Ceramic Based Resistive Sensors

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Abstract. This paper reviews the current status and research trends of two types of ceramic based resistive sensors, thermistors and gas sensors. The issues and challenges associated with their development for high temperature applications are examined and discussed. Worldwide research efforts in ceramic based resistive sensors, devoted mostly to resolve the issues of selectivity and stability, are also reviewed. These efforts tend to integrate the results obtained from both empirical and basic science approaches, and focus on various stages of sensor development, including development of new material systems, sensor fabrication and manufacturing techniques, and smart sensor arrays.

Keywords: resistive sensor, semiconducting gas sensor, thermistor

1. Introduction

The electrical resistance of ceramic materials is known to change with external energy inputs of various forms, including electrical, radiation, thermal, mechanical, magnetic, and chemical. Each phenomenon has been employed for various sensor/actuator applications, and is covered elsewhere in this issue. This review focuses on oxide based resistive sensors in which the electrical resistance or impedance changes in response to change in ambient temperature (thermoresistive) or chemical gaseous species (chemoresistive), i.e., thermistors and gas sensors, respectively. The ceramic based resistive gas sensors are often referred to as semiconducting gas sensors in the literature, as the sensing mechanisms are closely linked to the semiconducting nature of oxide materials.

There are several recent monographs and books on sensors which contain detailed account of ceramic based resistive sensors [1–7]. Notably, the sensor series, edited by Göpel et al. [3,4], contain updated overviews of various types of sensors. Issues and challenges associated with the development of semiconducting gas sensors and thermistors for high temperature applications (above $1000°(C)$) are the

focus of this review. Important research trends are also examined and discussed. Such a review is timely, as the development of resistive sensors appears to have come to a state where difficult issues are hindering their widespread applications, as was pointed out by Lampe et al. for ceramic gas sensors [8]. Similar difficulties were experienced in the authors' laboratory in the development of ceramic gas sensors and thermistors for high-temperature applications.

2. Semiconducting Gas Sensors

Semiconducting gas sensors were the most investigated solid-state resistive gas sensors in the past few decades, since the first product emerged in 1968 [7,9]. As with other types of sensors, the increasing interest and effort are in parallel with continuing technological progress and industrial needs. This includes the need to increase efficiency in combustion and other chemical processes, as well as the increasing concerns over environmental pollution and safety in industrial activities involving poisonous gases.

The base materials most widely used for semiconducting gas sensors are oxides, of which the conductivities are known to change with gas

composition in the surrounding atmosphere. Oxides such as ZnO, TiO$_2$, and SnO$_2$ are the most widely investigated. They not only have been adopted as the model systems for fundamental studies, but also as base materials for the development of various sensors for the detection of gases such as H$_2$, CO, NO$_x$, CH$_4$ and other hydrocarbons. Table 1 lists some of the SnO$_2$ based material systems reported in the literature for the detection of various gases.

The fact that a single oxide such as SnO$_2$ can be used as a base material for the detection of a variety of gases seems to suggest an unlimited potential for oxide based semiconducting gas sensors. There are, however, at least two issues, selectivity (or cross-sensitivity) and stability (or aging), which have limited their applications and further development. Poor selectivity toward the monitored gas or cross-sensitivity toward other gases makes a sensor's output unreliable. Also, aging or poor stability causes a sensor's calibration curve to drift with time.

In the past, there has been considerable effort to resolve the selectivity issue. The information summarized for SnO$_2$ in Table 1 indicates two commonly adopted approaches for improving selectivity. These are: (i) addition of suitable catalysts and/or dopants, and (ii) selection of appropriate operation temperatures. Other approaches, as summarized by Göpel et al. [11], include:

- development of *new* base oxides other than the *traditional* oxides such as SnO$_2$ and TiO$_2$.
- use of impedance (frequency modulation) instead of dc resistance measurements.

- use of filtration membrane or multilayer sensors for selective adsorption or reactions.
- using arrays of differential sensitive sensors in conjunction with pattern recognition and multi-component analysis.

In comparison to the selectivity issue, the problem of stability is rarely addressed in the literature. This does not mean that the stability issue has less impact on the usefulness of a gas sensor. It is rather an engineering issue often addressed at the prototyping and manufacturing stages, and is difficult to resolve due mostly to the lack of precise knowledge of the underlying physical and chemical processes.

Though the problems of selectivity and stability are considered as two major challenges to the development of oxide based gas sensors, the complexity varies with the sensing mechanisms utilized for specific applications. In general, based on the physical origins responsible for a sensor's response, two types of oxide gas sensors can be distinguished: bulk conduction based and surface layer controlled gas sensors. The latter is schematically illustrated in Fig. 1, which includes a limiting case where the surface layer extends to the intergranular contact and forms a potential barrier commonly known as the Schottky barrier. In the following, the sensing mechanisms of these two types of sensors will be briefly reviewed to provide background for the associated issues and challenges.

2.1. Bulk Conduction Based Gas Sensors

The bulk conduction based sensors involve gas-solid reactions in series with change in stoichiometry in the bulk (grains) of the sensor materials. In other words,
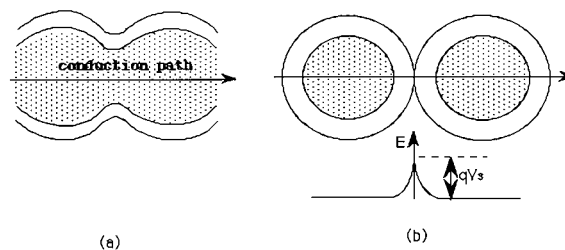
Table 1. SnO$_2$ based gas sensors for emission detection

Materials	Gas	Temperature (°C)	Ref.
SnO$_2$ + ThO$_2$ + SiO$_2$	CO	190–210	11
SnO$_2$ + Sb	CO	440–460	12
SnO$_2$ + Bi$_2$O$_3$	CO	430–500	13
SnO$_2$ + Pd + Cu	CO	100–200	14
SnO$_2$ + Sb$_2$O$_3$	H$_2$	180–440	15
SnO$_2$ + Pd	H$_2$	230–260	16
SnO$_2$ + In	H$_2$	330–380	17
SnO$_2$ + Bi$_2$O$_3$	NO$_x$	200–430	18
SnO$_2$ + Cd	NO$_x$	250–400	19
SnO$_2$ + V	NO$_x$	290–310	20
SnO$_2$ + Pd	NO$_x$	200–300	12
SnO$_2$ + Bi$_2$O$_3$	CH$_4$	480–520	21
SnO$_2$ + Bi	CH$_4$	430–480	22
SnO$_2$ + La$_2$O$_3$	C$_2$H$_5$OH	310–330	23
SnO$_2$ + Pd	C$_2$H$_5$OH	380–450	24

Fig. 1. Models for surface layer controlled gas sensing, showing two limiting cases: (a) continuous surface layer and (b) formation of a potential barrier across the intergranular boundary.

the change in bulk conductivity (σ) is a reflection of the equilibration between the oxygen activity in the oxide and the oxygen content (oxygen partial pressure, P_{O_2}) in the surrounding atmosphere. This can be described by the following equation:

$$\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right)P_{O_2}^{\pm\frac{1}{n}} \qquad (1)$$

Where σ_o is a constant, E_a is the activation energy for conduction, the value and sign of $1/n$ are determined by the type of dominant bulk defect involved in the equilibration process. The positive and negative signs of $1/n$ correspond to p-type and n-type conduction, respectively. In principle, all semiconducting oxides can switch from one type of conduction to another under certain conditions. Figure 2 shows such a transition in SrTiO$_3$ in the temperature range of 600 to 1000°C [25]. Nevertheless, in a given conduction regime, the sensitivity of a semiconducting gas sensor is determined by the value of $1/n$, according to Eq. 1. The higher the value of $1/n$, the greater is the sensitivity of the sensor. Since Eq. 1 describes a conductivity characteristic common to oxides, virtually all oxides are oxygen sensors. In practical applications, however, the usefulness of an oxide for oxygen sensing is determined by factors such as material stability, response time, and the temperature and oxygen partial pressure range of the conductivity regime (p- or n-type conduction). The latter is of particular importance, as the transition of the conduction mechanism (change in the sign and value of $1/n$) in an oxide may make the output unreliable.
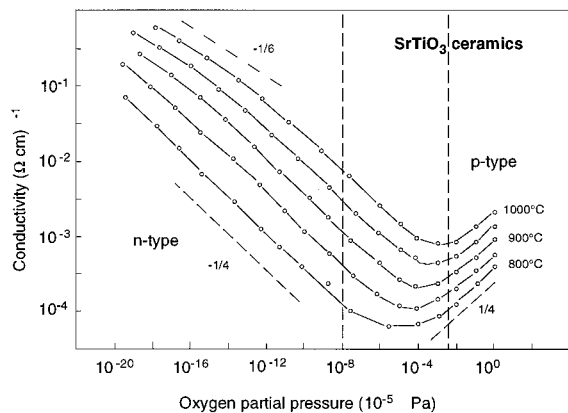
Many semiconducting oxide systems have been investigated for oxygen sensor applications, notably the automotive exhaust gas oxygen (EGO) sensors for air-to-fuel ratio control. TiO$_2$, Nb$_2$O$_5$, CoO, CeO$_2$, and SrTiO$_3$ are some examples. Despite their automotive applications, the development of bulk conduction based gas sensors are less attractive compared to that of surface layer controlled gas sensors. Four reasons are given here. First, bulk conduction based sensors are limited to direct monitoring of oxygen. Secondly, resistive type bulk conduction based EGO sensors have not been able to replace zirconia electrolytic type EGO sensors, due to lack of reliability. Thirdly, as bulk conduction based sensors rely on diffusion to change stoichiometry, response times are often slower. Finally, since the sensing behavior is mostly explainable and predictable based on well established thermodynamic principles [26], there is less incentive to study them in further details.

2.2. Surface Layer Controlled Gas Sensors

Surface layer controlled gas sensors utilize the change in the concentration of conduction electrons as a result of chemical reactions at the surface. These reactions, chemisorption and/or catalytic reactions, modify the defect states of the oxide's surface layer to a depth of a few micron or less. The working temperature of this type of sensor is usually lower than that of bulk conduction based gas sensors, typically 400–800°C, depending on the base oxide and the targeted applications. The temperature should be low enough to allow sufficient surface adsorption and slow down the bulk defect equilibration processes, but high enough for catalysis reactions and charge transfer between the surface layer and the bulk interior. The use of a particular catalyst (metal or oxide) for the detection of a specific gas species, is frequently determined by the chemisorption and/or catalytic reaction of the specific gas. For this reason, second phases or catalysts are normally added to the system to enhance sensitivity and selectivity (Table 1).

As depicted in Fig. 1, two cases are distinguished in surface layer controlled gas sensors. Both are characterized with a thin surface layer (1000 Å $-$ 1 μm), and rely on gas-solid reactions which change the trapping density either on the oxide surface (Fig. 1(a)) or at the intergranular interface (Fig. 1(b)). They are different in whether the surface layer is continuous or is interrupted by potential barriers

Fig. 2. Conductivity characteristics of SrTiO$_3$ [24].

across intergranular boundaries. It should be noted, however, that such a distinction is rarely supported by straightforward experimental evidence, and is often based on theoretical assumptions.

Gas sensor utilizing the presence of Schottky barriers at the grain-boundaries (back-to-back Schottky barrier) typically consists of *poorly* sintered body, porous thin- or thick-film, where the grains contact only at the neck through which the surface layers overlap. Figure 3 illustrates this arrangement and corresponding energy band diagram, using an *n*-type semiconducting oxide as an example. When exposed to oxidizing gas species such as oxygen, adsorption of oxygen on the surface results in removal of electrons from the conduction band by transfer to the oxygen (trapping the electron) thereby forming a Schottky barrier at the intergranular contact, resulting in a decrease in the conductance. The conduction is then determined by the height of the barrier (qV_s) at the intergranular contacts:

$$\sigma_s = \sigma_o \exp(-qV_s/kT) \qquad (2)$$

Where σ_s and σ_o are the conductivity and pre-exponential constant, respectively. When exposed to a reducing gas such as CO, the adsorbed CO reacts with the adsorbed O^- (or O^{2-}), releasing the trapped electrons back to the conduction band, subsequently lowering the barrier height and the resistance. At temperatures up to about 450°C, the characteristics of SnO_2- and ZnO-based CO sensors have been reported
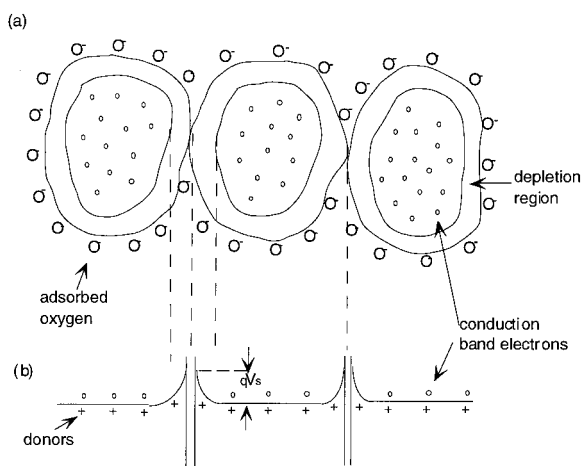
to follow the Schottky barrier controlled conduction mechanism [27,28]. This effect was also attributed to the sensing behavior of anatase titania (TiO_2)-based ceramic material CO sensors, recently developed in authors' laboratory [29–32]. Based on the ac electrical data combined with X-ray and XPS observations [32], the surface reactions tend to support a chemisorption process involving CO adsorption and ionization on the titania surface. Assuming that CO molecules adsorb directly on the exposed TiO_2 surface, according to:

$$CO(g) + TiO_2 \rightarrow CO_{ads}(TiO_2) \qquad (3)$$

The adsorbed species ionizes on the surface, releasing an electron into the conduction band:

$$CO_{ads}(TiO_2) \rightarrow CO_{ads}^+(TiO_2) + e^- \qquad (4)$$
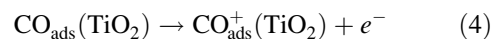
Upon increasing CO concentrations, more charge carriers (e^-) are released to the conduction band, and the resistance decreases. An increase in conduction band electrons effectively lowers the intergranular barrier height as well as the depletion region thickness. The decrease in depletion thickness is observed as an increase in the grain-boundary capacitance [32].

Surface layer controlled gas sensors are usually used for monitoring of gas species other than oxygen. It is important to note, however, these sensors may require an atmosphere of fixed (known) oxygen partial pressure to yield a reliable output. Oxygen may affect the chemisorption process, the barrier height, compete with the sensing gas (e.g., NO), or react with the bulk and subsequently change the surface condition. In some cases, a surface layer controlled gas sensor can be made to reduce or eliminate oxygen interference via the addition of a second phase and/or heat-treatment at elevated temperatures. The purpose is to fix or freeze the bulk defect concentrations. However, these sensors must be used at low temperatures to avoid interdiffusion or release of the frozen bulk defects.

As stated earlier, a major challenge of oxide-based chemical sensors is to make it selective to the targeted species in a gas mixture. In the authors' laboratory, anatase TiO_2 was found to be sensitive to both CO and H_2 [30,31]. This was resolved by the addition of a second oxide, such as alumina (Al_2O_3) or yttria (Y_2O_3). In the case of TiO_2-10 wt% Al_2O_3 (TA), the sensor response was exclusively dependent on the hydrogen concentration; the presence of CO or CO_2 did not affect the sensitivity. Conversely, the sensor

Fig. 3. Compressed powder model for gas sensor showing the (a) depletion region and (b) energy barrier (qV_s) at the intergranular contact.

based on TiO_2-10 wt% Y_2O_3 (TY) becomes exclusively a CO sensor with up to 400 ppm of H_2 [30]. Neither TA nor TY showed any interference from NO_x.

Though the addition of a second phase seems to be a feasible approach for achieving selectivity, the process of choosing the additive becomes a challenge due to the lack of basic understanding. Also, experience gained from empirical approaches or screen tests on one base material (e.g. SnO_2) often are not directly applicable to another (e.g. TiO_2). A sensor material system becomes even more unpredictable when it consists of more than two components, which is not uncommon as seen from Table 1 for SnO_2 based gas sensors. From the chemisorption point of view, complications may include co-adsorption and gas-gas interactions, when more than two potentially *active* gases are present.

The problem of stability associated with surface layer controlled gas sensors can be realized by considering the case of Schottky barrier controlled gas sensors. This type of sensor consists of incompletely sintered bodies in which the intergranular contacts are not identical. The electrical response can be considered as a collective phenomenon based on the existing distribution of contact areas and barrier heights. In other words, a Schottky barrier gas sensor can be considered as an assembly of micro-sensors at the intergranular contacts. At relatively high temperatures, this distribution may change with time due to the change in microstructure, and result in aging or long-term drift.

3. Thermoresistive Sensors: Thermistors

Thermistors are *therm*ally sensitive re*sistors* based on semiconducting oxides. Two types of thermistors are distinguished: NTC and PTC thermistors, according to the sign of the temperature coefficient of resistance. This review will focus only on the NTC thermistors, which are essentially bulk conductance based semiconducting sensors. NTC thermistors have several potential advantages over thermocouples and resistance thermometers (RTDs): (i) higher temperature capability; (ii) no requirement of special extension lead wires and connectors or cold junction compensation; (iii) high sensitivity and signal to noise ratio; and (iv) simple probe construction and signal conditioning leading to low system cost.

The electrical characteristics of NTC thermistors

follow Eq. (1) for bulk conductance based gas sensors. However, there are several differences between these two types of sensors:

- An NTC thermistor, utilizes the temperature dependence exponential term $(-E_a/kT)$ of Eq. (1), while a bulk conductance based gas sensor relies on the oxygen partial pressure term $(P_{O_2}^{\pm 1/n})$.

- NTC thermistors often operate in an atmosphere of constant or known oxygen partial pressure (P_{O_2}), while bulk conductance oxygen sensors work at a fixed temperature maintained by a built-in heater.

- Ideally, materials for NTC thermistors should have high E_a value for higher sensitivity, but small or negligible $P_{O_2}^{\pm 1/n}$ to avoid possible influence from the probing atmosphere. In contrast, materials for bulk conductance based gas sensors should have high $(1/n)$ value for higher sensitivity, and small E_a to minimize errors which could be induced by temperature fluctuation.

However, it should be noted that common low-temperature NTC thermistors do not generally show a P_{O_2} dependence because they are intentionally operated at temperatures below which little or no equilibration occurs between oxide and the gas phase.

The sensitivity of NTC thermistors, φ, is defined as the absolute value of the temperature coefficient of resistivity, α_T:

$$\alpha_T = \left(\frac{1}{\rho}\right)\left(\frac{\partial\rho}{\partial T}\right) = -\frac{B}{T^2} \tag{5a}$$

$$\varphi = |\alpha_T| = \frac{B}{T^2} \tag{5b}$$

where $B = E_a/k$ and is known as the beta factor of an NTC thermistor. It can be seen that φ is proportional to the activation energy of conduction; the larger the activation energy the greater the material's sensitivity to temperature excursion. Equation (5b) also indicates that φ has a strong nonlinear temperature dependence; it decreases with a factor of T^{-2} as temperature increases. For example, a semiconducting oxide with $E_a = 1$ eV has a φ value of about 0.009 at 850°C. At 1700°C, the value decreases to 0.003. This characteristic suggests that it is essential for a high temperature thermistor material to have an activation energy high enough to maintain its sensitivity at high temperatures.

The sensitivity φ defined by Eq. (5b) is called the normalized sensitivity, expressed in terms of percent

change in resistivity per degree change in temperature (%/°C). For practical applications, it is more useful to define the sensitivity as the actual change in resistivity per degree C (e.g., Ω-cm/°C). That is, by taking the temperature derivative of resistivity (ρ), the sensitivity ζ can be expressed as follows:

$$\zeta = \frac{d\rho}{dT} = -\rho \frac{B}{T^2} \tag{6}$$

Low-temperature NTC thermistors are widely used for temperature control and compensation in electronic devices/instruments. Such thermistors used in the temperature range of -100 to 500°C are typically made of transition-metal oxides such as nickel oxide (NiO), iron oxide (FeO), cobalt oxide (CoO), and manganese oxide (MnO) [33]. In the past, oxides of rare-earth elements such as Sm and Tb, have been considered for use at higher temperatures (up to 1000°C) as they are more refractory and usually have temperature coefficients of resistance (α_T) higher than those of the transition metal oxides [34]. However, reliable thermistors for applications near and above 1000°C, are yet to be developed. Typical problems associated with thermistors, such as stability and reproducibility, become even more complicated at high temperatures.

High-temperature NTC thermistor represents a potential area for new materials development. The activation energies and sensitivities (ζ at 1000°C) of yttria and calcium zirconate, along with some other oxides studied in the authors' laboratory are listed in Table 2 [35]. The sensitivities of thermocouple type K and S are also listed for comparison. Note that while thermocouples show changes of the order of hundredths of millivolt per degree change in temperature, ceramic thermistors show resistivity changes of the order of hundreds of Ω-cm.

Table 2. Activation energy (E_a) and sensitivity (ζ) of some of the high-temperature oxides studied (sensitivities of thermocouple type K & S listed for comparison)

Materials	E_a (eV)	ζ at 1000°C(Ω-cm/°C)
CaZrO$_3$	2.3	900
Y$_2$O$_3$	2.0	840
Al$_2$O$_3$	1.6	650
Dy$_2$O$_3$	1.5	300
MgO	1.4	230
Thermocouple Type K	N/A	0.0388 (mV/°C)
Thermocouple Type S	N/A	0.0115 (mV/°C)

Recent research in the authors' laboratory, indicates that the optimization of thermistor performance not only requires an adequate understanding of transport processes across grain boundaries and electrode interfaces, but also requires careful evaluation of environmental effects and packaging issues influencing the sensitivity and accuracy of the device. One of the challenges lies in eliminating the aging behavior that results in the long-term drift of the resistance reading. In the Y$_2$O$_3$-based thermistors, stabilizing the microstructure by doping with ZrO$_2$ seems to eliminate the aging problem [37]. The doping also eliminates the effect of humid environments and minimizes the oxygen partial pressure dependence [35].

Another challenge lies in selecting appropriate electrical contacts and lead wire materials as well as developing a technique to attach them to the sensor. For high-temperature applications, the choice of insulation material plays a critical role in a thermistor's reliability. Recent tests indicate that improving the accuracy of yttria-based thermistors requires developing suitable insulation material; alumina may not be the best choice.

Recently, the use of alumina as a lead wire insulation material for yttria-based thermistors was investigated in the authors' laboratory. The yttria-based thermistor was developed to monitor temperatures up to 1500°C. In the development of prototype thermistor probes, high-purity alumina (99.8% Al$_2$O$_3$) tubing was used for lead wire insulation. It was found that at temperatures above 900°C the alumina no longer provided adequate insulation. A significant leakage current existed across the insulation and formed a shunt circuit in parallel with the sensing thermistor, causing systematic temperature measurement errors at high temperatures. Also, the shunt resistance causing temperature measurement errors were found to vary with the type and concentration of impurities in the insulator.

4. Future Trends and Challenges

As pointed out in the previous sections, selectivity and stability are the major issues limiting wide spread applications and further development of oxide based resistive sensors. Current efforts to resolve these issues tend to integrate the results obtained from both empirical and basic science

approaches, and focus on various stages of sensor development, including development of new material systems for high temperature applications, sensor fabrication and manufacturing, and *smart* sensors (arrays) with signal conditioning and filtration. Also, it should be noted that due to the complexity involved in sensor development, research activities are moving more extensively towards multi-disciplinary collaboration.

4.1. Development of High Temperature Sensors

There is an increasing need for sensors capable of operating at high temperatures (near $1000°C$ or above) for measurement in industrial processes. In the aerospace industry, for example, there is a growing need for gas turbines to operate at higher temperatures for higher operational efficiency with reduced emissions. This requires applications of high-temperature sensors ($> 1000°C$) capable of accurate and reliable monitoring and control of turbine operational process variables, such as temperature, pressure, rotational speed, and exhaust gases. These high-temperature sensors demand higher temperature capability lead wire systems with stable electrical properties. Also, the increased need for in situ monitoring of potentially hazardous gases (e.g., CO, CO_2, NO_x, volatile organic compounds (VOCs) and unburned hydrocarbons), has stimulated considerable activity in the development of new gas sensor technologies.

There are several issues in the development of ceramic based resistive sensors, particularly for the sensing of specific gas species. First, past development on ceramic based sensors have been mostly focused on a few oxide systems (e.g., SnO_2 for gas sensors, and $Ni_xMn_yFe_{3-x-y}O_4$ for thermistors) for applications near $500°C$ and below. These oxide materials often lose their functionality at higher temperatures. Most oxides successfully used for developing specific gas sensors become bulk stoichiometric controlled semiconductor at high temperatures. Schottky barrier layer controlled gas sensors are more difficult to achieve (if not impossible) at higher temperatures, as the sensitivity tends to decrease dramatically due to the decrease in the barrier height. This means that new oxide materials need to be developed for higher temperature applications. This may also include the development of new catalysts and packaging materials and techniques.

4.2. Smart Sensors and Sensor Arrays

There is a trend towards the use of more sophisticated design concepts in the development of new sensor systems, notably so-called smart sensor systems, which combines sensing elements and signal processing, conversion and output units. This approach aims at simultaneous or sequential acquisition of more than one type of signal, mainly to resolve the problem of selectivity. This may include the use of more than two electrodes (arrays of electrodes) on a single sensor body, employment of sensor arrays made of many sensors or a multi-layer sensor with filtering membrane, and applications of artificial intelligence for pattern recognition [36]. The sensor arrays approach, proposed by Clifford [38], is quite appealing as it integrates the limited selectivity of each individual sensor for a finger-print like analysis. In applications, the objective of such an approach may be difficult to achieve, as a sensor array's functionality relies not only on the *right* combination or integration of different sensors but also depends on stability of individual sensors. Any change or drift in one of the sensors requires a system-wise re-calibration or re-programming of the pattern recognition part. In other words, potential applications of a sensor array system are determined by the availability of stable and reliable individual sensors.

Yet another approach was advanced by Malou [39]. Realizing the limitation of solid-state sensors, he proposes a hybrid between a sensor and an instrument. For example, a small array of sensor elements is combined with a short gas chromatograph (GC) column to optimize the MSI-301 Vapor Monitor system [40]. This instrument, shown in Fig. 4, is a temperature controlled GC typically used for analysis of ambient air. It is comprised of a sampling pump, a sample pre-concentrator, a GC column, and a Surface Acoustic Wave (SAW) detector. To increase the selectivity of this basic GC system, a small array of semi-selective chemoresistive elements was devised to replace the typical non-selective thermal conductivity detector. The use of GC column combined with a small array of semi-selective chemoresistive elements eliminates the need for large arrays of chemically ''selective'' compounds as in a *chemical nose*.
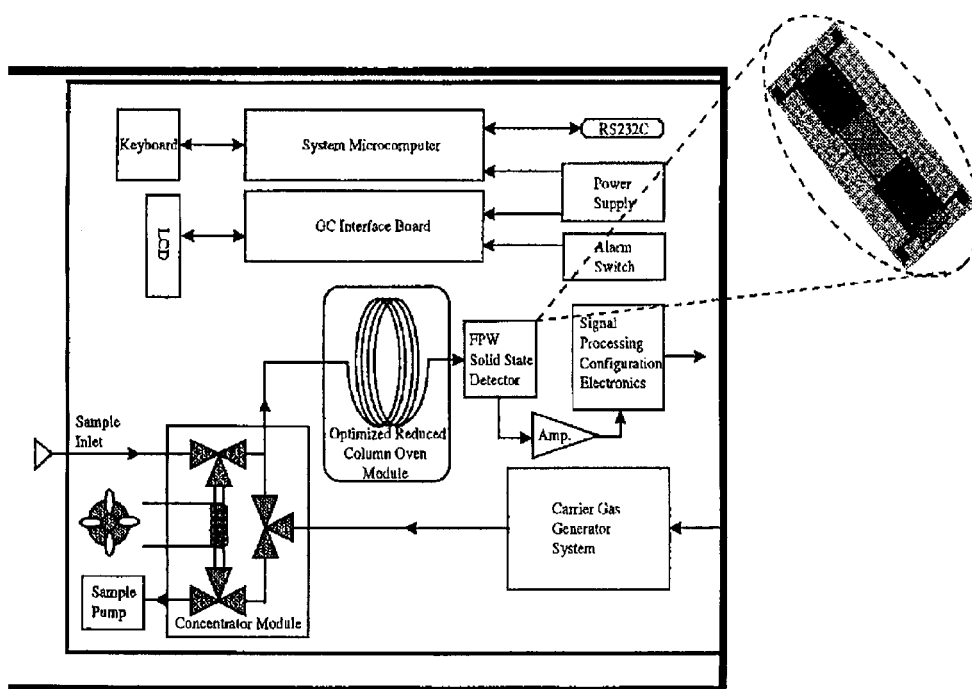
Fig. 4. Schematic of Modified MSI-301 gas chromatograph.

4.3. Device Fabrication and Manufacturing

From device fabrication and manufacturing points of view, besides the issues of poor selectivity and long-term stability, oxide based sensors are also plagued with issues such as poor reproducibility (unit-to-unit consistency) and power consumption (particularly for gas sensors to maintain a constant operating temperature). Poor reproducibility is due to poor control over raw materials and production conditions including forming, firing and electrode attachment [41]. Most of today's commercial sensor devices are produced either by typical ceramic fabrication (sintered body) or thick film processes. Sensors thus produced often have poor unit-to-unit consistency, and therefore require individual inspection and calibration.

Thin film fabrication processes and microma-chining, which are based on well-defined IC deposition and etching processes, are expected to improve the reproducibility and possibly lower the power usage beside its mass production capability [42–44]. However, there are at least two issues

accompanied with the application of IC techniques for the fabrication of oxide based sensors. First, the current thin film technology is mostly silicon based. The use of silicon substrate based sensors limits the upper operating temperature to about 200°C [45]. This not only limits the temperature operation window for optimum performance but also the choice of oxide systems for sensor development. For higher temperature operation, substrates such as TiO_2, Al_2O_3 and MgO have to be used. Here, however, proper selection of substrate and its orientation (single crystal) for a particular oxide system are critical. Otherwise, it may lead to compatibility and stability problems (arising from chemical and thermal mismatch), which may not compensate for benefits gained from the improved reproducibility. Secondly, it has been more difficult to make a compatible thin film as sensitive as the ceramic type thick film devices [46]. In summary, application of IC techniques becomes of obvious advantage only if thin semiconductor oxide films (e.g. tin oxide) can be made with the same sensitivity as the traditional thick sintered film [46].

5. Conclusions

Despite the many problems addressed above, the development of ceramic resistive sensors are expected to continue, and the market appears to be promising. Several emerging research trends contribute to such a perspective: (i) increased efforts in basic studies in recent years resulting in better understanding of sensing mechanisms; (ii) new and improved materials synthesis and device fabrication techniques, and (iii) development of sensors for more specific or focused applications rather than generic applications targeted at all markets. The last aspect is important in that it can help elevate the acceptance level of ceramic based resistive sensors and promote further development for specific sensors for use in various environments.

Development of resistive sensors for industrial applications appears to be more challenging than those for domestic applications. Selectivity and stability issues become even more challenging in harsh industrial environments with high temperatures, high pressures and dynamic gas flows. The increasing need for measurement in industrial processes and products, however, shows promising potential for future growth via innovative scientific and/or engineering approaches. This also opens new avenues of exploration, such as heating elements for high-temperature furnaces, insulating/sheathing materials, and electrical contacts and lead wire materials for high-temperature electronics. What makes this area exciting for future R&D is that the solution to the engineering and technological problems is closely linked with the fundamental knowledge and understanding yet to be uncovered.

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