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Gas Sensors for Monitoring Air Pollution

Kwang Soo Yoo

Department of Materials Science and Engineering, University of Seoul,
Korea

1. Introduction

The air pollution caused by exhaust gases from automobiles has become a critical issue. In some regions, fossil fuel combustion is a problem as well. The principal gases that cause air pollution from automobiles are nitrogen oxides, NO_x (NO and NO_2), and carbon monoxide (CO). Because NO_x gases with sulfur oxides (SO_x) emitted from coal fired plants cause acid rain and global warming and produce ozone (O_3) that leads to serious metropolitan smog from photochemical reaction, they must be detected and reduced [1-5].

In addition, as greater amounts of oil organic compounds are currently being produced by applied construction materials and households, the number of people who develop various symptoms after moving into a new apartment (*e.g.*, tickle, vertigo, headache, skin trouble) is increasing [6,7]. The principal gases that cause this phenomenon (called "sick-building syndrome") are formaldehyde (HCHO) and volatile organic compounds (VOCs) [8]. Especially, formaldehyde is the most dangerous among indoor pollutants as it could harm all kinds of organisms. Considering these, the allowed concentration of formaldehyde in the Netherlands and Germany is only 0.1 ppm [9,10]. Therefore, gas sensors with excellent reactivity and stability are needed.

The first decade of the 21st century has been labeled by some as the "Sensor Decade." A sensor is a device that converts a physical phenomenon into an electrical signal. As such, sensors represent part of the interface between the physical world and the world of electrical devices, such as computers. In recent years, sensors have received people's attention as one of the important devices in electronic systems and enormous capability for information processing has been developed within the electronics industry. Of all sensors, gas sensors and light sensors have been most actively studied [11-13]. The final goal of gas sensor development is to establish the array technology of multifunctional gas sensors that can monitor air pollution with low cost, and is to fabricate the electronic nose using this technology.

Gas sensors are defined as a device that can substitute for human olfaction, and there are many researches being conducted to monitor air pollution by using these gas sensors. Gas sensors can be classified into semiconductor-type, solid electrolyte-type, electrochemical-type and catalytic combustion-type. Among these, the semiconductor-type gas sensor, the most well-known, is operated by changing its conductivity when it is exposed to gas. The semiconductor-type gas sensor has the advantages of rapid reactivity, efficiency, and gas selectivity when suitable additives are applied to it [14,15]. Sensors made of inorganic materials are the most commonly used, especially ceramics. One reason is that many sensors are used in very severe conditions such as high temperature, reactive or corrosive atmosphere and high humidity, and ceramics are most reliable materials in these conditions. Another reason may be that the microstructure of ceramics can be controlled by process

conditions. In general, electrical, mechanical and optical properties of a material are controlled by changing its composition. In ceramics, however, these properties are also controlled by changing its microstructure [13]. The gas-sensing materials for semiconductor-type are SnO_2, WO_3, In_2O_3, perovskite-structure oxides, etc., and the electrolyte for solid electrolyte-type gas sensor is $Na_3Zr_2Si_2PO_{12}$ [1,2,4,16-19].

In this chapter, pollutants and sources of air pollution are briefly explained. Then environmental gas sensors for monitoring air pollution are introduced systematically and the fabrication methods and characteristics of each gas sensor are explained at length with recent research trends.

2. Air pollution [20]

Air pollution is the introduction of chemicals, particulate matter, or biological materials that cause harm or discomfort to humans or other living organisms, or cause damage to the natural environment or built environment, into the atmosphere. The atmosphere is a complex dynamic natural gaseous system that is essential to support life on planet Earth. Stratospheric ozone layer depletion due to air pollution has been recognized as a threat to human health as well as to the Earth's ecosystems. Indoor air pollution and urban air quality are listed as two of the world's worst pollution problems in the 2008 Blacksmith Institute World's Worst Polluted Places report [21].

2.1 Pollutants
A substance in the air that can cause harm to humans and to the environment is known as an air pollutant. Pollutants can be in the form of solid particles, liquid droplets, or gases. They may be natural or man-made [22]. Pollutants can be classified as primary or secondary. Usually, primary pollutants are directly emitted from a process, such as ashes from a volcanic eruption, the NO_x and CO gases from a motor vehicle exhaust or SO_x released from factories. Secondary pollutants are not emitted directly. Rather, they form in the air when primary pollutants react or interact. An important example of a secondary pollutant is ground level ozone - one of the many secondary pollutants that make up photochemical smog. Some pollutants may be both primary and secondary: that is, they are both emitted directly and formed from other primary pollutants. Causes and effects of air pollution are shown in Fig. 1.
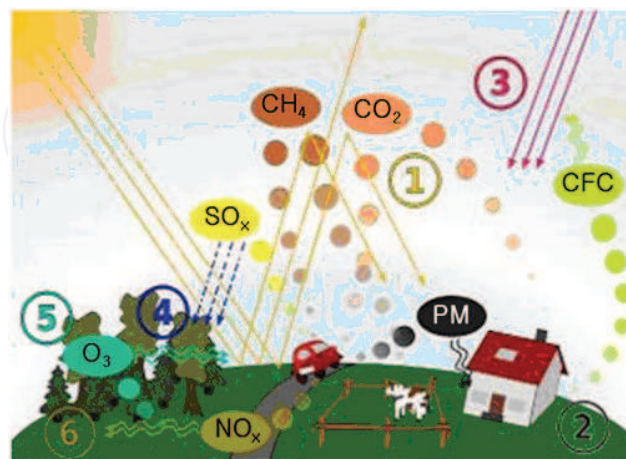

Fig. 1. Schematic drawing, causes and effects of air pollution: (1) greenhouse effect, (2) particulate contamination, (3) increased UV radiation, (4) acid rain, (5) increased ground level ozone concentration, (6) increased levels of nitrogen oxides [20].

2.1.1 Major primary pollutants

- Nitrogen oxides (NO$_x$): especially nitrogen dioxide (NO$_2$). NO$_2$ is emitted from high temperature combustion. Can be seen as the brown haze dome above or plume downwind of cities. This reddish-brown toxic gas has a characteristic sharp, biting odor. NO$_2$ is one of the most prominent air pollutants.

- Carbon monoxide (CO): CO is a colorless, odorless, non-irritating but very poisonous gas. It is a product by incomplete combustion of fuel such as natural gas, coal or wood. Vehicular exhaust is a major source of carbon monoxide.

- Carbon dioxide (CO$_2$): CO$_2$ is a colorless, odorless, non-toxic greenhouse gas associated with ocean acidification, emitted from sources such as combustion, cement production, and respiration.

- Volatile organic compounds (VOCs): VOCs are an important outdoor air pollutant. In this field they are often divided into the separate categories of methane (CH$_4$) and non-methane (NMVOCs). CH4 is an extremely efficient greenhouse gas which enhances global warming. Other hydrocarbon VOCs are also significant greenhouse gases via their role in creating ozone and in prolonging the life of CH$_4$ in the atmosphere, although the effect varies depending on local air quality. Within the NMVOCs, the aromatic compounds such as benzene, toluene and xylene are suspected carcinogens and may lead to leukemia through prolonged exposure. 1,3-butadiene is another dangerous compound which is often associated with industrial uses.

- Formaldehyde (HCHO): HCHO is the most dangerous among the indoor pollutants as it could harm all kinds of organisms. As great amounts of oil organic compounds are induced by applied construction materials and households, HCHO and VOCs are produced and cause various symptoms (called "sick-building syndrome") after moving into a new apartment [6-8].

- Ammonia (NH$_3$): NH$_3$ is emitted from agricultural processes. It is normally encountered as a gas with a characteristic pungent odor. NH$_3$ contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to foodstuffs and fertilizers. NH$_3$, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Although in wide use, NH$_3$ is both caustic and hazardous.

- Sulfur oxides (SO$_x$): especially sulphur dioxide (SO$_2$). SO$_2$ is produced by volcanoes and in various industrial processes. Since coal and petroleum often contain sulphur compounds, their combustion generates SO$_2$. Further oxidation of SO$_2$, usually in the presence of a catalyst such as NO$_2$, forms H$_2$SO$_4$, and thus acid rain. This is one of the causes for concern over the environmental impact of the use of these fuels as power sources.

- Particulate matter (PM): Particulates, alternatively referred to as PM or fine particles, are tiny particles of solid or liquid suspended in a gas. In contrast, aerosol refers to particles and the gas together. Some particulates occur naturally, originating from volcanoes, dust storms, forest and grassland fires, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols. Averaged over the globe, anthropogenic aerosols - those made by human activities - currently account for about 10 percents of the total amount of aerosols in our atmosphere.

Increased levels of fine particles in the air are linked to health hazards such as heart disease [23], altered lung function and lung cancer.

- Chlorofluorocarbons (CFCs): CFCs are harmful to the ozone layer emitted from products currently banned from use [24,25].
- Persistent free radicals connected to airborne fine particles could cause cardiopulmonary disease.
- Toxic metals, such as lead, cadmium and copper
- Odors such as from garbage, sewage, and industrial processes
- Radioactive pollutants produced by nuclear explosions, war explosives, and natural processes such as the radioactive decay of uranium.

2.1.2 Secondary pollutants
- PM formed from gaseous primary pollutants and compounds in photochemical smog: Smog is a kind of air pollution and the word "smog" means a portmanteau of smoke and fog. Classic smog (London type smog) results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog (photochemical or Los Angeles type smog) does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog.
- Ground level ozone (O_3) formed from NO_x and VOCs: O_3 is a key constituent of the troposphere. It is also an important constituent of certain regions of the stratosphere commonly known as the Ozone layer. Photochemical and chemical reactions involving it drive many of the chemical processes that occur in the atmosphere by day and by night. At abnormally high concentrations brought about by human activities (largely the combustion of fossil fuel), it is a pollutant, and a constituent of smog.
- Peroxyacetyl nitrate (PAN) similarly formed from NO_x and VOCs.

2.2 Sources
Sources of air pollution refer to the various locations, activities or factors which are responsible for the releasing of pollutants into the atmosphere. These sources can be classified into two major categories.

2.2.1 Anthropogenic sources (human activity)
- "Stationary Sources" include smoke stacks of power plants, manufacturing facilities (factories) and waste incinerators, as well as furnaces and other types of fuel-burning heating devices.
- "Mobile Sources" include motor vehicles, marine vessels, aircraft and the effect of sound etc.
- Chemicals, dust and controlled burn practices in agriculture and forestry management. Controlled or prescribed burning is a technique sometimes used in forest management, farming, prairie restoration or greenhouse gas abatement. Fire is a natural part of both forest and grassland ecology and controlled fire can be a tool for foresters. Controlled burning stimulates the germination of some desirable forest trees, thus renewing the forest.

- Fumes from paint, hair spray, varnish, aerosol sprays and other solvents.
- Waste deposition in landfills, which generate methane. Methane is not toxic; however, it is highly flammable and may form explosive mixtures with air. Methane is also an asphyxiant and may displace oxygen in an enclosed space. Asphyxia or suffocation may result if the oxygen concentration is reduced to below 19.5% by displacement.
- Military, such as nuclear weapons, toxic gases, germ warfare and rocketry.

2.2.2 Natural sources
- Dust from natural sources, usually large areas of land with little or no vegetation.
- CH_4 gas emitted by the digestion of food by animals, for example, cattle.
- Radon gas from radioactive decay within the Earth's crust. Radon is a colorless, odorless, naturally occurring, radioactive noble gas that is formed from the decay of radium. It is considered to be a health hazard. Radon gas from natural sources can accumulate in buildings, especially in confined areas such as the basement and it is the second most frequent cause of lung cancer, after cigarette smoking.
- Smoke and CO from wildfires.
- Vegetation, in some regions, emits environmentally significant amounts of VOCs on warmer days. These VOCs react with primary anthropogenic pollutants - specifically, NO_x, SO_2, and anthropogenic organic carbon compounds - to produce a seasonal haze of secondary pollutants [26].
- Volcanic activity, which produce sulfur, chlorine, and ash particulates.

3. Environmental gas sensors

A broad definition of environmental monitoring would include all aspects of air and water quality, soil contamination, electromagnetic radiation, noise, even heat release and light source pollution. However, the major environmental gas sensors are to monitor pollution in air, water, and soil as shown in Table 1 [27]. Environmental standard concentration and threshold limit value for six important gases of air pollution are listed in Table 2 [28,29]. Some information about gas sensors on the base of most familiar metal oxides and technological peculiarities of these sensors fabrication, which can be used for such selection, is presented in Tables 3 and 4 [30]. Gas sensors for monitoring principal gases among air pollutants are described in detail by using typical examples here.

	Fixed monitors		Mobile monitors	
	Stationary source	Ambient	Portable	Personal
Air	Industrial emissions, Leaks, Car exhausts, Biochemicals	Air quality	Air quality, Surveys	Gas alarms
Water	Drinking water, Effluent	Water pollution, Intake monitoring	Water pollution, Pollution tracing	Drinking water
Land	Waste disposal		Remediation, Leaks	

Table 1. Classification of Environmental Monitoring Applications [27]

Pollutants	Concentration			Ref.
	Environmental	TLV*	Request of sensors	
NO_x	Below 0.04-0.06 ppm (daily average)	NO_2: 3 ppm, NO: 25 ppm	0.01-0.3 ppm	28
CO_2	-	5000 ppm	200-400 ppm	28
CO	35 ppm† (1 h average)	50 ppm	0.1-10 ppm	28,†29
HCHO	-	1 ppm	-	29
SO_2	Below 0.04 ppm (daily average)	2 ppm	0-2 ppm	28
NH_3	-	25 ppm	-	28
O_3	Below 0.06 ppm (1 h average)	0.1 ppm	0-0.5 ppm	28
CFC**	-	-	20 ppt	28

*TLV: maximum exposure in 8 h period in 40 h work week
**CFC: Chlorofluorocarbon (Freon)
Table 2. Environmental Standard Concentration and Threshold Limit Value (TLV) of Air Pollution

Materials	Advantages	Disadvantages
SnO_2	High sensitivity, Good stability in reducing atmosphere	Low selectivity, Dependence on air humidity
WO_3	Good sensitivity to oxidizing gases, Good thermal stability	Low sensitivity to reducing gases, Dependence on air humidity, Slow recovery process
Ga_2O_3	High stability, Possibility to operate at high temperatures	Low selectivity, Average sensitivity
In_2O_3	High sensitivity to oxidizing gases, Fast response and recovery, Low sensitivity to air humidity	Low stability at low oxygen partial pressure
CTO ($CrTiO_x$)	High stability, Low sensitivity to air humidity	Average sensitivity

Table 3. Main Advantages and Disadvantages of Well-known Metal Oxides for Gas Sensor Applications [30]

Metal oxides	Detection gases	Operating temperature (°C)	Stability	Compatibility with IC fabrication
SnO_2	Reducing gases (CO, H_2, CH_4, etc.)	200-400	Excellent	Imperfect
WO_3	NO_x, O_3, H_2S, SO_2	300-500	Excellent	Low
Ga_2O_3	O_2, CO	600-900	High	Good
In_2O_3	O_3, NO_x	200-400	Moderate	Good
MoO_3	NH_3, NO_2	200-450	Moderate	Moderate
TiO_2	O_2, CO, SO_2	350-800	Enhanced	Moderate
ZnO	CH_4, C_4H_{10}, O_3, NO_x	250-350	Satisfactory	Good
CTO	H_2S, NH_3, CO, volatile organic compounds	300-450	High	Imperfect
Fe_2O_3	Alcohol, CH_4, NO_2	250-450	Low	Moderate

Table 4. Operating Parameters of Solid-state Gas Sensors on the Base of Metal Oxides and Technological Peculiarities of their Fabrication [30]

3.1 NO$_x$ gas sensor

Nitrogen oxide (NO$_x$) sensing materials reported by several investigators are WO$_3$, ZnO, SnO$_2$, In$_2$O$_3$, TiO$_2$, etc. Among these, WO$_3$ is known as the most promising NO$_x$ gas-sensing material [19,31-39]. These oxides have the advantages of rapid reactivity, efficiency, and gas selectivity when suitable additives are applied to them.

These sensing materials are oxygen-deficient nonstoichiometric compounds. The conductivity of these n-type semiconductors, such as WO$_3$ and In$_2$O$_3$, is estimated based on the electron created by the surplus metal. When sensing materials are exposed to oxidizing gases at temperature ranging from 200°C to 300°C, the concentration of electrons is decreased due to the reaction between the electron and the gas. Consequently, the conductivity decreases and the resistance increases.

As NO$_x$ is also an oxidizing gas, the concentration of electrons is decreased due to the reaction between the electrons in the sensing materials and NO$_x$ gas, as shown in the following equations:

$$NO + 2e^- \longrightarrow \frac{1}{2}N_2 + O^{2-} \tag{1}$$

$$NO_2 + 2e^- \longrightarrow NO + O^{2-} \tag{2}$$

Example [19]:

The powders of various gas-sensing materials were prepared using the solid-state reaction method, starting from the raw materials, WO$_3$ and In$_2$O$_3$. To improve the reactivity and sensitivity of the gas sensors, 0.1-wt% PdCl$_2$ was added as a catalyst. The powders were mixed, dried at 50°C, and then calcined at 1000°C. Thick-film NO$_x$ gas sensors were prepared on alumina substrate. The Pt electrodes were also printed with a silkscreen method before the deposition of the WO$_3$ and In$_2$O$_3$ gas-sensing layer. Schematic diagrams of the sensor are shown in Figure 2. To control the operating temperatures, a printing paste was used to form a Pt heater at the back of the alumina substrate. Pt wires were used as conductuve wires and were attached using silver paste.
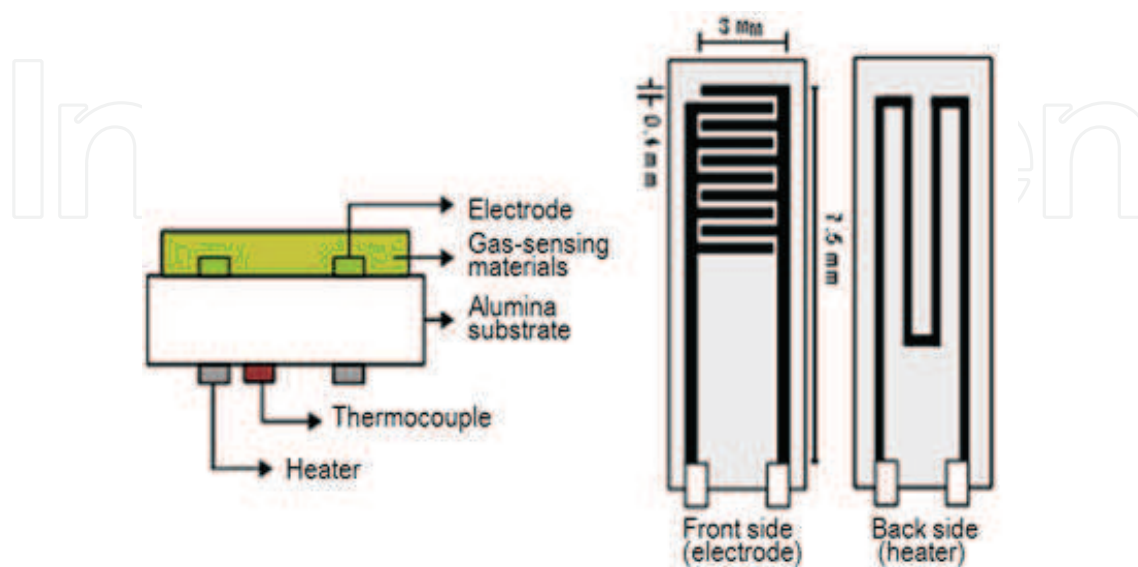

Fig. 2. Schematic diagrams of the gas sensor [19].

The gas-sensing properties were measured in a conventional gas-flow apparatus in the range of 1-5-ppm NO_x by mixing the parent gas (500-ppm NO_x in an N_2 balance) and dry synthetic air. The resistance of the sensor was calculated as:

$$R_s = R_L \left(\frac{V_C}{V_{RL}} - 1 \right) \tag{3}$$

where R_s is the resistance of the sensor, R_L is the resistance of the load which was controlled to fix the output voltage to the half of the input voltage because of the change the resistance of the sensor with the change of temperature. V_C is the input voltage and V_{RL} is the output voltage. The sensitivity (S), which refers to the resistance of a sensor that has been exposed to NO_x gas versus the resistance of a sensor that has been exposed to air, was calculated as:

$$S = \left(\frac{R_{gas}}{R_{air}} \right) \tag{4}$$

where R_{gas} is the resistance of the sensor that has been exposed to NO_x gas and R_{air} is the resistance of the sensor that has been exposed to air. In the gas mixtures of NO_x/air, the NO_x concentration varied from 1 ppm to 5 ppm.

As shown in Figures 3 and 4, when the sensors were exposed to NO_x gas, their resistance increased. Below 250ºC the resistance of the WO_3 and In_2O_3 were very high, so they could not detect the NO_x gas as there were hardly the resistance change of the WO_3 and In_2O_3. The highest sensitivities of the In_2O_3 to NO_x were at 300ºC, as were the highest sensitivities of the WO_3 to NO. The highest sensitivities of the WO_3 to NO_2 were at 250ºC, though.

Comparing the sensing property of In_2O_3 with that of WO_3, the sensitivities of In_2O_3 to NO were higher than those of WO_3 to NO, although they were similar. The highest sensitivity (R_{gas}/R_{air}) of In_2O_3 to 5-ppm NO was 10.22 when it was measured at 300ºC.
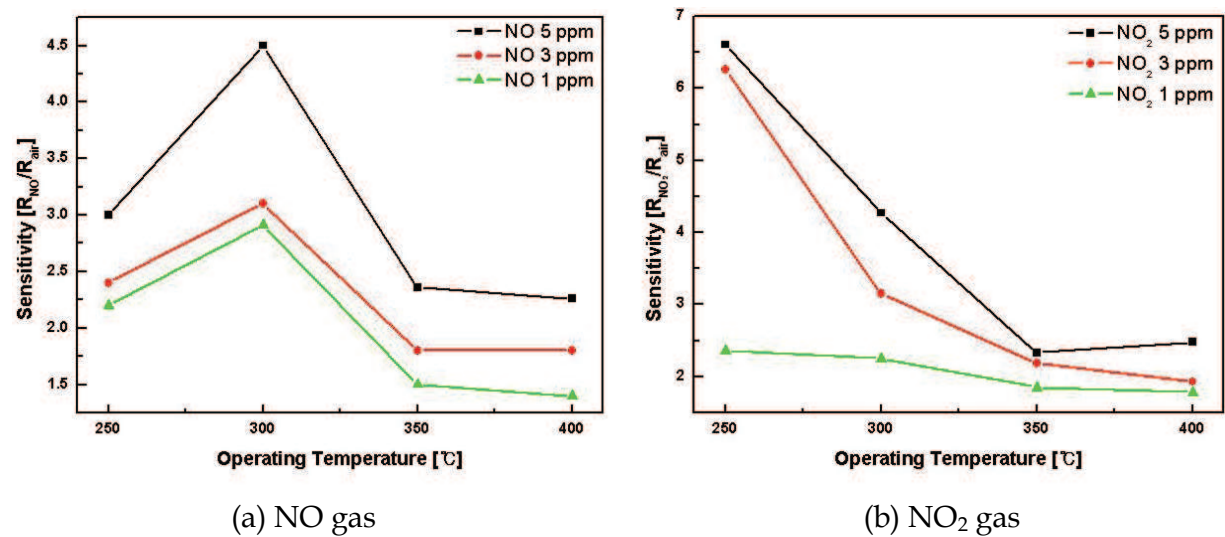

(a) NO gas   (b) NO_2 gas

Fig. 3. NO_x Gas-sensing properites of WO_3 [19].

(a) NO gas   (b) NO_2 gas
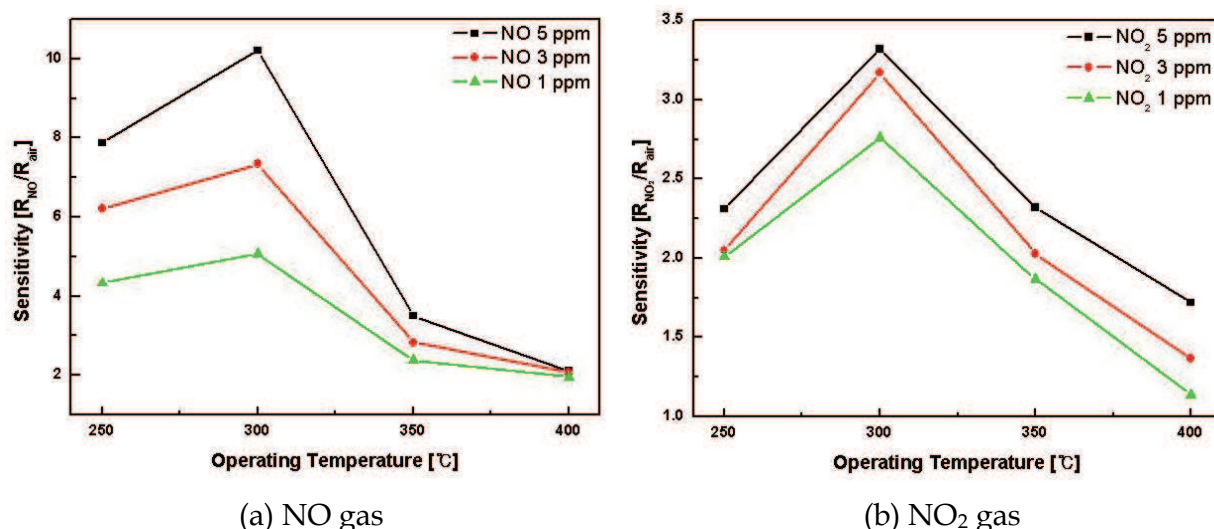
Fig. 4. NO_x Gas-sensing properites of In_2O_3 [19].

3.2 CO_2 gas sensor

Carbon dioxide (CO_2) sensors have been greatly demanded for monitoring or controlling CO_2 in various fields such as combustion process, biology, farming as well as air pollution. So far, many kinds of CO_2 sensors using various materials, such as solid electrolyte, mixed oxide capacitors, polymers with carbonate solution and so on, have been investigated [40-44]. Among them, solid electrolyte-type CO_2 sensors are of particular interest from the viewpoint of low-cost, high-sensitivity, high-selectivity and simple-element structure [45].

Most researches concerning the use of NASICON as active element for gas sensors have been focused on the $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ formula, in the composition range of $1.8 < x < 2.4$, because in this range, conductivity shows the largest value [46-48]. A commercial NASICON with a nominal-composition $Na_3Zr_2Si_2PO_{12}$ has been investigated as a CO_2 electrochemical sensor [49,50].

CO_2 sensing properties can be upgraded with auxiliary phases in sensing electrodes, which are binary carbonate systems such as Na_2CO_3-$BaCO_3$, Na_2CO_3-$CaCO_3$, Li_2CO_3-$BaCO_3$, and Li_2CO_3-$CaCO_3$. The binary systems bring about several advantages such as better long-term stability, quick response time, and resistance to water vapor interruption [18,40,51-54]. The device improved in this way has much increased feasibility in practice [55].

Example [18]

The NASICON powder was prepared using the sol-gel method, starting from the solutions of $ZrO(NO_3)_2 \cdot 8H_2O$, $NH_4H_2PO_4$, and $Na_2SiO_3 \cdot 9H_2O$. The solutions were mixed together to form a sol, which was further dehydrated at 80°C to form a gel. The gel was then dried at 120°C for 8 hours to form a fine dry powder, which was then ground and calcined at 750°C to eliminate the organic remains. Afterwards, the calcined material was reground.

The NASICON layer was screen-printed with a paste on the alumina substrate. The Pt electrodes were also screen-printed on the designated regions before and after the deposition of the NASICON layer. The assembly was sintered at 900°C, 1000°C, and 1100°C for 4 hours in air, respectively. After this, a series of auxiliary phases (Na_2CO_3-$CaCO_3$) was screen-printed on the Pt sensing electrode. The schematic diagram of the sensor is shown in Figure 5.
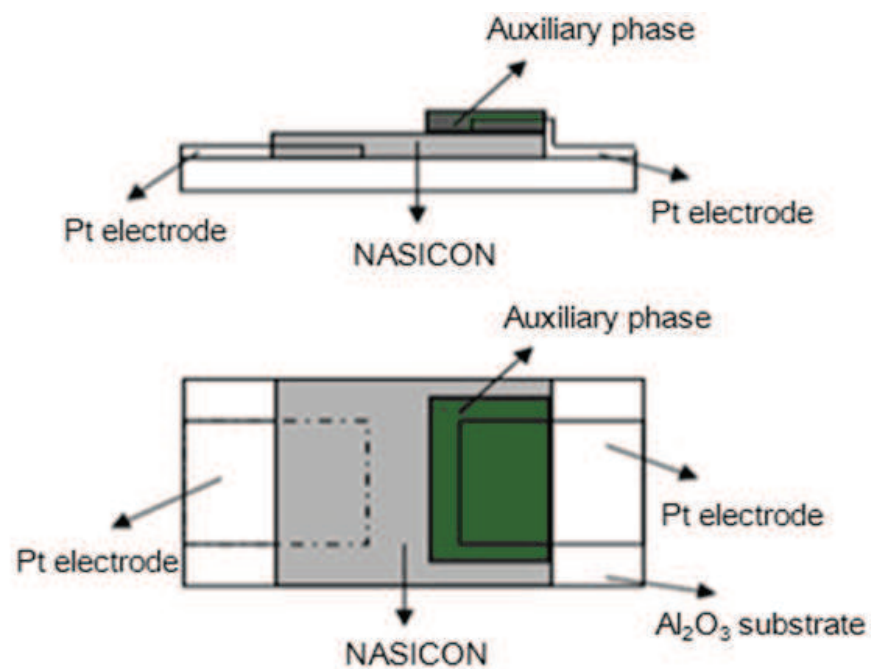
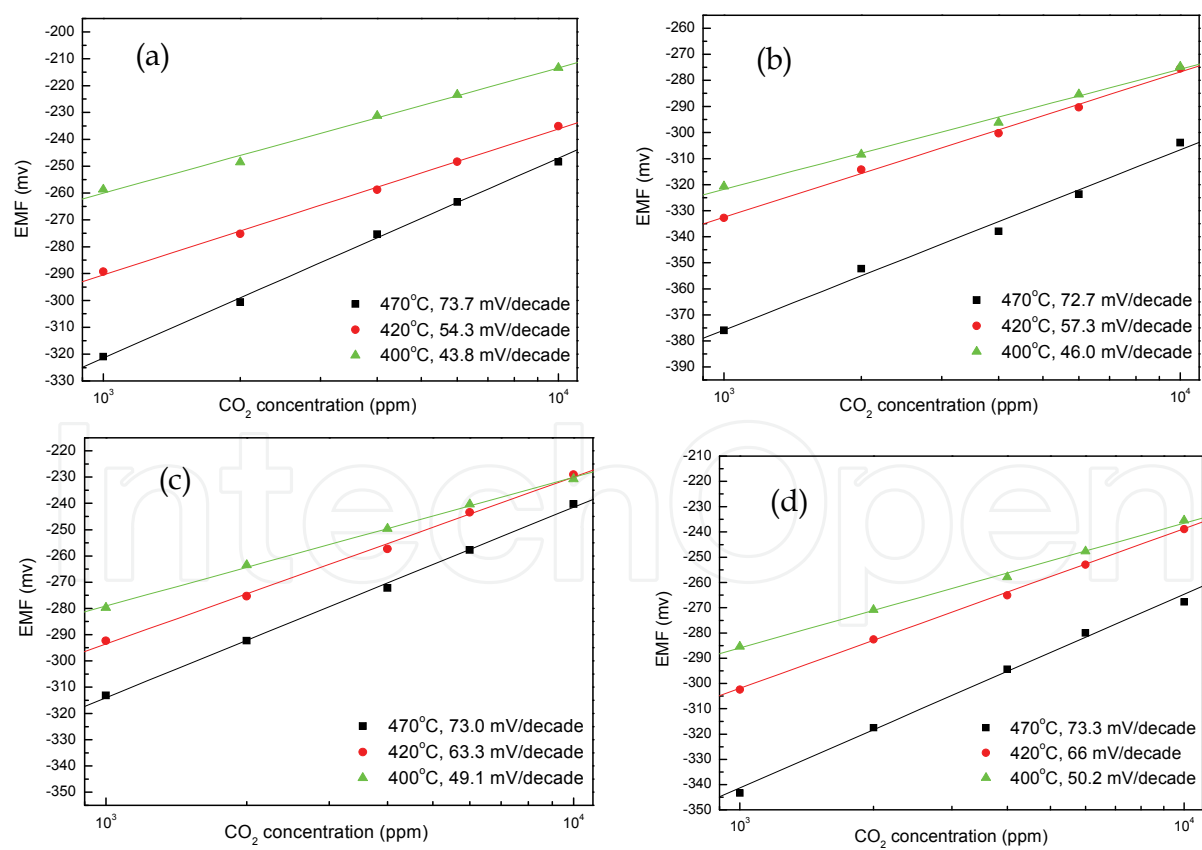Fig. 5. Schematic diagrams of the CO_2 gas sensor [18].

Fig. 6. CO_2 concentration vs. EMF for the CO_2 gas sensors attached with (a) Na_2CO_3-$CaCO_3$ = 1:0, (b) Na_2CO_3-$CaCO_3$ = 1:0.5, (c) Na_2CO_3-$CaCO_3$ = 1:1.5, and (d) Na_2CO_3-$CaCO_3$ = 1:2 [18].

Gas-sensing properties were measured in a conventional gas-flow apparatus by changing the mixing ratio between the parent gas (4% CO_2 in an N_2 balance) and dry synthetic air. The operating temperature was controlled by monitoring the applied voltage and current using the power supply. The sensors were exposed to the flow (100 cm^3/min) of the required sample gases. The gas mixtures of CO_2/air with the CO_2 concentration varied from 1,000 to 10,000 ppm.

Four types of sensors were fabricated from NASICON as a solid electrolyte. A series of Na_2CO_3-$CaCO_3$ mixtures at the molar ratio range of 1:0-1:2 was attached to the sensing electrode. Figure 6 shows the EMF response to CO_2 as a function of the CO_2 concentration at various temperatures. The EMF variation for each sensor at 470°C agreed well with the theoretical value of 74.0 mV/decade, based on a two-electron electrochemical reaction. As the temperature decreased, however, the slope tended to deviate from the ideal. Quite noticeably, the deviation could be suppressed very effectively with Na_2CO_3-$CaCO_3$ (1:2), which allowed 50.2 mV/decade to be kept at temperatures as low as approximately 400°C. An increase in the amount of $CaCO_3$ at the auxiliary phase is fairly effective for keeping the theoretical value at lower temperatures, whereas an adverse effect occurred when the $CaCO_3$ content was insufficient. The mechanism behind such improvements is not yet well understood, though. It requires further research.

3.3 HCHO gas sensor

Formaldehyde (HCHO) is an achromatic toxic gas and has a stimulating scent. When exposed to HCHO gas even just for a short time, a person may develop headache and vertigo, and when exposed to it for a long time, a person may develop asthma and other lung diseases. When exposed to high concentrations of HCHO, a person may develop pneumonia or edema of the lungs [9]. Considering these, the allowed concentrations of formaldehyde in Korea, Denmark, the Netherlands, and Germany are only 2 ppm, 0.2 ppm, 0.1 ppm, and 0.1 ppm, respectively [10]. Therefore, gas sensors with excellent reactivity and stability are needed. In view of the above, numerous attempts are being made to reduce the amount of HCHO in the air. Few studies have been conducted, however, on the detection and the measurement of the amount of HCHO gas in the air by using ceramic gas sensors.

HCHO sensing materials are perovskite-structure oxides (ABO_3) as the semiconductor type. ABO_3-type materials have the advantage of high stability. The sensitivity and selectivity of these kinds of sensors can be controlled by selecting suitable A and B atoms or through chemical doping with $A_{1-x}A_xB_{1-y}B_yO_3$ materials [56].

$La_{1-x}Sr_xFeO_3$ ceramics are ABO_3 perovskite materials. They are nonstochiometric compounds and p-type semiconductors whose conductivity is estimated through the holes created by the surplus oxygen therein. Substitution at the A-site of an element with a different valence (*e.g.*, the replacement of La^{3+} by Sr^{2+}) leads to the formation of oxygen vacancies and high-valence cations at the B-site, which results in a significant change in the catalytic activity [57-60]. When these sensing materials are exposed to reducing gases like CO, CH_4, and HCHO, their conductivity decreases, and their resistance increases because of the chemical surface reactions between the reducing gas and the surplus oxygen [61-63].

Example [17]

$La_{1-x}Sr_xFeO_3$ powders (x = 0, 0.2, 0.5) were prepared through the conventional solid-state reaction method, starting from raw materials of La_2O_3, SrO, and Fe_2O_3. The mixed powders were dried and were calcined at 1000°C.

The La$_{1-x}$Sr$_x$FeO$_3$ sensing layers were silkscreen-printed on the alumina substrate. The Pt electrodes were also silkscreen-printed on the designated regions before the deposition of the La$_{1-x}$Sr$_x$FeO$_3$ layer. Schematic diagrams of the sensor are shown in Figure 2.

The gas-sensing properties were measured in a conventional gas-flow apparatus by mixing the parent gas (10 to 50 ppm HCHO in N$_2$ balance) and dry synthetic air. The resistance of the sensor was calculated by using eq. (3). The gas sensitivity, which refers to the resistance of a sensor that has been exposed to HCHO gas versus the resistance of a sensor that has been exposed to air, was calculated as eq. (4). To confirm the selectivity of the sensors, the gas-sensitivities for CO$_2$, N$_2$, and C$_3$H$_8$ were also measured. The operating temperature was controlled by monitoring the voltage and current applied by using a power supply. The sensors were exposed to a flow (200 cm^3/min) of the required sample gases. Gas mixtures of HCHO/air with the HCHO concentration varying from 10 ppm to 50 ppm were used.

As HCHO gas is a reducing gas, free electrons are released due to the reaction between the surplus oxygen in the sensing materials and the gas [62], as shown in the following equation:

$$HCHO_{(gas)} + O^{2-}_{(ads)} = CO_{2(ads)} + H_2O_{(ads)} + 2e^- \qquad (5)$$
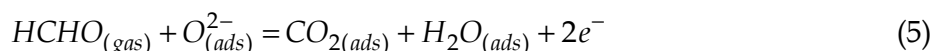
The sensing properties were improved by increasing the number of active sites of oxygen through the replacement of La with Sr. As shown in Figs. 7 to 9, when the sensors were exposed to HCHO gas, their resistance increased. As the reaction yield of the sensing material La$_{0.8}$Sr$_{0.2}$FeO$_3$ to the gas and the surplus oxygen increased, its sensing property was improved by increasing the resistance rather than the sensing property of LaFeO$_3$. The highest sensitivity (R_{gas}/R_{air}) of La$_{0.8}$Sr$_{0.2}$FeO$_3$ in 50 ppm was 14.7 when it was measured at 150ºC. The sensing property of La$_{0.5}$Sr$_{0.5}$FeO$_3$ declined, however, when the amount of surplus oxygen was decreased, despite the fact that the number of active sites of oxygen increased. The reason is assumed to be related to the microstructure of the sensor.
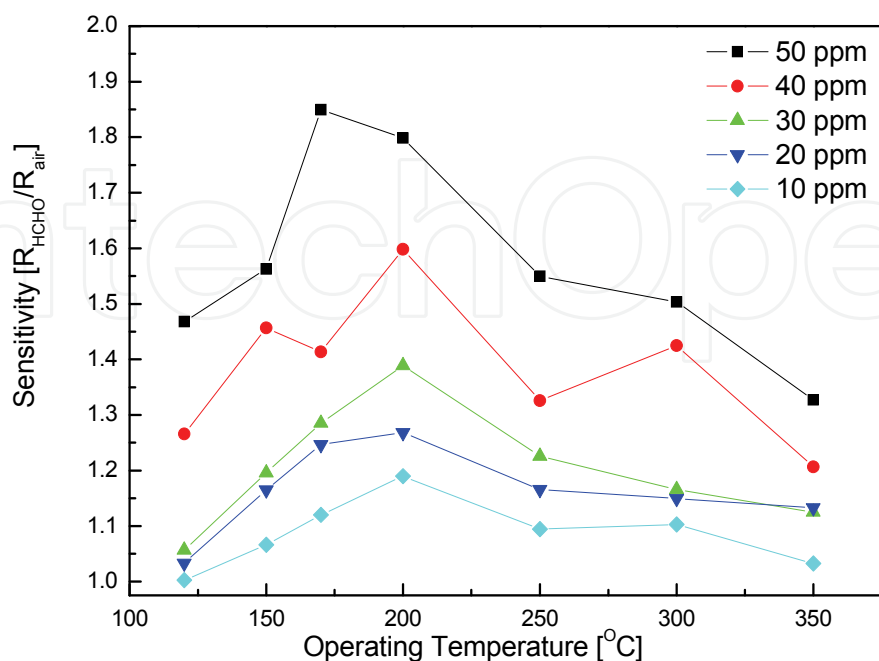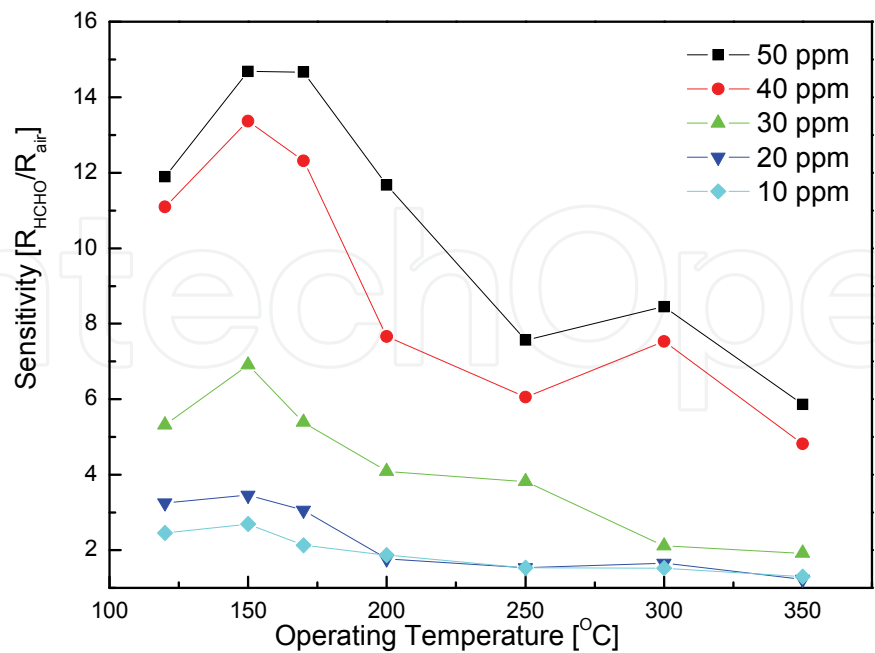

Fig. 7. HCHO Gas-sensing properties of LaFeO$_3$ [17].
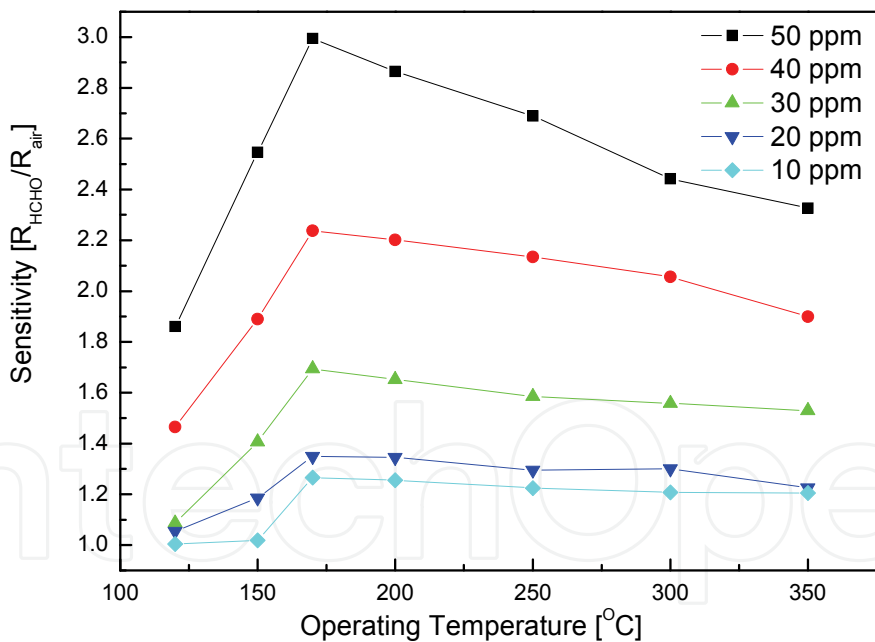
Fig. 8. HCHO Gas-sensing properties of $La_{0.8}Sr_{0.2}FeO_3$ [17].

Fig. 9. HCHO Gas-sensing properties of $La_{0.5}Sr_{0.5}FeO_3$ [17].

Considering the selectivity of the sensors, as shown in Table 5, the gas-sensitivity for HCHO gas was higher than those for other gases. As HCHO gas has a very strong reducing property, its sensitivity is over 2.5 because of the reaction between the surplus oxygen in the sensing materials and HCHO gas. On the other hand, other gases do not react to sensing materials, so their sensitivities were near 1. In particular, the $La_{0.8}Sr_{0.2}FeO_3$ sensor could selectively detect HCHO gas.

	$R_{3\%CO_2} / R_{air}$	$R_{2000ppmC_3H_8} / R_{air}$	$R_{50ppmHCHO} / R_{air}$
$LaFeO_3$	1.03	1.00	1.80
$La_{0.8}Sr_{0.2}FeO_3$	0.89	1.07	14.7
$La_{0.5}Sr_{0.5}FeO_3$	0.80	0.95	2.50

Table 5. Gas Selectivity of the Sensors Measured at 150℃ [17]

3.4 Other gas sensors
3.4.1 CO gas sensor
Carbon monoxide (CO) is a colorless, odorless, and tasteless gas which is slightly lighter than air. Because the development of CO gas sensors was urgent to avoid gas poisoning caused by imperfect combustion of kerosine or gas in a heater, many commercial SnO_2-based sensor devices have been realized by several investigators since 1980's. These gas sensors often operate at high temperature up to 400ºC, in order for high sensitivity.

Recently, in order to decrease the operating temperature, catalysts such as Pt, Pd, or Au [64] are added, and metal oxides (*e.g.* WO_3, In_2O_3 [65], MoO_3 [66], V_2O_5 [67]) are doped into the SnO_2 matrix. Especially, mixed oxides, normally tailored by doping metal cations into an oxide matrix, have attracted a great deal of interest in applications from catalysis to gas-sensing [67].

The electrochemical CO gas sensor is also useful for a fire alarm. If a sensor could detect CO in concentrations of 50-100 ppm, it could become a more useful fire detector than the smoke sensor [68].

3.4.2 NH$_3$ gas sensor
Ammonia (NH_3) is extensively used in preparing fertilizers, pharmaceuticals, surfactants, and colorants, with a global production. It presents many hazards to both humans and environment. Detection of NH_3 is required in many applications, including leak-detection in air-conditioning systems as well as in sensing of trace amounts of ambient NH_3 in air for environmental analysis, breath analysis for medical diagnoses, animal housing, and more [69].

Recently, various NH_3 gas sensors based on different sensing mechanisms have been developed. For example, the WO_3 nanofibers showed rapid response and recovery characteristics to NH_3, and gas-sensing mechanism was explained in terms of surface resistivity and barrier height model [70,71]. It was reported that polypyrrole (PPy)/$ZnSnO_3$ nanocomposites also exhibited a higher response to NH_3 gas [72], and by combining the merits of a chitosan polymer and a porous Si photonic crystal, the optical sensor showed high sensitivity, selectivity, and stability [69].

3.4.3 Others
Hydrogen sulfide (H_2S) is a colorless, very poisonous, and flammable gas with the characteristic foul odor of rotten eggs at concentrations up to 100 ppm. An ultrahigh sensitive H_2S gas sensor was developed utilizing Ag-doped SnO_2 thin film on the alumina substrate [73]. This Ag-SnO_2 nanocomposite showed excellent sensing properties upon exposure to H_2S as low as 1 ppm at 70ºC. Cuong *et. al.* [74] reported a solution-processed gas sensor based on vertically aligned ZnO nanorods on a chemically converted grapheme film. This sensor effectively detected 2 ppm of H_2S in oxygen at room temperature.

In addition, the sulfur dioxide (SO_2) gas sensor using an alkali metal sulfate-based solid electrolyte [75] and ozone (O_3) gas sensor of In_2O_3 thin-film type [76] were developed.

Recently, gas sensor array for monitoring the perceived car-cabin air quality was reported [34,77]. The technological process in microelectromechanical system (MEMS) metal oxide gas sensors in terms of stability and reproducibility has promoted the technology for mass market applications. Tille [34] suggested an automotive air quality gas sensor using micro-structured silicon technology as shown in Figure 10. The metallization and the gas-sensing layer were electrically isolated from the heating layer by a passivation. Reducing gases (*e.g.* CO, C_xH_y) result in an increase in conductivity and oxidizing gases (*e.g.* NO_2) produce a reduction in the conductivity of the metal oxide. For detection of various gases, several sensor elements such as SnO_2, ZnO, or WO_3 could be combined.
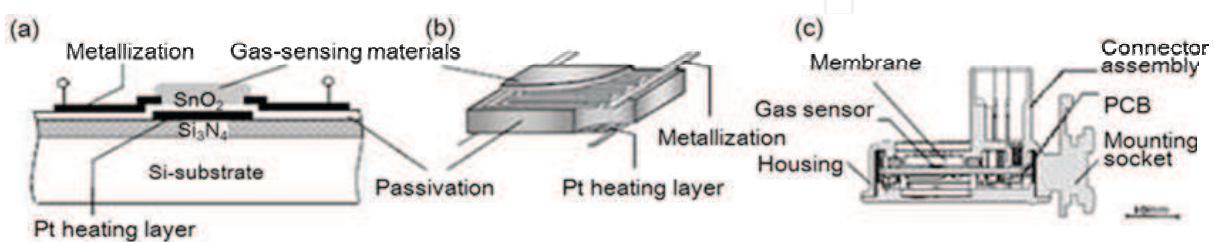

Fig. 10. Schematic illustration of a micro-structured metal oxide gas sensor (a) cross section; (b) metallization as inter-digital structure, and heating layer as platinum meander structure; (c) cross section of a typical automotive air quality sensor with embedded metal oxide gas sensor [34].

In the future, smart sensors with high sensitivity, good reliability, and rapid response by using MEMS technology and advanced signal processing should be developed.

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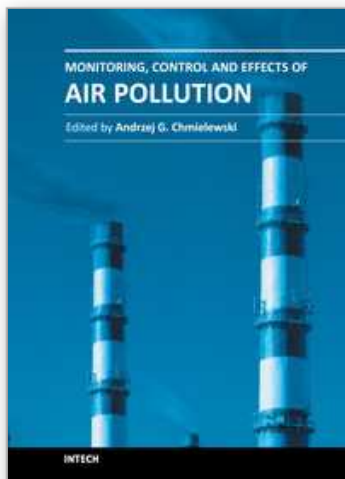
Monitoring, Control and Effects of Air Pollution

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The book addresses the subjects related to the selected aspects of pollutants emission, monitoring and their effects. The most of recent publications concentrated on the review of the pollutants emissions from industry, especially power sector. In this one emissions from opencast mining and transport are addressed as well. Beside of SOx and NOx emissions, small particles and other pollutants (e.g. VOC, ammonia) have adverse effect on environment and human being. The natural emissions (e.g. from volcanoes) has contribution to the pollutants concentration and atmospheric chemistry governs speciation of pollutants, as in the case of secondary acidification. The methods of ambient air pollution monitoring based on modern instrumentation allow the verification of dispersion models and balancing of mass emissions. The comfort of everyday human's activity is influenced by indoor and public transport vehicles interior air contamination, which is effected even by the professional appliances operation. The outdoor pollution leads to cultural heritage objects deterioration, the mechanism are studied and the methods of rehabilitation developed. However to prevent emissions the new technologies are being developed, the new class of these technologies are plasma processes, which are briefly reviewed at the final part of the book.

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