity for ammonia, acetone and ethanol. Due to the increment in the catalytic reactivity of the acetone at elevated concentrations, ZnO nano-particles exhibit exceptional sensitivity towards the gas ammonia and acetone at lower and higher concentrations of up to 150 ppm and above 150 ppm, respectively.
- A CO gas sensor that operates at room temperature and uses ZnO detecting film has been created. Sensor uses the mechanism of surface Plasmon resonance mechanism, which has been demonstrated as a possible contender for the commercial applications of the detection of CO. According to reports, this sensor has a wider range of CO concentration, webbed over the range of 0.5–100 ppm at the room temperature and a faster response time of roughly 1 s. It also has a higher sensitivity of about 0.091 ppm and has been demonstrated that these sensors are highly selective for CO, with barely any interference from any other gases, namely CO₂, NO_x, NH₃, LPG and H₂.

Figure 3 depicts photonic crystal gas sensor, as another type of optical gas sensor that is similar to one described above. The photonic crystals are mainly synthetic optical materials having periodic variations in value of the refractive index. According to photonic band gap theory, beams having the wavelength in range of photonic crystal band gap can be bound in and transmitted down the air channel having little energy loss in the case where the cladding of fiber has a higher refractive index compared to the photonic crystal core with air channels. Additionally, air passages act as the cells for the insertion of the molecules of the target gas, which alters core's refractive index of photonic crystal and hence, alters the output illumination.

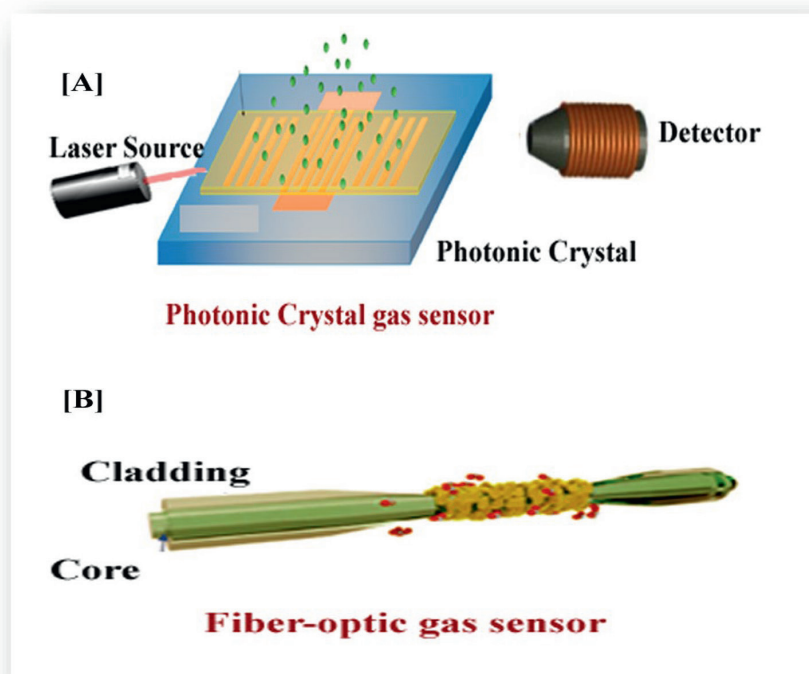


Figure 3. Schematic illustration of (A) photonic crystal gas sensor and (B) fiber-optic gas sensor.

Three patterns of varying sizes on a single substrate have been used to identify different VOCs using Si-based photonic crystals. By using electrochemical anodization to create mesopores of various sizes, the designs are etched onto the Si wafer. On a Si substrate, 8 nm of diameter mesopores were created in multilayers with 178, 229 and 300 nm of the vertical spacing, allowing the reflection of 430, 580 and 740 nm photons. Introduction of the analytes over this photonic crystal with several layer patterns raises the effective refractive index and changes the permitted wavelength of the reflected beam. When sensing capabilities of the devices were examined using methanol, ethanol, etc. in the nitrogen carrier gas presence, LOD in the ppm range was observed. Using this technique, analytes by calculating the shift in wavelength in time of each VOC.

Researchers have looked into self-assembling silica nanospheres to create photonic crystals for ethanol, water and carbon disulfide (CS₂) detection. On silica colloid drying over substrate and then annealing it at the temperature of 600°C for the sintering, the silica photonic crystal can be created. To improve the interaction with analytes, HKUST-1 can be coated on the nano-structured silica. Each silica nano-sphere has a diameter of around 300 nm and is arranged in a face-centred cubic configuration. For a gas-sensing test, when analytes are present, NIR light can be shone in the direction of the silica nanostructure. The predicted detection limit for water, ethanol and CS₂ is 2.6, 0.3 ppm and CS₂ is 0.5 ppm, according to tests on the sensing ability of these substances.

4. Conclusion

To conclude, optical gas sensing remains an important field that complements other gas detection technologies. The opportunities afforded by new technology, together with the challenges that remain, will make this an exciting and rapidly developing field for many years to come. Commercially available gas sensors are

rarely based on the optical principles, present article focuses over the broad overview of techniques involved in gas analysis and illustration of the detailed introduction of the optical-based gas sensors. Optical sensors including fiber-optic and photonic crystal gas sensors operate based on the detection of the light propagation through the device. Fiber-optic sensors detect analytes by measuring optical property changes of light such as wavelength, which is introduced on the polymeric sensing layer through optical fiber. These sensors have many advantages in high sensitivity, stability to environmental factors and long lifetime. However, needs of optical fiber in the structure make it difficult to be miniaturized. Photonic crystal sensors employ periodic arrangements of dielectric materials with various refractive indexes. Mid-infrared PhCs are a common example of these devices to detect common gases such as CO. These sensors can be developed using advanced micro-machining technology and, therefore, the dimension and shape of the device pattern can be precisely controlled, which on the other hand increases the fabrication cost.

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