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Environmental Gas Monitoring Sensors

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CONTENTS

1. INTRODUCTION

Present technological advancement, industrial revolution, and tremendous increase in transportations are degrading the environment with numerous common and non-common toxic gases which lead to atmospheric and water pollutions. The common gaseous pollutants are carbon monoxide (CO), oxides of nitrogen (NO_x), hydrocarbons (HC), and sulfur dioxide (SO_2). Besides these, there are other toxic gases also found in large quantities in some industrial belts and other places, they are volatile organic compounds (VOC), ammonia (NH_3), H_2S, O_3, CO_2 etc. Pollution is known to be hazardous to human health, brings about adverse effect to the environment and ecology. When people breathe the polluted air, pollutants come in contact with their lungs. The possible health effects of air pollutants that are toxic to human health include cancer, birth defects, damage to brain, nerves, respiratory system and so on. Air pollution also threatens plants, animals, natural environment, buildings, damage to property, tourism etc. Therefore, it is very essential to monitor these toxic gases in order to prevent the adverse effect to the environment and human health.

Environmental gas sensors help to detect toxic and dangerous gases in the atmosphere. They are not used to detoxify the pollutants but instead used to make sure that the pollution does not exceed beyond the permissible limit. Gas sensors are the devices that sense the pollutant gases qualitatively and quantitatively. By interaction with these gases there occurs the change in physical and chemical property of the sensor and converts it into a useful signal which helps to detect the toxic gases. Sensors aid to monitor and detect events as they happen. They also help to run the processes more efficiently and to limit the hazardous by-products. They can be located at a distance from the target to be monitored called as remote sensing or in situ or located at the site. Remote sensing systems are used for the environmental monitoring, also used in industries for the site monitoring, emission and plume gases monitoring, spill and leak detections. They are connected to larger control or data processing systems so that their readings can be analyzed. One of the goals in environmental sensor research is to make smart and intelligent devices. Table 1 shows the difference between analytical instruments and the gas sensors. Many sensors are used for more than one application. Frequently catalytic sensors are used in gas sensing devices. Electrochemical sensors react to variety of gases in air and industrial environment. Quite a few electrochemical devices for air monitoring are available commercially. Thin films or thick films are being used in many solid state gas sensors devices. Many new sensors have been developed and some are still in the research state, few to mention in the area like fiber optics, surface acoustic waves, acousto-optics, microwave based sensors etc.

2. AIR POLLUTION

The pollutant either gas, particles or foreign material or admixture of these which produce any measurable harmful effect on human beings, animals, vegetation or environment is said to be air pollutant. Air pollution is a burning problem the world over since industrial and nuclear revolution. Further, due to enormous growth in transportation, population and power plants, the usage of fossil fuels have increased tremendously, deteriorating natural atmosphere and public health. Yet the level of public concerns related to living and working in a healthy atmosphere has increased. Therefore, the demand for monitoring and controlling the indoor and outdoor atmosphere has also increased. As a result, intensive research progress has been made in various fields in an attempt to resolve the environmental problems.

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Table 1. Comparison between analytical tools and gas sensors.

Sr. No.	Factors	Analytical tools	Gas sensors
1	Accuracy	V. good	Good
2	Precision	Good	Good
3	Resolution	Good	Comparable
4	Process control	Cumbersome	Simple
5	Measurements	One at a time	Continuous
6	Measurement time	Quite long	Short
7	Cost	Expensive	Low
8	Size	Bulky	Compact (small)
9	Rigidity	Delicate	Rigid
10	Mass production	Not easy	Easy

Air quality monitoring is also very important for the control of industrial environment i.e., identifying and monitoring pollutants. All emission monitoring require appropriate gas sensing devices for effective control of pollutants. Sensors that monitor ambient air must have a broad analysis capacity. Sensors that monitor for fugitive emission can be specific to the particular gas as industry knows what gas could escape from which process line. A major application for air monitoring is stack gas monitoring and this can be accomplished by mounting the sensor device directly on the stack or the insertion of a probe. The sensors which can be applied include electrochemical, solid state, catalytic conversion, IR UV absorption, fiber optics, opacity monitors etc. and these are acceptable methods for stack gas monitoring.

2.1. Pollution Sources and Permissible Limit

Pollution sources are of two types; one is stationary source such as industries, power plants etc. and the other is mobile source, these include transportations including road, sea and air. In recent years, there has been tremendous increase in road transportations, due to which significant environmental deterioration has taken place especially in big and crowded cities. Transportation is the main source of CO and NO_x pollution. Whereas power plants which runs on fossil fuels, petroleum refineries and metal smelting industries are the largest source of SO_2 pollution. As a result, the regulation of pollution emission standards as well as atmospheric pollutants standards have been intensified world over. Table 2 gives briefly some common air pollutants, their permissible limits and environmental impacts.

3. TYPES OF SENSORS

Environmental gas monitoring sensors must be able to function under deleterious conditions, such as thermal and the chemical environment. Sensors for environmental sensing applications include solid state sensors, optical sensors, acoustics sensors, biosensors etc. Many other sensors are also used but their applications are very specific.

3.1. Solid State Gas Sensors

Solid state sensors are the devices of interdisciplinary branches that govern the modern sensing devices. Despite the rapid development of these sensors, not much is known about the sensing phenomenon and the mechanisms. Solid state devices hold the key to the development of inexpensive sensors for the range of various gas monitoring applications. Solid state sensors are capable of measuring the concentration of multiple gases. A lot of recent research and development has been focused on the development of solid state gas sensors and their performances have been improved considerably.

3.1.1. Semiconductor Sensor

Many semiconductor materials bring about gaseous reaction on the surface changing the electronic property which is essential criteria for semiconductor sensors. In other words semiconductor gas sensors function as gas sensitive resistors representing low cost rugged and simple indoor as well as outdoor gas monitoring sensors. Generally, the sensing devices are required to have several conditions such as sensitivity, stability, selectivity, response, recovery etc. Many

Table 2. Common air pollutants, their regulation values, detection methods and environmental impacts.

Sr. No.	Gas	Regulation values (ppm)		Detection methods	Environmental impacts
		Ambient air	In work place		
1	CO	1–40	50	NDIR, MS, GC, Gas sensor	Toxic, attacks hemoglobin
2	NO_x	10^{-2}–1	3–25	IR, MS, GC, Chemiluminescence, Gas sensor	Toxic, Acid rain
3	HC	10^{-2}–1	0.1–25	GC(FID), Gas sensor	Toxic, Photochemical smog
4	SO_2	10^{-2}–1	3	Spectrophotometer, UV-absorption, Pulsed fluorescence, Gas sensor	Toxic, Acid rain
5	O_3	10^{-3}–0.1	0.1	UV photometry, Gas sensor	Toxic
6	CO_2	350–5000	5000	NDIR, GC, Gas sensor	Green house effect

semiconductor gas sensors are specific to only certain gases. In fact, it is highly desirable to have highly specific selectivity so that no other gases can interfere during monitoring. This type of gas sensors was first used for the detection of gas leak and latter to detect alcohol in drivers, incomplete combustion in boilers and other gases.

The adsorption of gas or surface reaction on semiconductor changes the density of electrons in the sensor and this change brings about conductivity modulation. The surface reaction which takes place during the sensor response can be described in the following steps:

(i) Physical contact of the sensing gas molecules on the surface of the semiconductor.
(ii) Adsorption of the sensing gas molecules on the active site of the surface.
(iii) Reaction of the adsorbed molecules with oxygen or other gaseous species or decomposition to give the products.
(iv) Desorption of the products or adsorbed gas back in the stream, normally called as recovery of the device.

The above process of delivering electrons between the gas and semiconductor actually represent the gas sensitivity of the sensor. The change in the conductivity depends on the type of semiconductor and adsorbed gas. Table 3 shows conductivity and response expected for oxidizing and reducing gases on the semiconductors as a thumb rule which may deviate depending on the type of materials, gas, surface morphology, chemical environment, and acid-base sites on the surface.

Surface acid-base properties of the semiconductor greatly influence the adsorption process and can be modified by suitable additives. It is important for the sensor to detect basic gases like ammonia or acidic gases like SO_2 and NO_2. For example the modification of SnO_2 surface with basic oxides is preferable for H_2S adsorption [1]. Since the change in electronic property of the semiconductor is caused by a surface interaction or surface reaction, it is advantageous to maximize the specific surface area which is possible by nano particle technology, to intensify the gas response on the surface. Accordingly, commercial gas sensors must be highly porous oxide layer which are either printed or deposited on to the alumina substrate or chip. The electrodes are usually co-planar and located at the oxide alumina interface. A heater track is also necessary at the back side of the substrate to heat the sensor at the desired temperatures. Care should be taken to ensure the microstructure of the semiconductor, its thickness and temperature are optimized to improve the selectivity, sensitivity, speed and recovery. Many approaches have been attempted to modify the properties of the semiconductor sensors in order to obtain better sensitivity, selectivity, stability, response, repeatability, and reliability. If one achieves these three S and three R then it will be a real goal in sensor technology. The enhancement of the sensing properties of the sensor can be achieved by the development of preparation techniques like thick films, thin films, spray technique, sol-gel method, wet drying etc. and also by addition of the catalytic additives into sensors. Still the progress and the research in this area are going on at a tremendous pace to obtain 21st century sensors.

Table 3. Conductivity response for oxidizing and reducing gases on semiconductors.

Semiconductor	Oxidizing gases (such as O_2, O_3 etc.)	Reducing gases (H_2, NH_3, CO etc.)
P-type	Conductivity increases	Conductivity decreases
N-type	Conductivity decreases	Conductivity increases

Adsorbed oxygen plays important role in oxide semiconductors as an electron donor. The principle is based on the initial reversible reaction of the atmospheric oxygen with the lattice vacancies in the oxide and concurrent reduction in electrons concentration. This reaction generates various oxygen species (m) such as O_2^-, O^- or O^{2-} depending upon the temperature and pressure [2] and these species can react irreversibly with other adsorbed species. The electrical conductivity (σ) in a semiconductor sensor is also related to the oxygen partial pressure (P_{O_2}) [3].

$$\sigma \approx P_{O_2}^{-m} \tag{1}$$

where the exponent "m" lie in between 0.5 to 1.0 depending upon the type of reaction, pore size and particle density or microstructure of the surface. In ZnO, TiO_2 or SnO_2 which are widely used materials, the exponent m is known to be about 0.5. The ambient oxygen partial pressure and the humidity could be disadvantageous in a practical view point because both these can affect the sensitivity of the oxide semiconductor gas sensors. Sensor arrays of multiple sensors can be used to get different sensitivity pattern for the same gas and also for multiple gases. This can be utilized to identify qualitatively as well as quantitatively in an electronic nose system.

3.1.2. Capacitor Type Sensors

In capacitor type gas sensors, the change in the capacitance or dielectric constant of the film is measured between the electrodes as a function of partial pressure of the gas under test. It has been reported [4] that a spin coated polyphenylacetylene conducting polymer film responds to various gases like CO, CO_2, and CH_4 which are showing the change in dielectric constant with gas concentrations. Capacitance change of the capacitor type sensors is typically in the range of pF and depends very much on the operating frequency, humidity and temperature. Hagleitner and others [5] showed a capacitive micro-system with the ability to measure at different sensor temperatures for discrimination of ethanol, toluene and their admixtures.

3.1.3. Solid Electrolyte Gas Sensors

Solid electrolytes such as calcia and yttria stabilized zirconia have been used in electrochemical gas sensors to monitor CO, SO_2, and other gases. Ionic conductors like alkali metal sulfates of lithium, sodium and potassium show good cation conductivity at high temperatures. Zirconyl phosphate, antimonic acid, and dodeca-molybdophosphoric acid also exhibit protonic conductivity at room temperature and are used to detect CO_2 in air.

A NASICON is a solid electrolyte potentiometric gas sensing material consists of alkali metal carbonate as an auxiliary

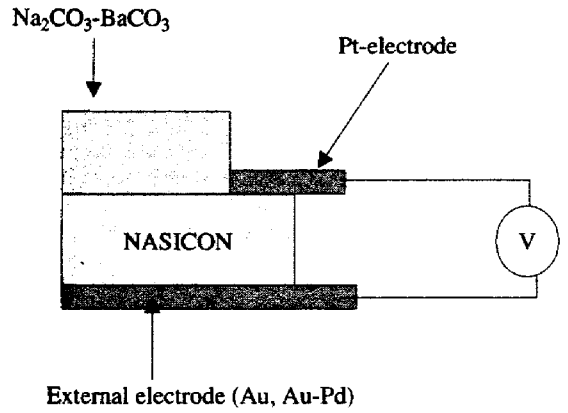

Figure 1. Cross-sectional view of the sensor.

phase and is known to be sensitive to CO_2. This type of solid electrolyte gas sensor can also be used for the detection of NO_2 and SO_2. The NASICON has the chemical formula as $Na_{1-x}Zr_xP_{3-x}O_{12}$, whereas some others have proposed with some variation of the composition [6]. Its frame work consists of SiO_4 and PO_4 tetrahedra linked by common oxygen octahedral [7] and the bonding are covalent. The Na^+ ions are located in interstitial spaces. The ionic conductivity is produced by Na^+ ions. It has been shown that the ionic conductivity is proportional to the sodium stoichiometry of the compound. Figure 1 shows the cross sectional view of NASICON sensor. The best conductivity has been obtained for the composition $x = 2$ or $x = 2.4$ [8]. At room temperature the conduction is purely cationic. There is also a LISICON gas sensor in which Li^+ is used instead of Na^+ as ionic conductor. This sensor exhibits a high sensitivity to CO_2, even at lower temperature.

3.2. Infrared Sensors

The infrared sensor for atmospheric gases and exhaust gases monitoring is useful and found to be suitable gas detection method. It is found that NDIR method is much simpler and easier to use. Many gas molecules selectively absorb the energy that corresponds to their own quantized vibrating energy which is usually found in an IR region. For example CO, CO_2, and CH_4 absorb 4700, 4250, and 3300 nm wave length respectively in an IR region. For most of the spectroscopic analysis, the radiation consists of a limited, narrow and continuous group of wavelength called a band. A narrow band width tends to enhance the sensitivity to both emission and absorption methods. In NDIR gas detection method monochromator is used to obtain a monochromatic beam from an IR source with a wide wave length range. Figure 2 shows the spectral response from various infrared light detectors [9]. In the wave length range of 4000 to 5000 nm, InSb, PbSe and HgCdTe have been used as the sensing materials for an infrared detector. However, these are needed to be used in the temperature range of 77 K to 196 K. PbSe, InAs, and PbS have also been used as an IR detectors for hydrocarbon gases in the range of 3000 to 5000 nm. IR detectors are used for detecting gases such as CO, CO_2, and HC using chromic filters in NDIR method.

3.3. Optical Chemical Sensors

An optical chemical sensor is a combination of the optical sensor and chemical sensor. This makes use of interaction

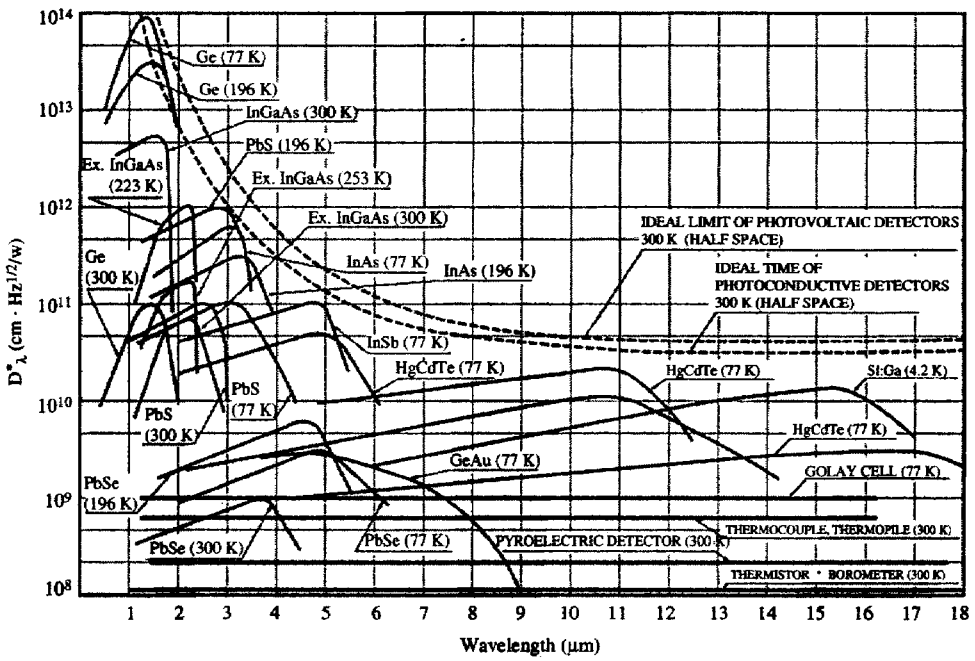

Figure 2. Infrared detectors. Reprinted with permission from [26], D. D. Lee and D. S. Lee, *IEEE Sensor J.* 1, 214 (2001). © 2001, IEEE.

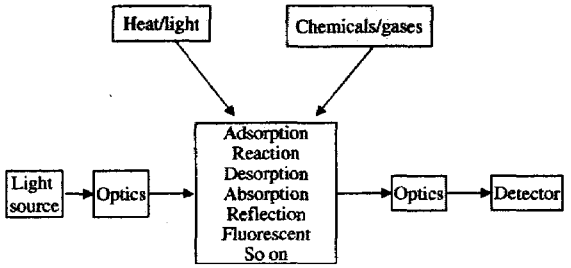

Figure 3. Optical chemical sensing system.

between the materials and optics [10]. Generally, the optical chemical sensor is based on spectroscopy. The basic idea of this sensor is to sense the chemical substances and their concentration. The interaction between the optics and materials are indicated in Fig. 3. The optical chemical sensor uses normally the intensity modulation of interaction between optical signals and the ingredient concentration and this is given by the following equation:

$$I = F(c, \lambda, t) \tag{2}$$

where I, c, λ, t is intensity, concentration, wavelength, and time respectively. This type of sensor has two advantages, one is the spectral signal determines concentrations of different chemicals/gases simultaneously and the other is the time dependence of the spectral signal. This type of sensor operate by making use of the interaction with light wave and the optical properties which the material posses. It offer many advantages [11] over others such as harsh environmental conditions, miniaturization, free from electromagnetic and electrical interference, rugged design, capability of remote sensing analysis, high sensitivity, high selectivity and good reliability. Detection of toxic gases such as NH_3, H_2S, Cl_2, SO_2, HCl etc. are possible by this device.

4. SENSING OF ENVIRONMENTAL TOXIC GASES

In order to minimize the damage caused by atmospheric pollution, monitoring, and control systems are needed that can rapidly and reliably detect and quantify the pollutant gases within the range of the regulation standard values. Solid state gas sensors which are compact, robust, with versatile applications and low cost can be effectively used in detecting and monitoring many of the toxic gases. Below mentioned are some of the common gaseous toxicants detection.

4.1. Carbon Monoxide Sensors

CO is colorless, odorless gas produced by incomplete combustion of fossil fuels and carbonaceous materials. It is formed as a by product of burning organic compounds. Automobile exhaust, furnaces, gas powered engines, water heaters, smoke from fire and tobacco also contributes to CO intoxication. The public health impact of CO has increased because of its ubiquitous environmental poison. CO toxicity causes impaired oxygen delivery to different organs of the body. CO affects several different sites within the body but it has profound impact on the organs with the highest required oxygen i.e., brain and heart [12]. Without oxygen vital organs heart and brain become deprived and will begin to deteriorate. To compensate, heart rate increases, breathing may be difficult and in most serious cases cardiac trauma, brain damage and coma results. Therefore, it is very essential to detect and monitor CO in indoors, traffic jam places etc. and this is possible by using the CO gas sensors.

Several investigators have reported CO gas sensors. Some have utilized changes in conductivity of semiconductors [13] and others utilized electrochemical oxidation of CO [14]. Semiconductor gas sensor is relatively low in price and can be used for long time. On the other hand, electrochemical CO sensor requires low power consumption because it can be operated at room temperature and gives quick response [14]. Electrochemical gas sensor detects gases by measuring electrical potential generated by oxidation/reduction reaction. Some of these sensors employing solid polymers electrolytes in place of aqueous electrolyte solutions have been reported [15, 16]. The use of polymer can decrease the total cell volume and becomes easier for handling the sensor. However, high performance, reproducibility and miniaturization of the sensors can be achieved using semiconductor techniques [17].

Semiconductor oxide sensors offer an inexpensive and simple method for monitoring CO gas. The change of the electrical resistance upon exposure to reducing CO gas has been used for gas detection. Many oxides such as ZnO, SnO_2, In_2O_3, CuO, WO_3 etc. have been used as CO sensor materials and also to find out important parameters like sensitivity, selectivity, response, recovery and reproducibility. Besides mixed oxides, mixed hetero-junctions, perovskites etc. have been reported [18, 19] as CO sensors. Figure 4 indicates temperature dependent sensitivity at different concentration of CO on SnO_2(Ca, Pt), SnO_2-TiO_2(Sb, Pt) and γ-Fe_2O_3. Many have proposed various reaction path ways for the detection and oxidation of CO on the surface of the semiconductors [20–23]. The basic principle for CO

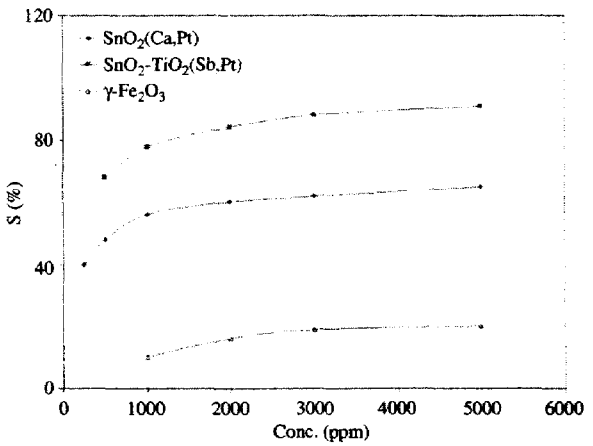

Figure 4. Carbon monoxide sensitivity of SnO_2(Ca,Pt), SnO_2-TiO_2(Sb,Pt), and γ-Fe_2O_3 thick films at 350°C. © 2004, Kodansha, Japan.

detection in semiconductor sensor can be shown by the following reaction scheme:

$$MO_{(s)} + CO_{(g)} \longrightarrow MO\ldots CO_{(ad)} \quad \text{(i)}$$

$$MO_{(s')} + 1/2O_2 \longrightarrow MO\ldots O_{(ad)} \quad \text{(ii)}$$

$$MO\ldots CO_{(ad)} + MO\ldots O_{(ad)} \longrightarrow MO\ldots CO\ldots O_{(ad)} + MO_{(s')} \quad \text{(iii)}$$

$$MO\ldots CO\ldots O_{(ad)} \longrightarrow MO\ldots CO_{2(ad)} \quad \text{(iv)}$$

$$MO\ldots CO_{2(ad)} \longrightarrow MO_{(s)} + CO_{2(g)} \quad \text{(v)}$$

(s), (s'), (g), (ad) represent active site for CO adsorption, active sites for oxygen adsorption, gas, and adsorbed species formed respectively.

Alternatively CO can also react with the lattice oxygen and can be shown alternative possible reaction mechanism:

$$MO_{(s)} + CO_{(g)} \longrightarrow MO\ldots CO_{(ad)} \quad \text{(i)}$$

$$MO\ldots CO_{(ad)} \longrightarrow M\ldots OCO_{(ad)} \quad \text{(ii)}$$

$$M\ldots OCO_{(ad)} \longrightarrow M[]\ldots CO_{2(ad)} \quad \text{(iii)}$$

$$M[]\ldots CO_{2(ad)} \longrightarrow M[] + CO_{2(g)} \quad \text{(iv)}$$

$$M[] + 1/2O_{2(g)} \longrightarrow M[]\ldots O_{(ad)} \quad \text{(v)}$$

$$M[]\ldots O_{(ad)} \longrightarrow MO_{(s)} \quad \text{(vi)}$$

(s), (g), (ad) indicate active site for CO, gas and adsorbed species formed respectively.

In reality the adsorbed CO gas which gives the signal for CO gets desorbed as CO_2 to recover the device. In most of the semiconductor devices the recovery in CO detection is quite good.

Semiconductor metal oxides gas sensors are considered as a modern technology for identification and measuring the concentration of CO gas. These semiconductor microelectronics devices offer a wide variety of advantages as mentioned in Table 1. In spite of these they suffer a lack of selectivity because most of these sensors are sensitive to wide range of oxidizing and reducing gases. Some have tried to improve the selectivity by optimizing the temperature, doping, use of filters, change of materials etc. [24]. The implementation of an array of semiconductors sensors combined with appropriate pattern recognition and classification tools looks to be fair approach to reduce this drawback [24].

4.2. Oxides of Nitrogen Sensing

Nitrogen oxides result from the combustion of fossil fuels such as transportation, natural gas, coal in power plants and high temperature burning. At present, transportation is the main source of NO_x emission. NO_x is well known to be harmful that damages respiratory system and main cause of acid rain. In order to control NO_x pollution, sensors are required for different purposes like exhaust monitoring, air monitoring and indoor control. In the case of monitoring exhaust gas, the high sensitivity to NO is desirable because most of the exhaust contains high level of NO and not NO_2. When NO comes out in air, it react with oxygen and gets converted to NO_2.

Many investigators have tried different types of NO_x sensors and some of them are summarized in Table 4. Among the semiconductor sensors, the use of phthalocyanine has been widely studied as NO_2 sensor [25]. The significant feature of phthalocyanine is their high sensitivity to NO_2 at ppb level but the major weak point is the stability at high temperatures. Semiconductor NO_x sensors using the metal oxides have been investigated by many workers. The sensitivity to NO_2 and NO is dependent on the oxide materials used. TiO_2 and WO_3 based sensors have shown good sensitivity to NO_2 above 1 ppm at 250–350°C [26] as shown in Fig. 5. The same oxide also show high sensitivity to NO, but sensitivity is lower than NO_2. The addition of noble metals (Pt, Pd or Au) or metal oxides such as TiO_2 and SnO_2 to WO_3 could enhance the sensitivity to NO and could be utilized for controlling combustion exhaust [26]. The metal oxides such as Cr_2O_3-Nb_2O_5 and Al_2O_3-V_2O_5 are known to exhibit high sensitivity to NO [27, 28].

There are also reports on solid electrolyte NO_2 sensors using Na^+ conductor as electrolyte and $NaNO_3$ as auxiliary phase [26]. With proper selection of the auxiliary phase, the NO_2 sensitivity can be improved to lower detection limit of 0.2 ppm. Some others reported [29] the use of sensor for NO exposure to a Pt-Yittria stabilized Zirconia interface which helps to promote the NO/NO_2 equilibrium prior to the gases reaching the electrochemically active interface.

The semiconductor oxides are most suitable materials to realize practical NO_x sensor for exhaust monitoring as they are stable in exhaust environment and their use for detecting gases in a simplified procedure as well as for continuous monitoring.

4.3. Hydrocarbon Gas Sensors

Hydrocarbon gases have come into wide use as fuels for home, industries, automobiles and many other combustion utilities because they are readily available and as a comparatively cheap source of energy for burning. They are also major component of the exhaust gases from the internal combustion engines and other combustion machines. As a result large amount of HC are discharged in the atmosphere either through exhaust gases or escapes by volatilization. Transportation, petroleum industries and refineries are the large sources of HC pollution. HC brings about pollution hazards to human health and the damage to the environment. In the atmosphere HC along with oxides of nitrogen undergo many photochemical reactions giving out toxic products such as peroxy acetyl nitrate (PAN) which is strong eye irritants and highly toxic to plants and vegetations.

Semiconductor metal oxides are widely used as gas sensors based on chemical reaction between a specific gas adsorbed on the surface and some adsorbed species like oxygen on the surface which bring about subsequent change in conduction electron density on the surface of sensing materials. Commonly accepted sensing mechanism is the oxidation of the adsorbed gas on the surface of the semiconductor. It is also well known that some specific catalysts promote the oxidation process. For example SnO_2, a representative material, some oxygen vacancies are assumed to be present in this oxide. The oxygen vacancies act as donors to increase the surface conductivity but the adsorbed oxygen species act

Table 4. Some recent reports on solid state gas sensors for detecting gaseous pollutants.

Pollutants and sensor materials	Sensing range	Temperature range (°C)	Year	Ref.
(I) CO				
Semiconductor type:				
Pt/SnO_2 thin film	200 ppm	100–250	2001	[43]
TiO_2/Fe_2O_3 thin film	50–300 ppm	200–500	2001	[44]
Pd/SnO_2 film	50 ppm	400–600	2001	[45]
NiO thin film	50–200 ppm	250–420	2001	[46]
Co-In_2O_3 thin film	250 ppm	350–500	2001	[47]
CeO_2/SnO_2 thick film	700–2800 ppm	250–450	2001	[48]
CuO/SnO_2 thick film	200 ppm	100–450	2002	[49]
Pt/SnO_2thick film	10–1000 ppm	70–250	2003	[50]
W-Mo/SnO_2 thin film	250 ppm	250–450	2003	[51]
SnO_2-$La_{.8}Sr_{.2}O_{.5}Ni_{.5}O_3$ film	250–1000 ppm	200	2003	[52]
In_2O_3 thin film	0.5%	100–450	2004	[53]
SnO_2-Co_3O_4 thick film	1000 ppm	100–500	2004	[54]
(II) NO_x				
Semiconductor type:				
In_2O_3-SnO_2 film	2–1000 ppm	200	1998	[55]
Pd, Pt, Au-WO_3 thin film	1–10 ppm	200	1998	[56]
TiO_2-WO_3 thick film	0.5–50 ppm	350	2000	[57]
NiPc thin film	5–500 ppm	160	2001	[58]
Au/Ru-WO_3 thin film	5–75 ppm	200–400	2001	[59]
Zn-Sn-Sb-O thin film	5 ppm	400–600	2001	[60]
SiC/In_2O_3 microhot plate	4–30 ppm	250–400	2001	[61]
Ge-As-Te film	0.05–1.5 ppm	R.T.	2001	[62]
SnO_2 thin film	1–3 ppm	R.T.–200	2001	[63]
Au/Zn-Fe_2O_3 thin film	2.5 ppm	150–400	2002	[64]
In_2O_3, SnO_2 film	50–500 ppm	54–120	2002	[65]
WO_3 thin film	0.2 ppm	200	2003	[66]
WO_3 thin film	3 ppm	35–100	2003	[67]
$SmFeO_3$ film	10 ppm	290–350	2004	[68]
Polyaniline thin film	3–50 ppm	R.T.	2004	[69]
Solid electrolyte type:				
NASICON/$NaNO_3$	1–800 ppm	150	1992	[70]
Y_2O_3-ZrO_2/$CdCr_2O_4$	20–200 ppm	500	1997	[71]
NASICON/Pyrochlore oxide	10–1000 ppm	400	2000	[72]
Pt/Nafion electrode	0–485 ppm	R.T.	2001	[73]
Pt-Au alloy Zirconia based	150 ppm	R.T.	2003	[74]
Au/PV composite	0.6–2.6 ppm	R.T.	2004	[75]
Capacitance type:				
NiO/ZnO	10–100 ppm	300	1995	[76]
$SrSnO_3$-WO_3	1–400 ppm	550	2000	[77]
MOS thick film Au gate	5–140 ppm	180	2002	[78]
(III) Hydrocarbons				
Semiconductor type:				
(Pt,Pd, Rh, Ir)/SnO_2 thick film	100–10000 ppm	50–400	1994	[30]
SnO_2-TiO_2(Sb,Pt), γ-Fe_2O_3				
K, Ca, Mg/SnO_2 film	500–10000 ppm	400	2001	[79]
Zn-Sn-Sb-O thin film	50 ppm	400–600	2001	[60]
Pd/SnO_2 nanoparticles	30–240 ppm	250–450	2001	[45]
Ruthenated SnO_2 thin film	1000 ppm	225–350	2003	[80]
SnO_2, ZnO, WO_3,In_2O_3 thick film	30 ppm	200–400	2003	[81]
Pd/SnO_2 thick film	400–1000 ppm	200–400	2003	[82]
Solid electrolyte type:				
Au, Pt/CeO_2 phosphate based	1–3%	600	2002	[83]
IV) SO_2				
Semiconductor type:				
CeO_2 film	10–1000 ppm	550	1995	[84]
SnO_2 film	1000 ppm	200–600	1997	[85]
Ag/WO_3 thick film	100–800 ppm	100–800	2001	[86]
Amminofunctional co-polymer	50 ppm	30	2001	[87]
Au,Ti/In_2O_3 thin film	10 ppm	300–450	2001	[88]
SnO_2, ZnO, WO_3, In_2O_3 thick film	25 ppm	200–400	2003	[81]
Solid electrolyte type:				
MgO-ZrO_2/$LiSO_4$-$CaSO_4$	20–200 ppm	700	1992	[89]
NASICON/Na_2SO_4, $BaSO_4$	5–100 ppm	300–550	1996	[90]
Y_2O_3-ZrO_2/$BaSO_4$, K_2SO_4, SiO_2	20–10000 ppm	650–1000	2000	[91]
Pt, Au, Pd/solid polymer electrolyte	25–500 ppm	R.T.	2002	[92]
(V) CO_2				
Semiconductor type:				
La_2O_3-SnO_2 film	2000 ppm	400	1993	[93]
SnO_2-La_2O_3 thick film	2000 ppm	400	2000	[94]
$BaTiO_3$-CuO-La_2O_3	1%	550	2000	[95]
LaOCl	2000 ppm	200–300	2003	[41]
Solid electrolyte type:				
NASICO/$NdCoO_3$	100–2000 ppm	200–300	2000	[96]
LISICON/Li_2CO_3, K_2CO_3, Na_2CO_3	500–10000 ppm	420	2000	[97]
$SC_2(WO_4)$-Zirconia	200–1000 ppm	550	2001	[98]
$LiCoO_2$-Co_3O_4/$LiCO_3$	200–3000 ppm	500	2001	[99]
NASICON-In_2O_3	3000 ppm	R.T.	2001	[100]
NASICON/Na_2CO_3-$BaCO_3$	200–2000 ppm	R.T.	2003	[101]
Capacitor type:				
CeO_2/$BaCO_3$/CuO	350–20000 ppm	550–650	2000	[102]
CuO-$BaTiO_3$	2%	R.T.–450	2001	[103]
(VI) O_3				
Semiconductor type:				
WO_3 thin film	10–160 ppm	200–400	2000	[104]
$Zn_2In_2O_5$-$Mg_2I_2O_5$ thin film	0.4–6 ppm	275	2000	[105]
In_2O_3-MoO_3film	200 ppb	R.T.–400	2000	[106]
WO_3 thin film	54 ppb	200–400	2002	[107]
ZnO thin film		R.T.–400	2003	[108]
VII) VOCs				
Semiconductor type:				
Al, Pt, Pd/SnO_2 film	50–5000 ppm	300	1997	[109]
SnO_2 film	0–3000 ppm	400	2001	[110]
Cu/polyaniline	10–50 ppm	R.T.	2001	[111]
Pd/SnO_2 thick film	200 ppm	200–400	2003	[82]

continued

Table 4. Some recent reports on solid state gas sensors for detecting gaseous pollutants (Continued).

Pollutants and sensor materials	Sensing range	Temperature range (°C)	Year	Ref.
TiO_2 thin film	100–2000 ppm	160–400	2003	[112]
Cu, Au, Ag, Pt/In_2O_3-SnO_2 film	220–900 ppm	R.T.	2003	[113]
Au, Pt, Pd/SnO_2 thick film	1000–5500 ppm	R.T.	2003	[114]
(IX) NH_3				
Semiconductor type:				
Au,Ru/WO_3 thin film	1–10 ppm	200–400	2001	[59]
Acrylic acid/polyaniline	1–600 ppm	R.T.	2001	[115]
Au,Ti/In_2O_3 thin film	100 ppm	300–450	2001	[88]
SnO_2 film	100–1000 ppm	100–400	2002	[116]
Polyaniline film	4–1000 ppm	R.T.	2002	[117]
CuBr microsensor	0–50 ppm	R.T.	2002	[118]
MoO_3 thin film	3–100 ppm	450	2003	[119]
CuBr thin film	1–50 ppm	R.T.	2003	[120]
(X) H_2				
Semiconductor type:				
SnO_2-CeO_2 with Pt coil	1–1000 ppm	30–500	1998	[121]
Pd/InP	15–10000 ppm	20	2002	[122]
Polysilicon/Pd	100 ppm	R.T.	2002	[123]
In-SnO_2 thin film	500–3000 ppm	50–250	2003	[124]
SnO_2 thin film	0.5 %	300	2003	[125]
SnO_2 thin film	1–4 %	100–700	2003	[126]
Pt/NiO thin film	0.025–10 %	80	2004	[127]

as acceptor to decrease the surface conductivity [30, 31]. The binding states of the oxygen species relevant to the surface reactions are known to influence the surface composition and the temperature of the semiconductor oxides. Oxygen is adsorbed from air forming adsorbed species [2] and reacts with the adsorbed HC on the surface to give out oxidation products. Earlier in situ FTIR studies of CH_4 oxidation on Rh added SnO_2 had shown the absorption bands for CO_2 and H_2O which are the products of total oxidation of hydrocarbon [30]. This indicates that the final products of CH_4 oxidation are CO_2 and H_2O. The total surface oxidation reaction may be assumed in a simplified way as shown below:

$$2s + CH_{4(g)} \longrightarrow s\ldots CH_{3(ad)} + s\ldots H_{(ad)} \quad \text{(i)}$$

$$2s + O_{2(g)} \longrightarrow 2s\ldots O_{(ad)} \quad \text{(ii)}$$

$$s + s\ldots CH_{3(ad)} \longrightarrow s\ldots CH_{2(ad)} + s\ldots H_{(ad)} \quad \text{(iii)}$$

$$s\ldots O_{(ad)} + s\ldots H_{(ad)} \longrightarrow s\ldots OH_{(ad)} + s \quad \text{(iv)}$$

$$s\ldots CH_{2(ad)} + s\ldots O_{(ad)} + s \longrightarrow s\ldots CO_{(ad)} + 2s\ldots H_{(ad)} \quad \text{(v)}$$

$$s\ldots CO_{(ad)} + s\ldots O_{(ad)} \longrightarrow s\ldots CO\ldots O_{(ad)} \quad \text{(vi)}$$

$$s\ldots OH_{(ad)} + s\ldots H_{(ad)} \longrightarrow s\ldots OH\ldots H_{(ad)} \text{vii} \quad (3)$$

$$s\ldots CO\ldots O_{(ad)} \longrightarrow s + CO_{2(g)} \quad \text{(viii)}$$

$$s\ldots OH\ldots H_{(ad)} \longrightarrow s + H_2O_{(g)} \quad \text{(ix)}$$

Here, s, ad, g represent active site on the surface, adsorbed and gaseous species respectively. Active sites for CH_4, O_2 and hydrogen may not be same that depends upon the surface composition, nature of the sites, acidic-basic character, valence state of the metal etc.

Among many metal oxides semiconductor tin oxide is of interest as an important material for gas sensing devices. Some addition of active metals such as Pt, Pd, Rh, Ir, and some metal oxides play an important role in promoting sensitivity of hydrocarbon gases. Also promoting the grain size is useful parameter for improving sensing properties. Figure 6 shows the sensitivities of SnO_2-TiO_2(Sb, Pt) thick films to different hydrocarbons. Butane showed high sensitivity almost more than 90%, methane gave around 60% and propane was in between at 3000 ppm concentration. This indicates that smaller the carbon number lower the sensitivity on these type of sensors.

There may be some factors which affect the potential barrier height across the grain boundary of the sintered polycrystalline sensors, thus effecting sensor resistance. Oxygen

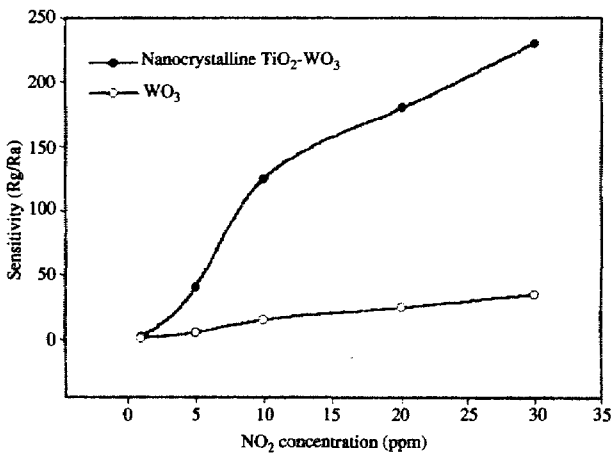

Figure 5. Sensitivity of TiO_2-WO_3 and WO_3 gas sensors as function of NO_2 gas concentration. Reprinted with permission from [26], D. D. Lee and D. S. Lee, *IEEE Sensor J.* 1, 214 (2001). © 2001, IEEE.

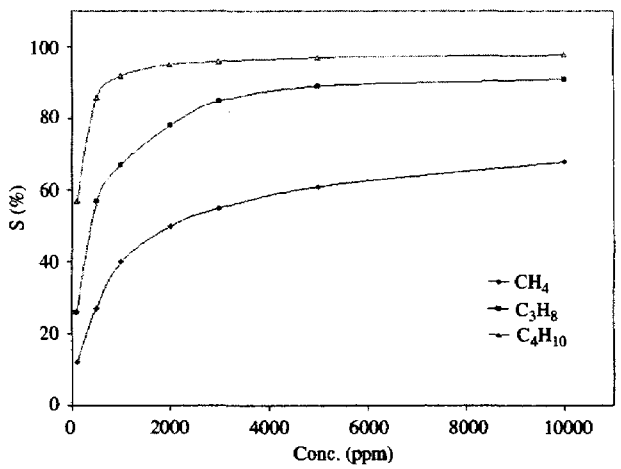

Figure 6. Sensitivity of SnO_2-TiO_2(Sb,Pt) thick film to various hydrocarbons at 350 °C. © 2004, Kodansha, Japan.

adsorbed on the oxide surface can remove an electron from the semiconductor to form either O_2^- at low temperature or O^- or O^{2-} at high temperatures, there by reducing the Schottky barrier height in grain boundary [30]. Another effect is that oxygen adsorbed on the catalyst removes electrons from the catalyst and subsequently the catalyst removes electrons from supporting semiconductor. Because Pt has a higher work function than SnO_2 or TiO_2, the electrons from SnO_2 or TiO_2 are pumped into and tied up at the Pt sites, resulting in the formation of Schottky barrier across the grain boundary of the Pt and SnO_2 or Pt and TiO_2.

Figure 7 depicts the response to different hydrocarbon gases at 300 °C on γ-Fe_2O_3 device. Here also butane showed higher sensitivity than CH_4 and C_3H_8.

Several factors need to be considered with regard to the preparation and the operation in developing an efficient and reliable sensor device. Thick film devices prepared by co-precipitation of the composite oxides, SnO_2-TiO_2 (Sb, Pt) has been found to be promising sensor for hydrocarbon detection. Also γ-Fe_2O_3 made it possible to detect hydrocarbon gases with good selectivity at relatively low operating temperature of 300 °C. Detailed history of the recent work has been cited in Table 4.

4.4. Sulfur Dioxide Sensors

Sulfur dioxide gas in the environment is a major source for the acid rain, corrosion and health hazards. The major industrial sources of SO_2 emissions are coal burning in power plants, petroleum refineries and metal smelting industries. Once the gas escapes in the atmosphere then one cannot prevent the environmental hazards caused by this gas. In the past many lives have been claimed by this gas along with particulates especially in London air pollution episodes in 1952 and 1956 also New York episode in 1963. Therefore, it is very essential to prevent the escape of this gas beyond permissible limit. Control and monitoring the toxic gas at the pollution source is very important. Present analytical tools such as spectroscopic West-Gaeke method, UV fluorescence, Gas chromatography techniques etc. are very good

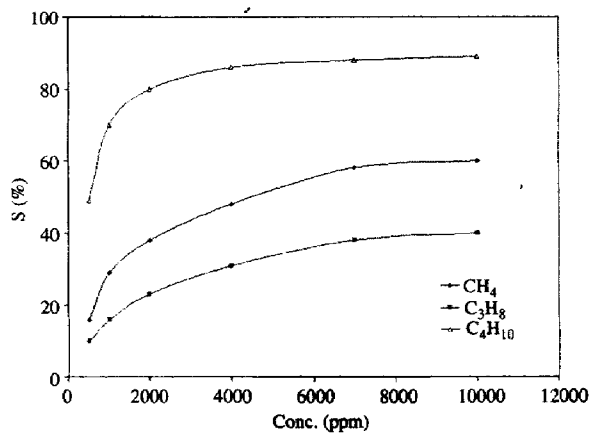

Figure 7. Sensitivity of γ-Fe_2O_3 thick Film to various hydrocarbons at 300 °C. © 2004, Kodansha, Japan.

but comparatively slow, time consuming and non continuous methods. Hence the monitoring at the pollution source by semiconductor device or by solid electrolyte type device is quite desirable.

A gas concentration cell method using a solid electrolyte has been investigated for SO_2 detection [32]. The advantage of this technique is that SO_2 monitoring is simple, selective, continuous and low cost. As the electrolytes, β-alumina, NASICON and alkali metal sulfates are used. The cell of SO_2 gas sensor with solid electrolyte is expressed as below [31]:

$$\text{Pt, } O_2, \text{ } SO_2, \text{ } SO_3/Na^+ \text{ based solid electrolyte}/SO_3, \quad SO_2, \text{ } O_2, \text{ Pt} \tag{4}$$

In SO_2 compartment, $NaSO_4$ decomposes to $2Na^+$, SO_3, $1/2O_2$, and $2e^-$. On other side, Na_2SO_4 is formed from an ambient SO_2 gas.

Different sulfate based solid electrolyte have been applied to this type of sensors, thereby combining NASICON with another Na+ ions as solid electrolyte and Na_2SO_4 as an auxiliary phase. These sensors have shown quite good sensitivity, selectivity and linearity to SO_2 gas. The cell composition is expressed as below [33]:

$$\text{Pt, } SO_2, \text{ } O_2/Na_2SO_4\text{-}BaSO_4/\text{NASICON}/Na_2SiO_3/SO_2, \quad O_2, \text{ Pt} \tag{5}$$

where, Na_2SiO_3 is the reference electrode in air and the binary composite of Na_2SO_4 and $BaSO_4$ as an auxiliary phase. The e.m.f. of this sensor can be expressed using Nernst equation for the detection of SO_2 in air as follows [26]:

$$E = E_o + \frac{RT}{2F} \ln P_{SO_2} \tag{6}$$

where R, T, F, P_{SO_2} represent gas constant, measuring temperature, Faraday constant, and partial pressure of SO_2 respectively. The e.m.f. of the NASICON SO_2 sensor with Na_2SiO_3 as reference electrode and Na_2SO_4as auxiliary electrode is proportional to the SO_2 gas concentration is shown in Fig. 8 [26].

Semiconductor SO_2 sensor with SnO_2 was first reported by Lalauze and others [33]. There after SO_2 sensing properties on semiconductor metal oxides, such as CeO_2 and SnO_2 have been studied [33, 35]. Among the oxides, WO_3 showed high SO_2 sensitivity at 400 °C, accompanied by increase in resistance, but resistance decreased with SO_2 at temperatures higher than 500 °C. Addition of Ag 1% by weight was found to be most effective for improving the SO_2 sensitivity [36].

4.5. Carbon Dioxide Sensors

CO_2 is the constituent of air and is non toxic. But if the concentration of CO_2 increases above normal natural concentration level then it is harmful and the main cause of green house effect. CO_2 sensing is necessary to maintain the level and to prevent its increase in the atmosphere. NDIR is one of the methods for detecting CO_2 gas. The absorbance for

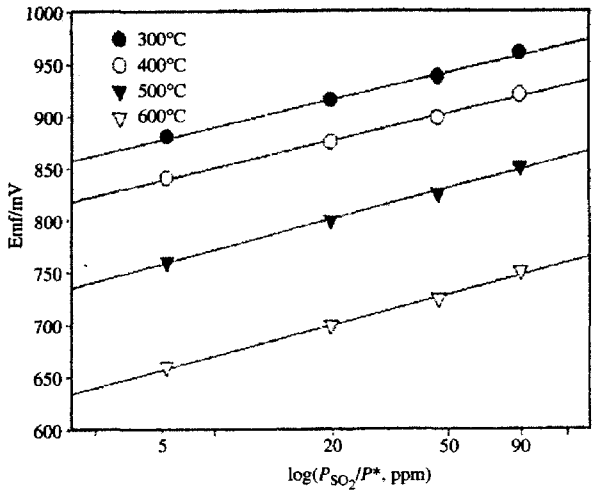

Figure 8. Emf response of NASICON to SO_2 sensor. Reprinted with permission from [26], D. D. Lee and D. S. Lee, *IEEE Sensor J.* 1, 214 (2001). © 2001, IEEE.

CO_2 is around 4250 nm wavelength and by using a filter that can only transmit a beam with a 4250 nm wavelengths, the absorbance beam can be detected. The out put is expressed as a function of CO_2 concentration.

The solid state CO_2 sensor based on electrochemical was reported in 1977 [37], since than lot of research have been conducted. NASICON and LISICON CO_2 sensor are used with an attached auxiliary phase of an alkali metal carbonate and are recognized as exhibiting a good linearity to CO_2 concentration.

Capacitor type CO_2 sensors are implemented using composite ceramics such as CeO-$BaCO_3$/CuO and CuO-$BaTiO_3$ [38, 39]. These sensors exhibit good sensitivity and selectivity to CO_2 in the concentration range 100 to 10, 000 ppm. Furthermore, the semiconductor CO_2 sensor using La_2O_3-SnO_2 has been investigated [40]. Recently, the use of LaOCl powder as a new material for CO_2 based on resistive change is reported [41].

4.6. Other Gas Sensors

Due to the severe regulation on the emission of VOC indoor and outdoor, the main cause of sick-house syndrome, lot of efforts have been put in detecting different VOCs. Many VOC's such as methanol, carbon tetrachloride, benzene, toluene, nitrobenzene etc. are widely used and important organic solvents with wide-spread applications. However, they are highly toxic and often fatal to human beings. Wide range applications, toxicity and implications make imperative the need of the development of reliable and selective sensors. It is assumed that for VOC on SnO_2 sensor, work through the oxidation resulting the consumption of adsorbed oxygen on the sensor surface resulting in decrease in resistant, although there is some knowledge about surface reactions of VOC's, most of which the actual interaction is not very clear [82]. Conducting polymer such as polypyrrole, polyaniline, polythiophene etc. and also metal substituted polymers are being explored for many VOC compounds such as chloroform, CCl_4, benzene, toluene etc. [111].

Sensing other gases such as O_3, ammonia, H_2, humidity etc. in air is also important for the safe and comfortable environment. Several ppm of O_3concentration in air has been reported with an In_2O_3-based semiconductor [42]. The recent work on other gases has been cited in Table 4. Research on solid state sensors are also going on for other miscellaneous gaseous pollutants. Still further research and development on solid state gas sensor are needed to meet the demands for safe and healthy environment.

5. CONCLUSION

A brief overview of gaseous environmental pollutants, emitting sources, sensing mechanisms of some solid state sensors and sensing of gases have been presented. Precise and accurate monitoring of pollutants is very important to prevent environmental hazards or accidents. Analytical and conventional instruments for monitoring gaseous pollutants are bulky, time consuming and expensive. Whereas, solid state gas sensors are compact, robust, inexpensive and monitoring continuously. Most of the solid state sensors work above room temperature to maintain the sensing activity as a result requires lot of power consumption. Minimization of power consumption during sensor operation is essential for practical sensors. Lot of efforts are put to minimize the power consumption by considering the several points such as miniaturization, new sensing materials, new techniques and sensing device morphology. Thick and thin films are suitable for miniaturized sensors with low power consumption and suitable for practical use.

GLOSSARY

Precision Degree of accuracy of the scale used to measure how closely the results can be reproduced.

Accuracy Measured value lies how close to the true or accepted value.

Fugitive emission These are the emissions to the atmosphere resulting from leaking pipe sources and equipments such as valves, pump seal connections, compressor seals, pressure valve etc. In general these emissions are not observable, but can be measured at low concentration at each source by gas sensors.

Adsorption It is a surface phenomenon and are of two types. One is chemisorption and other is physisorption. Chemisorption is a chemical reaction on the surface of the film or solid forming chemical bonds. Physisorption is a weak force of adsorption without chemical bonds.

Monochromator A filter for passing a single wavelength when scanned through a wide wavelength range.

Active site It is a site or point having force of attraction for the gas molecule either by accepting or donating electron.

Desorption Adsorbed molecule when leaves the active site from the surface is called desorption.

Sensitivity The minimum concentration of gas that is detectable, is the main measure of sensor performance. In other words it is the ratio of change in output and change in input signal.

Selectivity (Selective gas affinity) This should be high enough to differentiate the desired gas species from the rest of the analyte mixture.

Response Time necessary for the response curve to reach around 90% of its end value. Or time needed to reach the final value of the reading (true value of the measured signal).

Repeatability It is defined as the percent error between the reading generated by a second application of calibration gas and the bench mark value, compared to the range. It is obvious that both the readings must be taken at the same conditions. In other words, the ability to give repetitively the same value when the same input is measured.

Reliability The probability that the sensor operates the expected time correctly.

NDIR Non dispersive infra red spectrometer is an analytical tool which detects certain gases at particular wavelength in the ir region.

Perovskite It is a material composition of ABO_3 type where A and B are trivalent metal with three atoms of oxygen.

Dielectric constant A number that indicates the magnitude of the shift in a solid of positive and negative charges in opposite directions when a voltage is applied across the solid.

Calcia It is calcium oxide of the composition CaO.

Yttria It is yttrium oxide of the composition Y_2O_3.

Zirconia This is zirconium oxide of the composition ZrO_2. It is a white powder having both acidic and basic properties.

Schottky barrier It is the potential barrier in the metal—semiconductor contact and also can be said as a rectifying interface between a semiconductor and a metal.

Acid rain Sulfur dioxide and oxides of nitrogen under go chemical reaction forming aerosols of sulfuric and nitric acids in the atmosphere and the rain water becomes acidic because of these acidic aerosols. This is called as acid rain.

Green house effect Some trace gases (CO_2, N_2O etc.) absorb infrared radiations and reradiate back in the earth atmosphere, effectively storing some of the heat in the atmosphere, resulting net warming of the surface and the process is called as green house éffect.

Sick house syndrome An acute incidence of indoor air pollution that can occur in closed or poorly ventilated houses, buildings, auditoriums, Offices etc.

R.T. Room temperature measurements.

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