An Overview of Metal Oxide Semiconducting Sensors in Electronic Nose Applications

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Abstract

Accurate analysis of electronic nose depends on several factors such as sensor types, pattern recognition algorithm, ambient temperature and humidity. The sensor is one of the important factors for effectively and accurately odor measurement of electronic nose. This study aimed to propose the advantages and disadvantages of MOS metal oxide semiconduting sensors,

one of the most used sensors, by analyizing performance, structure, operation principles of them. Consequently we aimed to extract beneficial information about electronic nose studies based on MOS sensors.

1.INTRODUCTION

In recent years, electronic noses have been widely used in various fields such as quality control of foods and beverages, public safety, air protection and medical applications. Major

advances in information and gas sensor technology could enhance the diagnostic power of future bio-electronic noses and facilitate global surveillance models of disease control and management Odor Category such as [1-7]:

- Detailed Description Of Odor (Disease, Marker Chemical, Breath, Sweet)
- Fruity; alcoholic (Alcohol abuse, phenol exposure, Ethanol, Phenol)
- Minty, wintergreen (Patient covering alcohol abuse, Menthol, wintergreen)
- Fruity; pear-like (Chloral hydrate poisoning, Chloral hydrate)
- Dried malt, burnt sugar, yeast-like (Methionine malabsorption)
- Violets (Turpentine poisoning, Turpentine)
- Sweet mouth (Portacaval shunt, portal vein thrombosis, diphtheria, Musty)
- Rancid butter (Hypermethioninemia)
- Rancid butter, fishy, musty (Tyrosinosis, tyrosinemia)
- Musty fish, raw liver, new-cut clover (Hepatic failure, Mercaptans)
- Feculent (Intestinal obstruction, esophageal diverticulum, Foul)
- Foul, putrid (Lung abscess, intranasal foreign body, Bad breathe, Infection: teeth, nose, tonsil, stomach, esophagus)
- Ozaena, very foul odor (Infection or cancer of nose or sinuses)
- Severe bad breath (Trench mouth, amphetamine abuse)
- Garlic (Phosphorous, arsenic, malathion poisoning)
- Rotten eggs (Hydrogen sulfide poisoning)
- Pungent, unpleasant, heavy (Schizophrenia; trans-3-methyl-2-hexanoic acid, Other)
- Bitter almond

Electronic nose is a detection system which consists of a multisensor array with partial specifity and appropriate pattern recognition software, capable of idetifying and recognizing odors [8]. Electronic Nose mimics the human sense of smell by generating a unique response to each odorant. The system detects the odour by an array of sensors and transduces the gaseous molecules into electrical signals. Electronic nose measurement is influenced by certain factors, such as sensor type, pattern recognition system, humidty and temperature of ambient. Using an appropriate sensor type for any chemical odorant or mixture extremely effects measurement accuracy of e-nose. In this study, we have investigated Metal Oxide Semiconducting - MOS sensors, which are widely used in many VOC analysis applications. We have aimed to propose strength and weakness of MOS sensors by analyzing their structure and operating factors.

Sensors in an array are the main components of the electronic nose. Because the sensitivity and specifity of sensors mostly influence accuracy of detecting and recognizing of odorants. The role of sensors in electronic nose is human receptors. When an odor is presented to the sensors, they generate a unique response to the odor to be considered as a signature or characteristic of the odor. Each sensors reflects unique response to the odor. The responses of each sensors comprise the characteristic of the odor. The output of odor sensors is then filtered and converted to the digital form by a transducer. Then, the digital output is processed for classification and recognizition by pattern recognition algorithm. Schematic view of electronic nose can be seen in Figure 1 [9].

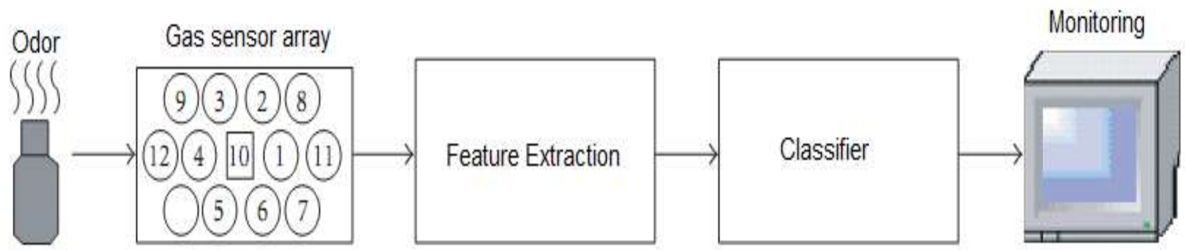

Figure 1. A shematic view of Electronic Nose System

2.Principles of Sensor System

In their widely accepted definition, International Union of Pure and Applied Chemistry (lUPAC) define the sensor that "a chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated" [10].

Chemical sensors typically are composed of two main parts, a receptor and a transducer. The receptor converts chemical information into a form of signal, which can be measured by the transducer. Basically, the gas sensor operates interacting between gas molecules and sensor-coated or sensing materials which enable electrical current passing through the sensor. The modulated electrical current then is converted to a recordable signal [11].

There are many different types of electronic nose sensors ranging from metal-oxide gas sensors (MOS), metal-oxide semiconductor field effect transistors (MOSFET), conducting polymer gas sensors, acoustic wave gas sensors, quartz crystal microbalance sensors (QCM), surface acoustic wave devices (SAW), field-effect gas sensors, electrochemical gas sensors, pellistors, fiber-optic gas sensors. As well as sensor technology, the type of sensing material influences measurement of gas molecules of odors. They are categorized in regard to additive doping materials, the type and nature of the chemical interactions, the reversibility of the chemical reactions and running temperature. The generic types of sensors involved with its sensing element are summarized in Table 1. [12]

Table 1. Types and mechanisms of common electronic-nose gas sensors

Sensor Type	**Sensing Material**	**Detection Principle**
Acustic sensors: Quartz crystal microbalance (QMB); surface acoustic wave (SAW)	Organic or inorganic film layers	mass change (frequency shift)
Calorimetric; catalytic bead	pellistor	temperature or heat change
Metal-oxide semiconductor field effect transistors (MOSFET)	catalytic metals	electric field change
Conducting polymer sensors	modified conducting polymers	resistance change
Electrochemical sensors	solid or liquid electrolytes	current or voltage change
Fluorescence sensors	Fluorescence-sensitive detector	fluorescent-light emmissions
Infrared sensors	IR-sensitive detector	Infrared-radiation absorbtion
Metal-oxide semiconductor (MOS)	doped semi-conducting metal oxides (SnO2, GaO)	resistance change
Optical sensors	photodiode, light-sensitive	light modulation,

		optical changes

Transducer devices in electronic-nose sensors have various types which are based on certain principles, such as electrical measurements, including changes in current, voltage, resistance or impedance, electrical fields and oscillation frequency as well as measurements of mass changes, temperature changes or heat generation. The light characteristics such as changes in light absorbance, polarization, fluorescence, optical layer thickness, color or wave length are utilized as transducing priciple for measuring optical sensors.

Sensor performance is measured by a set of parameters. Certain important parameters and their behaviors can be defined as [13]:

- *Sensitivity:* It is a change of measured signal per analyte concentration unit that has been more and more attention, and many studies have been conducted to enhance the sensitivity of sensors.
- *Selectivity:* It refers to capabilities of the sensor's response towards a group of gas analytes or a single one.
- *Stability:* This parameter defines the ability of the sensor that provides reproducible results for a certain period of time.
- *Detection limit:* The parameter is utilized to state the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- *Response time:* It is the time that involves for measurement of gas analyte.
- *Recovery time:* It is the time that occurs during recovering to the sensor's initial or baseline value.
- *Life cycle* is the period of time that denotes the maximum time over continuously operating of the sensor.
- *Operating temperature:* The temperature with minimum and maximum values for effecitive analysis.

For reliable and ideal measurement of an analyte, the sensor should meet certain parameteres. These parameters are high sensitivity, dynamic range, selectivity and stability; low detection limit; good linearity; small hysteresis and response time; and long life cycle.

3.Structure of Metal Oxide Sensors (MOS)

Metal Oxide Semiconductor (MOS) was a first developed sensor array, which detected 20 odours[14]. MOS sensors are relatively simple electronics featured by high sensitivity (in the order of parts per billion ppb), low cost, high speed response. The MOS sensors consist of sensing element, sensor base and sensor cap. Figure 2a and 2b illustrates a basic structure of MOS sensor [15]. The sensing element contains a sensing material and a heater. According to the target odorant or gas, different materials such as Tin dioxide (SnO2), Tungsten oxide (WO3) are used as a sensing element. The gas molecules, known also Volatile Organic Compounds (VOCs) interact with a doped semiconducting material deposited between two metal contacts over a resistive heating element, which operates from 200 °C to 400 °C. Once a VOC passes over the doped oxide material, the resistance between the two metal contacts changes according to the concentration of the VOC. The registered signal depends on the change of resistance produced by the gas flow during the measurement [16].

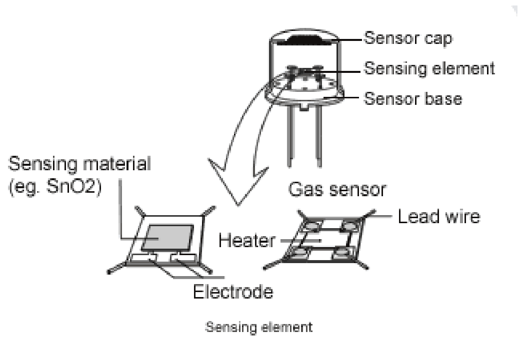

Figure 2.a) Structure of the MOS Sensor

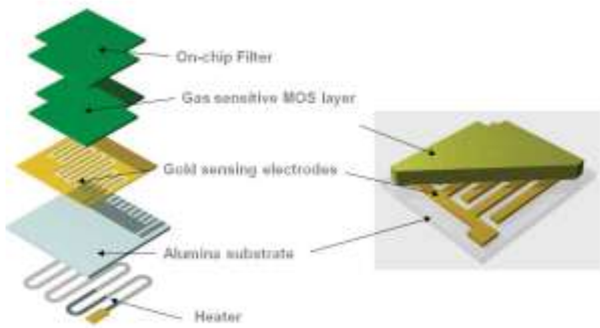

Figure 2.b) General form of MOS Sensor

(Courtesy of Capteur Sensors and Analysers)

3.1. Advantages of MOS sensors

Metal-oxide sensors are widely used in many sensor based applications, e.g. electronic noses. The MOS sensors are known as the most used sensors in the market because:

1. MOS sensors responds to a wide range of compounds such as oxidizing compounds (zinc-oxide, tin-dioxide, titanium-dioxide, iron oxide) and some reducing compounds, mainly nickel-oxide or cobalt-oxide [17]
2. MOS sensors are characterized by high sensitivity (sub-part per billion ppb levels for some gases) to the oxidizing and some reducing compounds.

3. Compared to other analytical instruments, MOS are far more inexpensive.
4. MOS sensors have a short response time to the analytes.
5. With its small size, MOS sensors are compatible with intregrating into analyzing instrument.
6. Since MOS sensors are relatively simple electronics they are easily fabricated.
7. MOS sensors have ability to operate in high temperature and pressure.
8. They have long lasting life to operate.

3.2. Disadvantages of MOS Sensors

Despite many advantages of MOS sensors, there are some challenges to overcome. These are:

1. High selectivity of MOS sensors influences the analysis. Because they are sensitive simultaneously to wide range of reducing and oxidizing gases. For instance, a typical carbon monoxide (CO) sensor may respond significantly to hydrogen, ethylene, and isobutylene. When these gases are presented, the sensor would response as CO presence, which may not be true.
   It is very difficult to achieve an absolutely selective metal oxide gas sensor in practice, and most of the MOS sensors have cross-sensitivity at least to humidity and other vapors or gases.
2. MOS sensors cannot operate at high temperature. Because MOS sensors are less sensitive with high temperature. Thus, the sensitivity of sensors reduces with high temperature.
3. Operation of MOS requires more power compared to the of others as a result of working at high temperature.
4. MOSs are susceptible to humidity causing drift on analysis.
5. Accuracy rate of gas analysis is low compared to the other analyzing instruments.
6. Their low stability and long range drift are imptortant issue. This causes uncertain results and the need to frequently recalibrate or replace sensors [18].

4.MOS Sensors in Applications

Since 1962, several studies have been conducted on gas analysis based on metal oxide semiconducting sensors. It is diffucult to review all studies about MOS sensors due to high number of studies on them. We were able to briefly propose a literature review based on MOS sensors applications.

In 1962, Saiyeama et. al. first introduced MOS sensors using zinc oxide thin film layers[19]. After this time, several studies conducted using different doping and sensing materials. In 1982, the first sensor array were designed using MOS sensors which detected 20 gases [14].

As the discovery of the hundred VOCs existed in human breath, MOS sensor arrays have been used to detect disease diagnosis such as lung, liver, asthym failures. Through numerous studies on diseases diagnosis from breath analysis, we were able to report some of the outstanding studies about MOS sensors. Blatt et. al. concluded remarkable detection results of lung cancer diagnosis using MOS sensors[20]. In another research, Guo et. al. conducted a study on diagnosis on diabetes, renal disease, and airway inflammation using mos sensor array, and they resulted that breath analysis can be employed for early diagnosis of many diseases [21]. MOS sensors have been used extensively to measure and monitor trace amounts of environmentally important gases such as carbon monoxide and nitrogen dioxide. In another study, the human body armpit could be detected by MOS sensors [22]. With the power of neural network as pattern recognition Bucak and Karlik evaluated performance of the application developed for hazardous odor recognition using OMX-GR electronic nose equipped with a MOS sensor [6]. They achieved hundred percent success rate of classification for hazardous odor recognition system based. Using a novel fuzzy clustering neural network algoritm, Karlik and Yuksek conducted a real time odor analysis by an electronic nose instrument sensed by a MOS sensor [9]. They concluded that based on a neural network, electronic nose with MOS sensor could be used to recognize odor compounds.

5. CONCLUSIONS

In this study, we aimed to give general perspective about MOS sensors. To achive this, this study observed operation principles, measurement parameters, sensing material of MOS sensors. Despite its some drawbacks for analysis, the results reflect that MOS sensors are reliable and prominent materials for odor analysis. It can widely be employed as an array sensors in electronic nose applications.

The classification performance of an e-nose device is highly dependent upon the quality of the features extracted from its sensors' dynamic response. Although some improvement in an e-nose device was achieved in terms of increasing classification performance, reducing the number of sensors, combining multiple classifiers for dissimilar odor datasets, and extending application to odor mixture analysis, further improvements are necessary if an e-nose is to become a smarter and smaller device. Ideally, if the response of the sensor to an odor is consistent to the same odor over time (reproducibility), high classification performance can be easily obtained from simple classifier algorithms. However, reproducibility is not achieved in practice because of the interaction of the odor with the sensor's surface and several interfering environmental factors, such as temperature and relative humidity which results in an inconsistent sensor's response[23]. Consequently, reliability of e-nose device could be improved by further developing sensor technologies.

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