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Review of Gas Sensors used in Electronic Nose and Odor Sensing Technology

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***Abstract*— Over the last decade, there have been major advances in the area of "e-sensing", in both, technical and commercial aspects. An e-nose is a device that mimics human olfactory system. It perceives odor/flavor and characterizes each odor with a unique signal pattern. E-nose comprises of sensor block followed by an analysis block which performs feature extraction and pattern recognition. This paper reviews different types of gas sensors employed in electronic noses till date. It describes the operating principles of major sensor types and their applications. It lists the various advantages and disadvantages of all the mentioned types that are used in e-nose.**

Keywords—Electronic nose (e-nose), Quartz crystal microbalance (QCM), conducting polymers, Surface acoustic waves (SAW), metal oxide semiconductor field effect transistor (MOSFET), optical sensors.

I. Introduction

THE electronic nose (e-nose) is the closest electronic equivalent to the human nose. They respond to a wide range of compounds, and the data is processed in real time using advanced pattern recognition and artificial intelligence techniques, hence enabling the users to readily extract relevant information that is also reliable. Electronic nose devices have been largely advanced during the last twenty years due to the discovery of new applications in diverse fields of research and applied sciences. Also, advances in sensor technologies and microcircuits have helped. E-nose helps in identification, comparison, quantification, data storage and retrieval of different odors. This document is a review of gas sensors that are used in e-nose. E-Nose is more efficient than gas chromatography and mass spectrometry because the latter techniques are not portable, expensive and usually do not work in real time.

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The e-nose simulates the mammalian olfactory responses and hence attempts to emulate the mammalian nose. Fig 1 shows the scheme of the human olfactory system and Fig 2 portrays how an e-nose follows the same principles.

The odor under test is made to pass across an array of sensors which induces a reversible chemo-physical change in the sensing material, hence causing a change in its electrical properties. These changes are converted to electrical signals using transducers and are processed using a pattern recognition system. Hence, every array produces a response pattern that is unique for a given odor.

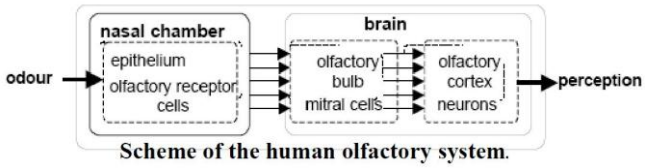

Fig 1. Scheme of the mammalian olfactory system [10]

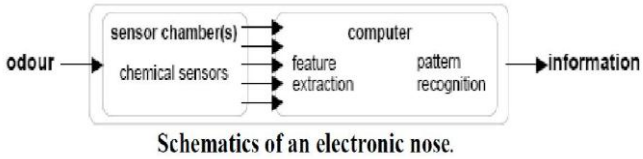

Fig 2. Electronic nose based on the human olfactory system [10]

The most commonly employed sensors in e-nose, namely optical sensors, MOSFET type sensors, conducting polymers, quartz crystal microbalance and surface acoustic wave sensors, are dealt in section II, in the same order.

II. Sensors used in e-nose

A. *Optical Sensors*

Optical sensors are a common type of sensors that are used in e-nose. They detect and measure the modulation of light properties such as wavelength, polarization, absorbance and other optical properties. Commonly used and the simplest optic sensors use colour changing indicators such as metallopophyrins, to measure absorbance with an LED and photodetector system upon exposure to gas analytes [1].

Two types of optical sensors are the colorimetric and fluorescence sensors. Thin films of dyes that respond to chemicals are used in colorimetric sensors, while fluorescence sensors detect fluorescent light emitted by the gas analytes at a low wavelength.

The sides or tips of the optical fibers are coated with fluorescent dye impregnated polymer, as shown in the fig 3. On interacting with the gas analytes, the dye's optical properties change, such as wavelength shift, intensity change, spectrum change or lifetime change [2][3]. It was proposed that these changes can be used for measurement of odour responses [25][26].

The nature of the fluorescent dye or a mixture of dyes is the most important factor that affects the sensitivity of the optical sensors. The nature of the polymer controls the response of the sensors [2][3]. Adsorbents, such as alumina, can be added to the polymer to improve the response by lowering the detection limits of the sensor [4].

Optical sensors coated with polyanaline have been found to detect ammonia at concentrations as low as 1ppm and the linear dynamic range was between 180 and 18,000 ppm[5].

Optic sensors have been used for the development of nucleic acid probes for various genomic applications, microbial pathogen detection methods, and live cell based sensors for monitoring specific chemicals and toxins in the environment [6]. Kuang *et al.* developed an *Escherichia coli* living bacterial cell-based optical fluorescence biosensor array to detect the presence of genotoxins (toxins that cause DNA damage) in the environment.

Optical sensors have a number of advantages over other sensor transduction mechanisms. Gas sensors that use optical fibres achieve high sensitivity, selectivity and stability than non-optical methods. They have a low response time and are not deteriorated performance-wise, by environmental changes [7]. Sensor designs are highly versatile and numerous configurations are possible.

However, there are several disadvantages associated with optical sensors. The cost of these sensors is comparatively high, and the sensors have a reduced lifespan due to photo-bleaching effects [2]. Temporal responses remain consistent and are unaffected by photo-bleaching [4].

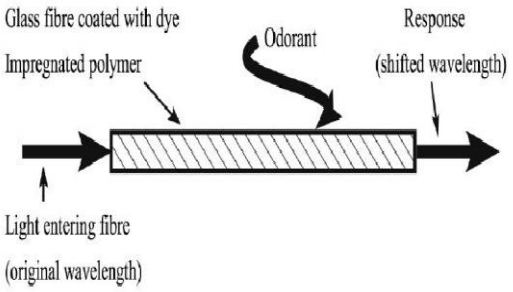

Fig 3. A gas optical fiber sensor. The odorant interacts with the material and causes a shift in the wavelength of the propagating light wave. [8]

B. *Metal-Oxide-Semiconductor Field-Effect-Transistor type gas sensor and its use in the e-nose*

The term Metal-Oxide-Semiconductor describes the different layers of a MOSFET. The gate is a metal contact, mainly polycrystalline silicon. The gate is attached to an oxide insulator, which is next to a semiconductor. All MOSFET devices have three terminals: source, drain and gate. The source provides charge carriers (electrons for an n-type MOSFET, and holes for a p-type MOSFET), and the drain collects the charges. The structure of a MOSFET is shown in fig 4.

The MOSFET sensors were firstly reported by Lundström in 1975 based on the tendency of a number of metals to adsorb and dissolve hydrogen [11].

The MOSFET sensor is used as a transducer that converts the chemical signals to electronic signals.

This sensor works on the principle that the threshold voltage of the MOSFET changes when the poly silicon of the gate reacts with certain gases. This happens due to some changes in the work functions of the metal and oxide layers [3].

IEEE Spectrum September 1998, Volume 35, Number 9, pp. 22-34

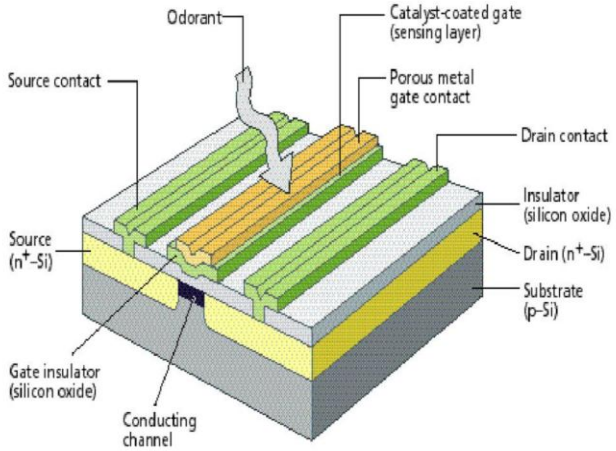

Fig 4. The structure of a MOSFET [9]

The primary operating mechanism is conductivity modulation of the channel by field effect. Changes in the drain-source current and the gate voltage have been used as the response mechanisms for the MOSFET gas sensors as they are affected by changes in the work function [2][12]. A polycrystalline semiconductor has a grainy structure, and hence, by coming into contact with other grains, can alter its conducting properties. The electric properties at the surface of the thin-film and the surface boundaries of the grains are affected by the adsorption and desorption of gas molecules.

There are widely two types of adsorption phenomena; physisorption and chemisorption. Physisorption is based on Van-der-Waals forces, which are forces of electrostatic nature. Chemisorption is caused by stronger covalent forces (Geistlinger *et al* , 1993).

The change in the threshold voltage or the drain-source current has been found to be in direct relation to the amount of analyte. Thick films have been used to detect hydrogen and hydrogen sulphide while thin films are more porous and
can detect amines, alcohols and aldehydes [13].

For the physical changes in the sensor to occur, the metal- insulator surface must be easily accessible to the gas. Therefore, either a porous gas sensitive gate
material is used to facilitate diffusion of gas into
the material [14] or polymers are used as agate materials [15]. These MOSFET sensors that use polymers as gate materials are more commonly called as PolFETs, and can be operated at room temperature.

The operating temperature for these MOSFET sensors varies between 50-170° C [13]. The higher the temperature,higher are the response and recovery times [16]. The gate metal thickness is altered to provide different selectivity patterns to different gases [17]. The composition of the catalytic metal also affects the sensitivity of the sensor. According to Kalman et al., the detection limit of MOSFET devices for amines and sulphides was 0.1 ppm with Pt, Ir and Pd gates and the maximum response was approximately 200mV.

The main advantages of using MOSFET sensors in an e-nose are, since they are micro-fabricated (by CMOS technology), they have a good reproducibility and hence are low cost. They are also small in size. MOSFET are robust sensors with low sensitivity to humidity. Their robust characteristic makes them particularly useful in environmental applications. They show good sensitivity to toxic and flammable substances.

The disadvantage is that the catalyzed reaction products must penetrate the catalytic metal layer in order to affect the gate; the package must therefore have a window for gas inlet. MOSFET sensors also undergo baseline drift [2]. The operating temperature also has serious effects on the sensitivity of the sensor, and hence, can be a major difficulty in hand-held e-nose.

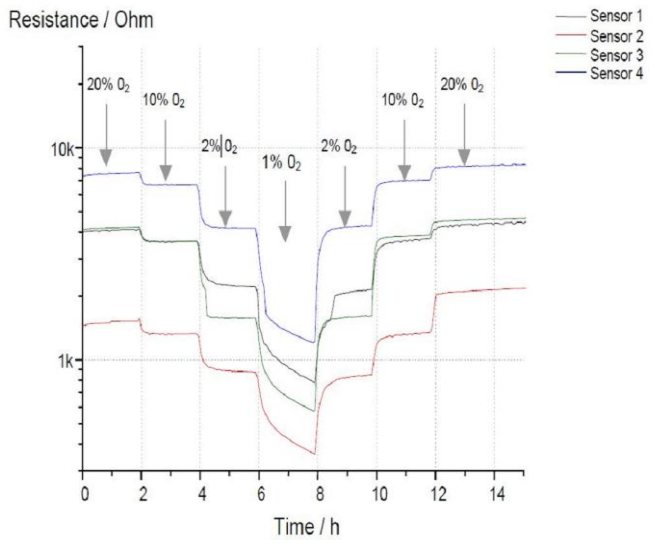

Fig 5. Resistance measurement of a thin-film of tin dioxide, four different sensors, at approximately 400°C for different oxygen concentrations in N_2. The measurement has been performed in IPM´s gas laboratory. The deposition technology for these layers and the one used for the MOSFET gas sensors analysed in this work are the same. [18]

C. *Surface Acoustic Wave Sensors*

Surface Acoustic Wave sensors (SAW) are a type of microelectromechanical system (MEMS). They sense a physical phenomenon based on the modulation of surface acoustic wave. SAW technology is based on the principle of piezoelectric effect. It converts electrical energy into an acoustic wave using an interdigitated transducer (IDT). The acoustic wave travels across the surface of the device substrate to another interdigitated transducer (IDT), which converts the acoustic wave back to an electrical signal. The characteristics of surface acoustic wave can be modified by the change in the surface properties which result due to several physical phenomena.[8]

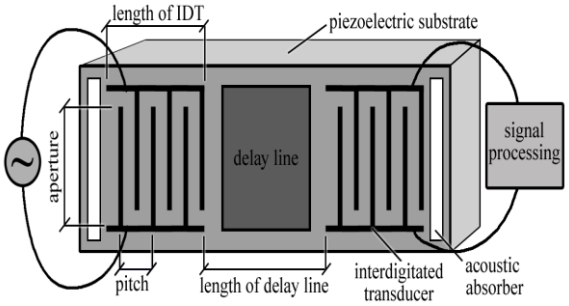

Fig.6: General structure of a surface acoustic wave sensor with signal processing unit and with connections to an ac voltage. In some sensors, reflectors replace the acoustic absorbers in order to reduce the insertion loss. By replacing the output of IDT and coupling its input to an RF antenna rather than a voltage source a wireless surface acoustic wave sensor can be made.

The basic SAW device is shown in fig 6. (Jared Kirschner, 2010). It consists of piezoelectric substrate, an input interdigitated transducer on one side of the surface, and a second, output interdigitated transducer on the other side of the substrate. The space between the IDTs, across which the surface acoustic wave propagates, is known as the delay line. A gas sensitive membrane is placed between the two transducers. An ac signal is applied across the input IDT. This creates a two dimensional wave that propagates along the surface of the crystal at a depth of one wavelength. [3]. The mass of the gas sensitive membrane changes on interaction with a compatible analyte. This alters the frequency of the wave. The change in the frequency is given by equation 1.

$$\Delta f = \Delta f_p . c_v . k_p / \rho_p \quad (1)$$

Where Δf_p is the change in frequency caused by membrane, c_v is the vapor concentration, k_p is the partition coefficient, ρ_p is the density of the polymer membrane used [2],[3],[12]. Generally liquid crystal or polymeric sensitive membranes are

used. Photolithography, screen printing techniques [20], dip coating and spin coating techniques are used to produce SAW devices commercially.

The operating frequencies for SAW devices range from 100 to 400 MHz [3]. The sensitivity of the SAW device to a particular odor depends on the sensitivity of the gas sensitive membrane used. The sensitivity is defined as differential response, i.e. Δf_p/ppm of odour [3][21]. System detection limits are in the parts per trillion ranges. SAW devices are relatively cheaper than the QCM because of the fact that the three dimensional MEMS processing is not required. Differential measurements eliminate common mode effects. SAW devices have high sensitivity and fast response time. They can detect a broad spectrum of odors because of the availability of the wide range of gas sensitive coatings. [22][23]. The fabrication of the SAW devices is compatible with the current planar IC technology. However, due to the high frequency of operation, they have poor signal to noise performance. [17]. Another disadvantage of these devices is the requirement of the frequency detectors, whose resonant frequencies can drift as the active membrane ages [24].

D. *Quartz Crystal Microbalance*

Quartz is a crystal that experiences the piezoelectric effect. The applications of piezoelectric effect are numerous and in various fields. It has been employed in high power sources, sensors, actuators, frequency standards, motors, etc. The work function of the crystal is well understood. Applying alternating current to the quartz crystal will induce oscillations. With an alternating current between the electrodes of a properly cut crystal, a standing shear wave is generated. The Q factor, which is the ratio of frequency and bandwidth, can be as high as 10^6. Such a narrow resonance leads to highly stable oscillators and a high accuracy in the determination of the resonance frequency.

This property of precision and ease is exploited in the concept of QCM sensor. When the sensor is exposed to atmosphere, it adsorbs certain gases and the mass of the crystal changes. This leads to a change in the very stable frequency produced by the crystal, by measuring the change in the frequency we can analyse the atmosphere/gas. With some simplifying assumptions, this frequency change can be quantified and correlated precisely to the mass change using Sauerbrey's equation(1957). This is demonstrated by equation 2.

$$\Delta f = \frac{-2 * fro^2}{A * (\rho q * Gq)^{.5}} \Delta m_q \qquad (2)$$

Where: Δf is the frequency change due to addition of mass Δm_q onto the vibrating quartz surface area A , with the resonant frequency f_{ro} , = 2.648 $g\ cm{-}3$ ρ_q is quartz density and = 2,947x1011 g cm-1 s-2 G_q is its shear modulus.

The advantage of using QCM is that they have fast response times, typically 10s [27], however, response times of 30 s to 1 min have been reported [22].

QCM gas sensors have many disadvantages which include complex fabrication processes and interface circuitry, [2], and poor signal to noise performance due to surface interferences and the size of the crystal [2].

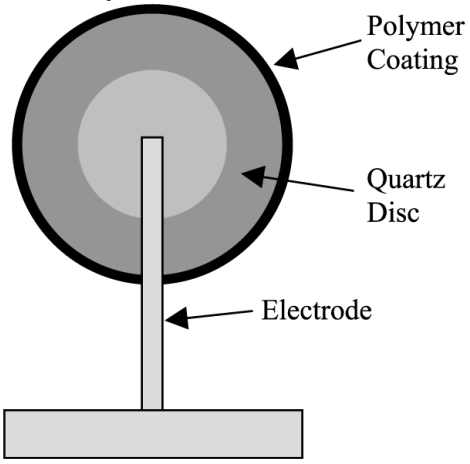

Fig 7. Quartz crystal microbalance with polymer coating [8]

E. *Conducting Polymers*

A polymer is a chemical compound or mixture of compounds consisting of repeating structural units created through a process of Polymerization.

Polymers exhibit both metallic and semi-conductor properties which is a unique nature. They conduct electricity due to the presence of alternate single and double bonds in the backbone structure. The backbone pi-electrons also induce other electronic properties such as low energy optical transitions, high electron affinity and low ionization potential. These polymers are generally known as intrinsically conductive polymers (ICP) or electro active polymers. These properties of ICPs' are exploited in the building of an electronic nose/Gas sensor.

As gas sensors, polymers adsorb gases which leads to the change in their conductance i.e their resistance [28][16]. The key advantage of these polymers is that they exhibit high sensitivity to very minor perturbances. Typically polymers such as polypyrole, polythiophene and polyanaline are employed in gas sensors [29]. Generally an array of sensors is used to detect and analyze a characteristic odor.

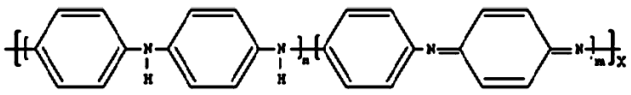

Fig 8. Structure of polyaniline[31]

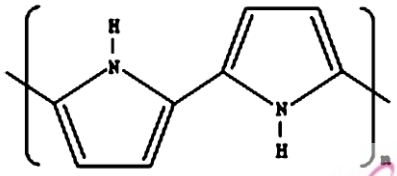

Fig 9. Structure of polypyrole[31].

The conductivity of ICPs is affected in a number of ways.

1. Interchain conductivity (due to alterations in the backbone).
2. Intermolecular conductivity (due to electron hopping to different chains).[30]
3. Ionic conductivity (due to proton tunneling induced by hydrogen atoms).[12]

ICP are fabricated either electrochemical techniques or by chemical polymerisation. To apply voltage across the ICP and to measure the change in its resistance/conductivity when exposed to certain gases (in case of e-nose), polymers are fabricated between two inter-digitised electrodes. These sensors can be built in nanoscale and microscale as well which makes it.

ICPs have a number of advantages when used in e-nose systems. Increased discrimination when developing sensor arrays can easily be achieved with these materials as a wide range of ICPs are available on the market [12].

ICPs are cost effective and they also provide fast response, recover quickly and have a wide range of working temperatures. This makes them one of the most widely used gas sensors.

The disadvantages concerning ICP being used as sensors are listed below:

-The signal transduction mechanisms are poorly understood.

-The properties of the ICP slowly drift through time and hence frequent replacement of the sensor is required.

-They have very short lifetime around 9-18 months when exposed to atmosphere due to oxidation. [17]

1. Electronic nose sensor technologies

Sensor type	Principle of operation	Fabrication methods	Availability	Sensitivity	Advantages	Disadvantages
Metal oxide	Conductivity	Microfabricated	Commercial, many types	5–500 ppm	Inexpensive, microfabricated	Operates at high temperature
Conducting polymer	Conductivity	Microfab, electroplating, screen printing	Commercial, special order only	0.1–100 ppm	Operates at room temperature, microfabricated	Very sensitive to humidity
Quartz crystal microbalance (QCM)	Piezoelectricity	Screen printing, wire bonding, MEMS	Commercial, several types	1.0-ng mass change	Well-understood technology	MEMS fabrication, interface electronics
Surface acoustic wave (SAW)	Piezoelectricity	Microfab, screen printing	Commercial, several types	1.0-pg mass change	Differential devices can be quite sensitive	Interface electronics
MOSFET	Capacitive charge coupling	Microfab	Commercial, special order only	Parts per million	Integrated with electronic interface circuits	Odorant reaction product must penetrate gate
Optical	Fluorescence, chemolumines-cence	Dip coating, MEMS, precision machining	Research	Low parts per billion (ppb)	High electrical noise immunity	Restricted availability of light sources

Fig 10. Table summarizing the sensor types and details as mentioned above (IEEE Spectrum September 1998) [32].

Conclusion

This paper discussed in detail about the major types of gas sensors used in e-nose namely optical sensors, MOSFET type sensors, SAW sensors, QCM sensors and conducting polymers. The operating principle, manufacturing techniques, advantages, disadvantages and applications of each type have been explained in this paper. Fig 10 provides a brief comparison of the various sensor types used in e-nose.

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