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MEMS/Nano-technologies for Smart Air Environmental Monitoring Sensors

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Abstract

The importance of air quality monitoring is rapidly increasing. Even though state-of-the-art air quality monitoring technologies such as mass spectrometry, gas chromatography, and optical measurement enable high-fidelity measurement of air pollutants, they cannot be widely used for portable or personalized platforms because of their high cost and complexity. Recently, personalized and localized environmental monitoring, rather than global and averaged environmental monitoring, has drawn greater attention with the advancement of mobile telecommunication technologies. Here, micro- and nano-technologies enable highly integrated and ultra-compact sensors to meet the needs of personalized environmental monitoring. In this paper, several examples of MEMS-based gas sensors for compact and personalized air quality monitoring are explained. Additionally, the principles and usage of functional nanomaterials are discussed for highly sensitive and selective gas sensors.

Keywords: gas sensor, MEMS sensor, nanomaterials, air quality sensor

1. INTRODUCTION

Air pollution is becoming an increasingly serious problem every year. Air pollution caused early death of 7 million people globally in 2012, according to the World Health Organization (WHO). It is especially prevalent in industrial and metropolitan cities. Significant gases that contribute to air pollution include sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen oxide (NOx), ozone (O_3), particulate matter (PM), and volatile organic compounds (VOC). SO_2 gas is generated from the oxidation of sulfur-containing materials. The major sources of SO_2 are from combustion of fuels (such as coals and petroleum) in power plants, refinery facilities, and household fireplaces. CO gas is generated from the incomplete combustion of carbon-containing materials. This can bind with hemoglobin to form carboxyhemoglobin (COHb) and inhibit the oxygen supply in the lungs, and therefore can result in suffocation.

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NO_X gas is formed when ambient nitrogen is oxidized at high-temperature, high-pressure conditions (such as in car engines, power plants, and chemical factories). Although it is less toxic than CO, it can react with moisture to form nitric acid vapor, which causes problems in the lungs. O_3 gas is generated when VOC, NOx, and CO gases undergo photochemical reactions under ultraviolet light. It can cause various respiratory problems (such as asthma, pulmonary inflammation, and lung disease). PM is a collection of solid particles and liquid droplets suspended in the air, which originate from rocks, soil, automobile emissions, chemical plants, and other sources. PM can cause a number of health effects such as lung irritation, asthma, and heart problems. VOC is a collection of organic chemicals with high vapor pressure such as toluene, acetone, benzene, and xylene, which often exist in aerosol sprays, cleaners, paints, and solvents. They can cause several health problems, such as headache, dizziness, and damage to the liver and kidneys.

The abovementioned air pollutants can cause serious damage to human health, and therefore their continuous monitoring is crucially important. There are established monitoring technologies and systems that are already being used in public locations and the data from these platforms are compared with the standard criteria. These methods include pulsed ultraviolet fluorescence, non-dispersive infrared, chemiluminescence, ultraviolet photometry, and beta ray absorption. Pulsed ultraviolet fluorescence uses the fluorescence light from gas molecules that are under ultraviolet (UV) illumination, whose wavelength range depends on the type of gas. The fluorescent light is passed through a bandwidth filter, followed by detection with a photomultiplier tube (PMT). In the non-dispersive infrared method, infrared (IR) light is passed through a gas chamber and absorbed by gas molecules. Strong absorption occurs at particular wavelengths, which depend on the type of gas molecule. The light intensity is decreased according to the Beer-Lambert law and can be detected by IR photodetectors. The chemiluminescence method depends on the reaction of a particular target gas and light emission from the reaction. For example, NO molecules can react with O_3 molecules, forming NO_2 molecules and generating infrared light with a peak wavelength of λ = 1200 nm. In the ultraviolet photometric method, the absorption of light at particular wavelength is strong, depending on the type of target gas. For example, O_3 has a strong UV absorption at λ = 254 nm. At this wavelength, other gases such as CO, CO_2, NO, and NO_2 do not interact with light, which provides very high selectivity to O_3 gas. The beta (β) ray absorption method is typically used for particulate matter (PM) monitoring. In this method, the intensity of the beta ray is attenuated by the PM concentration.

Although these methods are very accurate and well-established, they are expensive and complicated, and thus are not appropriate for personalized environmental monitoring.

2. SOLID-STATE GAS SENSORS

Compact, inexpensive, and simpler sensors based on solid-state devices have been developed as alternatives to the abovementioned standard air quality monitoring systems. Although they do not provide high accuracy as compared to the standard air quality monitoring methods, they are very useful for low-power, personalized, and mobile gas detection. Conventional solid-state gas sensors include metal oxide-based chemiresistive sensors, electrochemical sensors, and catalytic reaction sensors. First, metal oxide-based chemiresistive sensors utilize the change in electrical resistance of metal oxide films by reaction with reducing or oxidizing gases. For example, n-type metal oxide semiconductors (such as SnO_2) absorb oxygen molecules from the ambient air, forming negative oxygen ions, which results in the generation of an electron depletion layer at the surface. If the metal oxide film is exposed to reducing gases such as hydrogen, surface-adsorbed oxygen molecules react with the reducing gas, reducing the depletion layer and increasing free electrons in the metal oxide. As a result, the electrical resistance of the metal oxide film is decreased. Second, the electrochemical sensor is based on the electrical potential or current generated by an electrochemical reaction of gases with solid electrolyte materials. In an amperometric sensor, electrical current generated between working and counter electrodes is measured. In a potentiometric sensor, the Nernst potential generated between working and reference electrodes is used. In both cases, the current or potential is determined by the concentration of the target gases. In addition, by choosing appropriate solid electrolytes, selectivity to a particular gas can be obtained. As an example, CO molecules can react with H_2O on the working electrode and generate H^+ ions, which then can transport through a proton ion conductor and finally react with O_2 molecules to form an H_2O molecule at the counter electrode. This series of reactions generates an electrical current between the working and counter electrodes. In a catalytic reaction sensor, temperature change from a catalytic chemical reaction is detected. Typically, this sensor is fabricated on a ceramic body coated with catalysts, where a temperature sensor continuously monitors the change in temperature from the catalytic chemical reaction. If a combustible gas is exposed, a catalytic reaction occurs at the surface of the sensor and increases the temperature, which is monitored by a resistive temperature detector (RTD).

All of these solid-state gas sensors are fabricated in compact packaging and sold at much lower prices than the standard air quality monitoring systems, which were mentioned in Section 1. However, these solid-state sensors are still bulky and expensive, and require large electrical power for applications in the next generation of IT platforms such as wearable electronic devices or mobile telecommunication gadgets. Therefore, new platforms for gas sensors should be developed for these applications in order to achieve truly personalized environmental monitoring.

3. MEMS TECHNOLOGIES FOR INTEGRATED GAS SENSORS

In the previous section, the needs of ultra-compact, low power, highly integrated gas sensors for wearable, Internet of Things (IoT), and telecommunication devices were briefly discussed. Micro-electromechanical systems (MEMS) technology is among the essential and promising developments that can meet these requirements. MEMS devices consist of micromachines for sensors, actuators, and electronic circuits in single chip, and are typically fabricated by microfabrication processes on silicon substrates. MEMS technology can optimize device performance by accurate control of electrical characteristics via doping, surface coating, gate potential application, or temperature modulation with integrated microheaters. Examples of MEMS-based chemical sensors include:

- Chemical field-effect transistor (ChemFET) sensor: An array of multiple ChemFETs can be used to detect pH in a liquid environment in real time [1]. Hizawa et al. realized a 10 × 10 ChemFET array device with integrated circuits for real-time 2D mapping of pH. Here, the surface charge of a ChemFET changed by pH modulates a potential well, which results in a charge transfer to the readout circuit. Miniaturization of the sensor array in microscale and integration with signal processing circuits enable novel applications such as real-time 2D imaging of micro-chemical environments.
- Microcantilever array sensor: An array of microfabricated cantilevers functionalized with different receptor molecules can be used as chemical sensors [2]. Here, the reaction of target molecules causes mechanical deflection by increasing the mass or surface stress. As an example, a microcantilever sensor array was used for the detection of biomolecules such as DNA by surface coating with various DNA oligonucleotides. Lange et al. [3] developed a polymer-coated resonant cantilever array for sensing volatile organic compound (VOC) gases. By the reaction with gas molecules, the resonance peak of the microcantilever is changed, which is then detected by using integrated piezoresistive sensors.
- Surface acoustic wave (SAW) sensor: This type of sensor is based on the modulation of surface acoustic waves by the chemical reaction of target molecules. Here, acoustic waves are generated by the excitation of a piezoelectric substrate with an input transducer (IDT). After travelling through the surface, acoustic waves are detected by output electrodes. A chemical reaction on the substrate alters the characteristics of surface acoustic waves. In the work of Sehra et al. [4], an electronic tongue based on surface acoustic waves was developed that can discriminate between different liquid chemicals. Their device could differentiate between the four basic flavors (sourness, saltiness, bitterness, and sweetness) because of their different relative permittivity and conductivity. Varghese et al. developed a SAW sensor for ammonia (NH_3) gas sensing [5]. By combining piezoelectric ST cut quartz crystals with a nanoporous anodized aluminum oxide (AAO) layer, they could detect NH_3 gas with a frequency shift of ~0.001% per percentage of NH_3, and realized a fast response time (30–40 sec) at room temperature. Here, the nanoporous AAO surface provides a high surface area for improved reaction with the target gas.

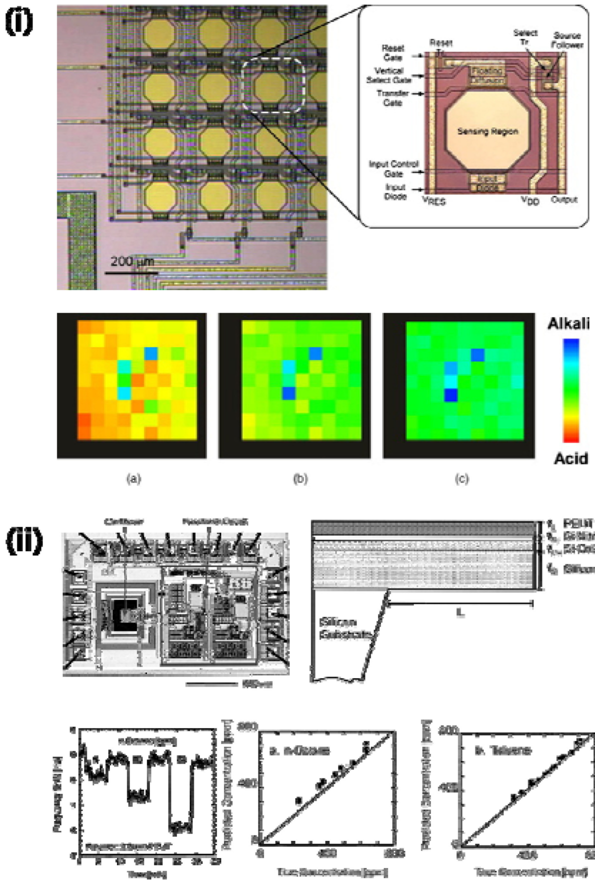

Fig. 1. Examples of MEMS chemical sensors: (i) 10 × 10 ChemFET sensor array for 2D pH mapping (reproduced from [1]); (ii) Microcantilever sensor for the detection of VOCs (reproduced from [3]).

- Chemoresistive sensor: As explained above, metal oxide thin films or metal oxide particles change their electrical resistance by chemical reactions with reducing or oxidizing gas molecules. They exhibit different responses depending on their semiconducting behaviors (i.e., n-type or p-type). However, this type of sensor requires a high operating temperature (300–400 °C) for vigorous reactions with gas molecules, and therefore requires high electrical power for heating. A MEMS platform such as a suspended MEMS plate or bridge structures coated with sensing materials enables miniaturization of the heated sensing area and thus can minimize the heating power consumption. Another challenge of metal oxide-based chemoresistive gas sensors is relatively low selectivity to particular target gases, which can be partially solved by using an array of heterogeneous metal oxide materials. Guo et al. [6] developed a 4 × 4 array of gas sensors with metal oxide materials on MEMS microheaters and on-chip electronic circuits. By using suspended microheaters, heating zones could be isolated from electronic circuits and a highly integrated gas sensor array with on-chip electronics could be realized.

- Microcalorimetry sensor: The enthalpy and heat capacity of a sensing structure can be changed by chemical reaction with target gas because most chemical reactions involve heat absorption or extraction. Examples of calorimetric chemical sensing include flammable gas sensing in a catalytic reaction chamber and glucose sensing on an oxidize-immobilized sensor. In the work of Yasuda et al., a catalytic microcalorimeter was developed for the detection of carbon monoxide (CO) [7]. The change in temperature from the catalytic reaction with the target gas is measured by an integrated platinum thin film-based resistive temperature detector (RTD). Selective detection of CO could be realized by using catalytic molecular sieves.

4. ONE-DIMENSIONAL NANOMATERIALS FOR GAS SENSORS

As mentioned previously, MEMS technology can realize highly compact, low-power, and integrated gas sensing devices for mobile and personalized sensing applications. Another innovative technological approach for chemical sensors is nanotechnology in which functional nanostructures are used as the device components. Unique physical and chemical properties of nanostructures, such as high surface to volume ratio, quantum confinement, bandgap tuning, and high chemical reactivity enable the dramatic improvement of chemical sensors.

Among several types of gas sensors, semiconductor-based chemoresistive sensors are the most widely used because of their simple working principles, device structures, and instrumentation. For gas sensor applications, metal oxide nanowires, carbon nanotubes, and conductive polymer nanofibers are being used as sensing materials. As mentioned earlier, chemoresistive gas sensors are based on the change of charge carrier density in the depletion layer and resultant electrical resistance by reaction with gas molecules. One-dimensional (1D) nanomaterials have large surface-to-volume ratios and thus provide higher sensitivity and response speed. Various approaches for the synthesis, surface functionalization, and integration of 1D nanomaterials are utilized in order to enhance the sensitivity, selectivity, and response speed of gas sensors.

Metal oxide-based chemoresistive gas sensors have been actively developed because of their simplicity as well as high

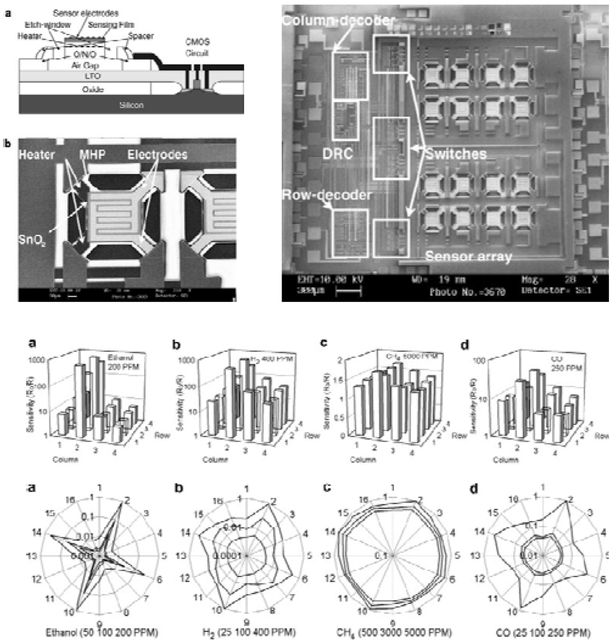

Fig. 2. MEMS chemoresistive gas sensor array: 4 × 4 array of gas sensors with metal oxide materials on MEMS microheaters and on-chip electronic circuits (reproduced from [6]).

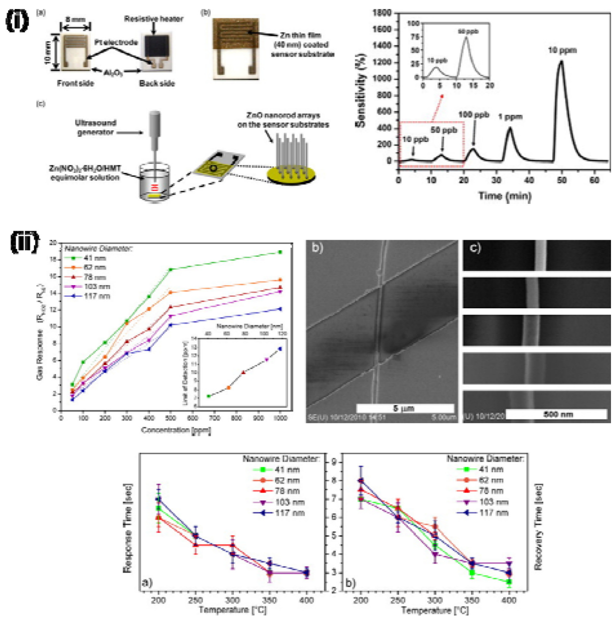

Fig. 3. 1D nanomaterial (metal oxide)-based gas sensors: (i) ZnO nanorods for NO_2 gas detection (reproduced from [8]), (ii) SnO_2 nanowires for NO2 gas detection (reproduced from [9]).

sensitivity. Tin oxide (SnO_2), copper oxide (CuO), tungsten oxide (WO_3), zinc oxide (ZnO), and indium oxide (In_2O_3) nanowires can function as sensing materials for various types of gas analytes. As mentioned previously, metal oxide materials require high operational temperatures for vigorous reaction with target gas molecules and therefore require high electrical power to heat the sensing materials. Alternatively, surface functionalization of metal oxide nanomaterials with catalytic metal nanoparticles or in-situ doping with appropriate impurities can be used to reduce the operating temperatures while maintaining high sensitivity and response speed. A few examples of metal oxide nanomaterial based chemoresistive gas sensors and their operation mechanisms are listed in the following:

ZnO nanorods for NO_2 sensing: Vertically aligned ZnO nanorods (average diameter ~50 nm) were synthesized by using a sonochemical reaction method on a Pt electrode-patterned alumina substrate [8]. This sensor exhibited a very low detection limit of 10 ppb for NO_2 gases.

SnO_2 nanowires for NO_2 sensing: SnO_2 nanowires with various diameters (40–120 nm) were synthesized by chemical vapor deposition (CVD) and used for the detection of NO_2 gas [9]. The smaller the nanowire diameter was, the higher the sensitivity became because of the increased surface to volume ratio.

TiO_2 nanowires for CO and NO_2 sensing: TiO_2 nanowires were synthesized by using a hydrothermal reaction, followed by surface modification with Pt nanoparticles via sputtering [19]. The sensitivities of TiO_2 nanowires to CO and NO_2 gas could be enhanced by surface coating with Pt nanoparticles. The Pt nanoparticles spill the gas molecules onto the surface of the TiO_2 nanowires and thus increase their reactivity with gas molecules.

Conductive polymers (such as polypyrrole (PPy), polyaniline (PANI), and polythiophenes (PTs)) and carbon nanotubes (CNTs) are excellent materials for gas sensors because of their high sensitivities to target gases at room temperature. Their sensor characteristics can be enhanced by surface coating or doping with metal nanoparticles or metal oxide materials. Conductive polymers and CNTs possess mechanical flexibility and thus have been actively developed for flexible electronics platforms.

- PANI nanofiber-based room temperature sensor: PANI nanofibers were synthesized by using a wet chemical reaction [11]. The PANI nanofiber sensor could detect 10 ppm of NH_3 with moderate response and recovery times of 427 and 180 s at room temperature.
- CNT and PPy composite sensor: PPy, CNT, and their composite sensors were fabricated and used for the detection of NO_2 gas [12]. Single wall carbon nanotubes (SWCNTs) and PPy were fabricated by DC arc discharge with a mixture of graphite powders and wet chemical reaction, respectively. The CNT/PPy composite exhibited improved sensitivity of several times that of PPy or SWCNT single-material sensors.
- PPNI and TiO_2 composite sensor: PANI and PANI/TiO_2 composite sensors were developed and utilized for the detection of NH_3 and CO gases [13]. Both PANI and PANI/TiO_2 thin films could be synthesized by using a wet chemical method. The PANI/TiO_2 composite sensor exhibited higher sensitivity, faster response, and faster recovery to NH_3 and CO gases because the junctions of PANI and TiO_2 provide a positively charged depletion layer that enhances the electron migration from TiO_2 to PANI.
- Flexible gas sensor by SWCNT on polyimide substrate: Flexible gas sensors consisting of SWCNTs on a polyimide substrate were developed by Wang et al. [14]. The sensor could detect 1 ppm dimethyl methylphosphonate (DMMP) vapor and exhibited stable response even under mechanical bending because of its mechanical flexibility and robustness.

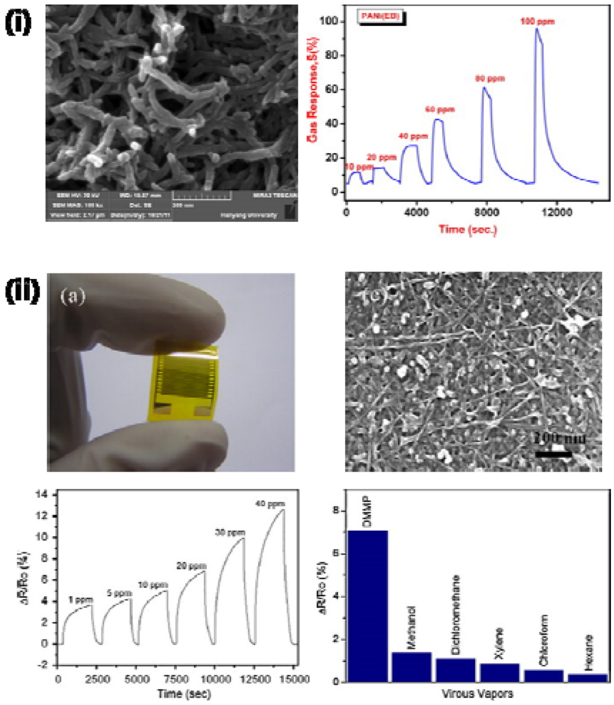

Fig. 4. Gas sensors based on conductive nanofibers and carbon nanotubes: (i) polyaniline nanofiber sensor for NH_3 detection (reproduced from [11]), (ii) carbon nanotube sensor for DMMP detection (reproduced from [14]).

5. CONCLUSIONS

In this article, we discussed the new technologies for personalized air quality monitoring. Although solid-state gas sensors such as conductometric or electrochemical sensors have fulfilled the needs of personalized gas sensing, they are not satisfactory for application to the next generation mobile, IoT, and wearable applications because of their limited functions, high power consumption, and large size. MEMS enables highly integrated and multifunctional gas sensors. In addition, by using functional nanostructures with MEMS devices, we can further enhance the performance of gas sensors, which have higher sensitivity, reduced power consumption, and smaller size. It is believed that the micro- and nano-technology will revolutionize the paradigm of gas sensors and improve the quality of our lives by realizing truly personalized air environment monitoring.

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