Development of chemical sensors for monitoring environmental emissions

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ABSTRACT

The need for sensing and monitoring equipment pervades nearly all manufacturing and industrial processes. The purpose of such requirements encompass a range of objectives, including improvement in process efficiency and the reduction of emissions into the environment. The type of monitoring equipment currently in use in manufacturing facilities is first identified and alternate methods and monitoring technologies are introduced. The advantages and limitations of emerging devices, such as those based on chemical sensors for the detection and quantification of gaseous analytes, are described. The in-house research effort in chemical sensors which is ongoing at NRCC is introduced. Complex metal oxides of the perovskite family are the focus for the sensor materials component of the project. Thin films of the perovskites are grown by pulsed excimer laser deposition onto selected substrates for comprehensive evaluation of gas sensor functionality. This exploits the changing electrical resistance of the semiconducting films when they are at elevated temperatures and exposed to gaseous mixtures. The goals of the activity in chemical sensor development include improvement of the sensor performance by materials modification, and the integration of the sensor thin films into silicon based sensor arrays by using micromachined fabrication methods. The details of sensor data obtained with $SrFeO_{2.5+x}$ and related compounds when exposed to oxygen and carbon monoxide are reported. The chemical tunability of the response of sensor materials to specific analyte gases is outlined with relation to metal substitution in the perovskite structure. The development of sensor array devices of the electronic nose type, where the sensor film is integrated with silicon microhotplates, is described.

INTRODUCTION

Nearly all industrial processes and manufacturing technologies depend upon the use of some form of sensor or monitoring equipment to facilitate operation. Parameters which are monitored or measured can be diverse. Depending on the process, they may include chemical and physical quantities or states which can be in a variety of combinations of gas, liquid and solid phases. The range of analysed concentrations, although again dependent on the specific process, can be over several orders of magnitude; parts per billion to tens of percent. This presents a challenge to sensor and monitoring technologies. The driving force behind the requirement for monitoring can be efficiency; (*eg* driven by product or process improvement, minimising operator involvement, more efficient use of feedstock which generally means decreased costs), improved productivity, improved safety and also responding to regulatory issues. The latter need increases annually, and is particularly driven by the requirement in most jurisdictions for emissions monitoring and control (1). The areas of regulatory requirements generally relate to toxic or other hazardous emissions such as greenhouse gases with respect to global warming. Whatever the motive, the use of sensors in an appropriately selected mode can have a positive impact on the environment by, in combination, improving product yields, reducing wasteful use of feedstock and by limiting plant emissions.

In the past, the type of sensing and monitoring equipment used in established manufacturing and industrial facilities has been influenced heavily by what was available and already developed for use in analytical laboratory situations. In some cases these systems are amenable to modification to give field usability, and even some degree of portability. Amongst these types of equipment and techniques, (2), are gas/liquid chromatography, mass spectral analysis, emission spectroscopy, absorption spectroscopy, colourimetric analysis (*eg* Dreager tubes), chemiluminescence and x-ray fluorescence. Some versions of these techniques are suitable for on-line use with near realtime results of several seconds to a few minutes, whilst others operate in batch mode and with a consequent delay in results of up to several minutes or hours. The instrumentation with faster response can be used to rapidly feedback and optimise process conditions. Whatever the equipment of this type, it is high cost and requires regular operator intervention to ensure calibration and adequate maintenance. The size, cost and maintenance prohibit the general deployment of equipment of this type in multiple locations, so comprehensive plant, fence-line and multi-point analyses are not usually obtained. Also, domestic use is not likely because of the high capital cost involved in purchase and installation.

To address the limitations above, alternate means of detection have been explored by a large number of groups in the research and development field. The impetus has been from both the viewpoint of decreasing the cost and of increasing access and implementation of monitoring and sensor devices (3). One broad family of such an emerging technology for gas phase emissions is based on the exploitation of solid state

chemistry to provide a sensing or detection device. Similar technologies are also being explored for liquid phase monitors. This type of device is generically known as a chemical sensor. These devices exploit in some form, the chemistry which occurs when a target analyte gas is in contact with a specific sensor material. Accompanying the chemical reaction or interaction in the sensor material are associated changes in one or more physical properties which can be directly measured to provide a means of sensor signal transduction. A large number of combinations of chemistries and transduction modes have been identified, (*eg* semiconductor, potentiometric, amperometric, catalytic, optoelectronic *etc*), and exploited by various research groups. Some of these are reviewed elsewhere (4). Advantages conferred upon such sensor devices include compact size, reduced cost of manufacture, real time analysis, arrays, integration with other technology platforms and multi point deployment. Some versions of these are currently available for domestic carbon monoxide monitoring, for example.

Chemical sensors can, however, have some limitations when compared to the larger, available analytical tools. Generally, they are less specific to a given analyte and can exhibit interferences with other gases, particularly those which possess similar chemistry. Consequently, for effective deployment, some information or pre-assessment of potential interferences in the ambient is sometimes needed such that the sensor and its application are appropriately matched. Significant research effort is currently focussed onto the improvement of the functionality of sensor materials and associated integrated sensor systems.

The current research activity at the National Research Council of Canada has objectives directed toward the development of new chemical sensor materials and sensor technology which has improved functionality for use in gas sensing applications. A goal of this development is the integration of the materials into platforms and environments which are compatible with sensor arrays, silicon microtechnology and the measurement of single components in multi-component gas mixtures. A particularly promising family of compounds, the non-stoichiometric perovskites with generic formulation $ABO_{2.5+x}$, and where A and B are metallic elements, have been identified for application in sensor studies (5). These materials when fabricated as thin films offer high potential in gas sensor development. Reviewed here are some results obtained which highlight the structural chemistry of these materials, their characterisation and gas sensor functionality. Some of the beneficial modifications to sensor functionality which result when changes are made to the perovskite chemical or structural composition are also reported.

EXPERIMENTAL

A number of experimental procedures are used in sequence to create a prototype sensor device which has sensor material based on the parent perovskite composition $SrFeO_{2.5+x}$. Outlined in this section are the techniques and apparatus which are used to prepare the bulk powder ceramic materials, the measurement of structural, phase and thermodynamic

properties, the deposition of perovskite thin films and the determination of gas sensor functionality of gas sensor prototypes fabricated from the thin films.

Perovskite Preparation and Characterisation

The parent perovskite ceramic materials are prepared by the sintering reaction at high temperatures of the precursor metal oxides and carbonates. For preparing $SrFeO_{2.5+x}$, stoichiometric proportions of $SrCO_3$ and Fe_2O_3 are initially intimately mixed by grinding before being thermally treated in a tube furnace under flowing argon in a series of programmed temperature steps to 1150°C for a period of 4 days. Further details are reported elsewhere (5). The reaction product is then characterised by elemental analysis using the technique of inductively coupled plasma mass spectrometry and x-ray diffraction to determine chemical and phase purity, respectively. For the preparation of substituted perovskites based on $SrFeO_{2.5+x}$ where the Fe is partially replaced by another transition element, Co for example, a third precursor compound, in this case Co_3O_4, is added to the initial reactants in the desired stoichiometric proportion prior to sintering. Subsequent preparation steps are then as given above.

Measurement of Phase Equilibria

The thermodynamic properties of the non-stoichiometric perovskites in bulk powder form upon reaction with oxygen are primarily measured to determine the pressure *vs* composition isotherms and phase equilibria which exist over temperature ranges of interest in sensor applications. To determine phase relationships the powdered perovskites are subjected to gas titration with O_2. This technique is done by containing the perovskite powder (approximately 5 g) in a stainless steel reactor which is surrounded by a furnace, and O_2 is then added/removed from the sample by a series of controlled and incremental pressure changes in the gas phase. The reactor is attached to a stainless steel manifold which facilitates gas handling and serves as a gas burette. The quantity of O_2 which is in the gas and solid (perovskite) phase is calculated by using volumetric techniques in the calibrated apparatus. Experimental precision permits measuring incremental oxygen stoichiometric units to $\Delta x = 0.01$. Some additional details of the technique used are described elsewhere (6).

Thin Film Deposition

Thin films of the perovskite materials are grown by the technique of pulsed laser deposition, (PLD). Targets for use in the PLD process are prepared from the parent powder perovskites by isostatic pressing into pellet form, followed by sintering at temperatures up to 1200°C to produce a mechanically robust target structure. An excimer laser (Lambda-Physik LPX 305i) operating with Kr/F ($\lambda = 248$ nm) is used as an energy source for the process. The target is placed in an evacuable steel deposition chamber where focussed incident laser radiation is directed upon it. The resultant plume of material ablated from the target is deposited onto a substrate located about 5 cm from

the target surface. A diagram of the PLD chamber and overall apparatus are shown in Figures 1 and 2, respectively. Other details have been reported earlier (7).

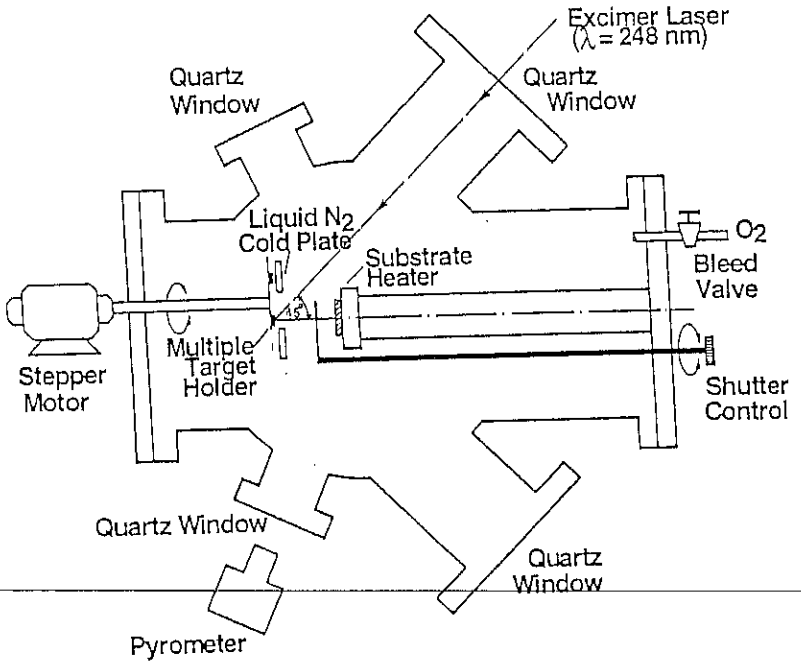

Figure 1 — Pulsed Laser Deposition Chamber

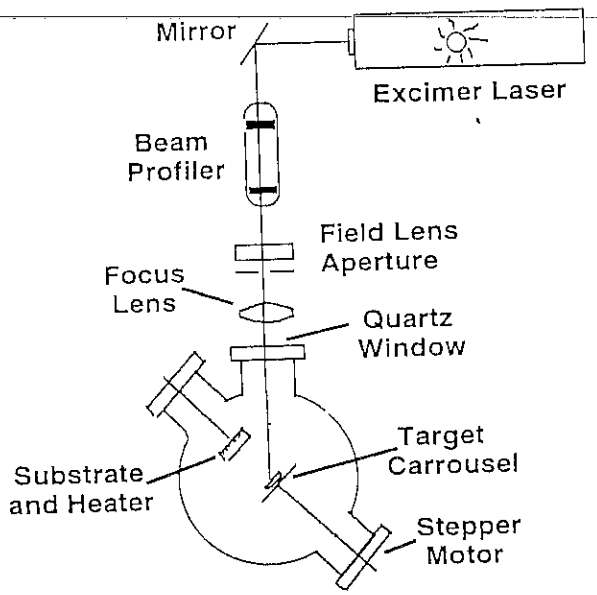

Figure 2 — PLD System Schematic

Typical conditions for the PLD process are: laser energy 600 mJ; fluence at target 1.5 $J.cm^{-2}$; pulse rate 8 Hz; pulse duration 25 ns; chamber pressure during deposition 150 mTorr O_2; substrate temperature 650°C; substrate area 2 cm^2. The majority of the data reported here are for sensor prototypes with films deposited by PLD onto a substrate of single crystal alumina, $(1\bar{1}02)$, sapphire.

Gas Sensor Functionality

The gas sensor functionality of the perovskite films are determined by measuring the electrical resistance changes which accompany the chemical changes that occur upon exposure of the sensor film to the analyte gas mixture. The thin films are fabricated into prototype sensor assemblies by masking and evaporating a thin layer of gold onto the film to provide two electrodes separated by about 1 cm. Electrical contact to the electrodes is achieved either by bonded gold wire or by direct contact to gold wire sheathed in thin bored ceramic tubing. The assembly is mounted onto a heater surface inside a stainless steel chamber with about 1 L volume, as shown in Figure 3. The chamber is attached to a gas delivery manifold equipped with gas sources, mass flow controllers and valving to permit controlled gas flow over the sensor film under test. A gas chromatograph is connected in parallel to the chamber to provide independent measurement of the gas phase composition. In a typical experiment the sensor film is heated to an elevated temperature and gas mixtures are delivered to the test chamber at

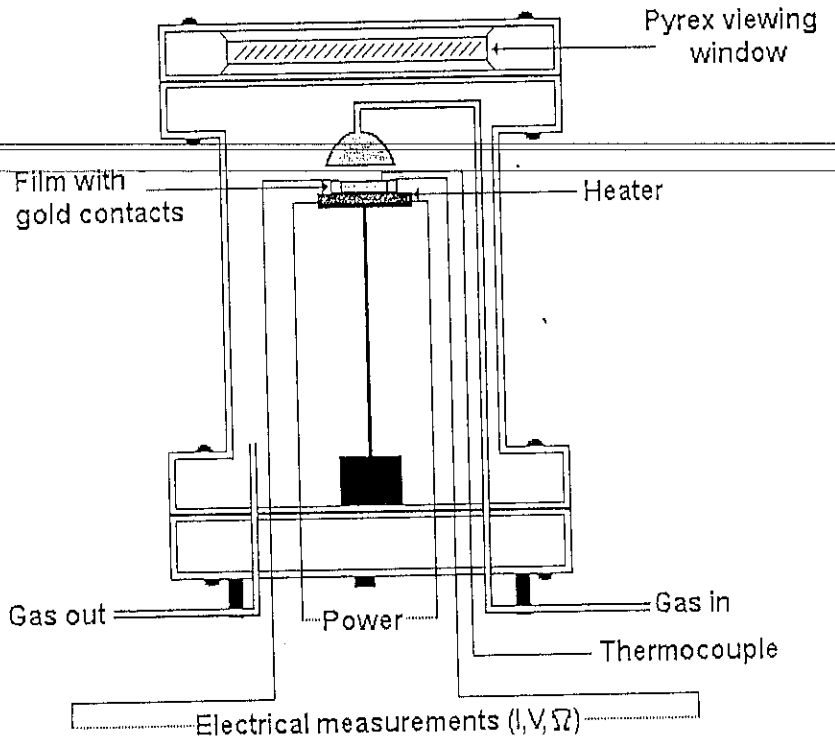

Figure 3 — Gas Sensor Functionality Chamber

200 cm^3 per minute with sensor film resistance being continuously recorded. The chamber system is under PC control of temperature and resistance data acquisition. In order that the kinetics of the chemistry which occurs with the sensor films is rapid, and that a fast sensor response is consequently obtained, the films are operated at elevated temperature. For the majority of the work reported on sensor functionality, temperatures in the range between 450°C and 500°C have been used. These temperatures are sufficiently high that the kinetics of sensor response are rapid. The gas compositions used in the current studies were O_2/N_2 mixtures with O_2 concentrations from ppm to 100% levels, and also CO mixtures at concentrations of 10 ppm to 1000 ppm in either N_2 or air. In addition to sensor functionality data which was obtained isothermally, in order to determine some other physical properties such as activation energies, for example, the resistance properties of the films were also obtained under dynamic thermal conditions with temperature being varied linearly at rates of ±10°C/minute in the range from ambient to 500°C.

RESULTS AND DISCUSSION

Phase Relationships in $SrFeO_{2.5+x}$

The phase relationships determined in recent studies (8) and by others (9,10) can be summarised in the reduced phase diagram shown in Figure 4. The maximum O_2 pressure used to obtain this data is approximately 1.5 atm. Four phases, denoted BM,

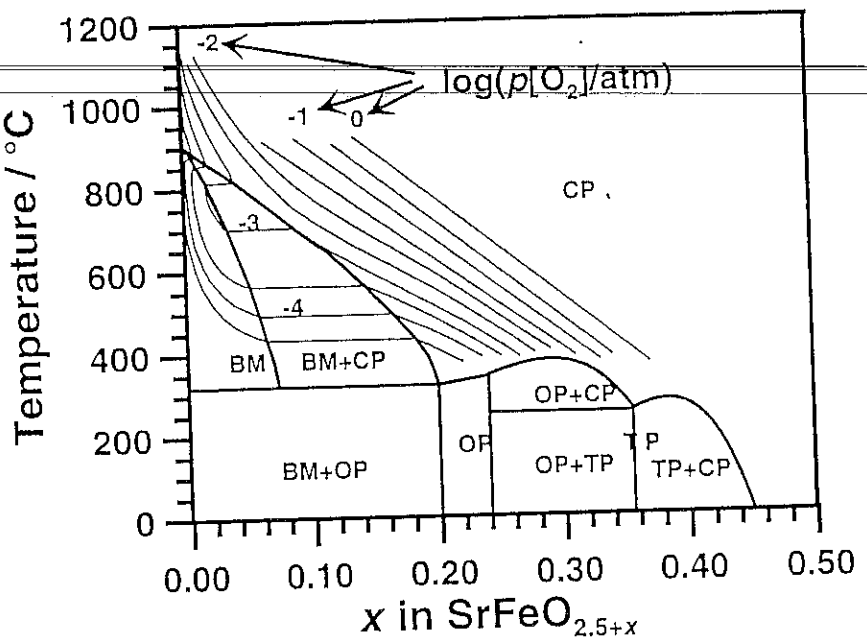

Figure 4 — Reduced Phase Diagram for the $SrFeO_{2.5+x}$ + O_2 System Based on Refs (8-10).

OP, TP and CP, exist over the oxygen stoichiometric range $0 < x < 0.5$ and for $0 < T < 1050°C$. At the upper composition limit of $x = 0.45$ at these $p(O_2)$, the CP phase is close to cubic, and the fully stoichiometric cubic perovskite CP phase (*ie* for $x = 0.5$) can only be attained either at very high $p(O_2)$, (9), or by using anodic oxidation techniques (11). At the lower composition limit the orthorhombic brownmillerite phase BM exists. Two phases of intermediate oxygen composition also exist which are defined by ordering in the oxygen sub-lattice: these are orthorhombic, OP, and tetragonal, TP, phases which are based on distortions on the cubic perovskite structure.

The physical properties of the films exhibit large changes over the range of phases in $SrFeO_{2.5+x}$. Two examples are the electrical resistance (8) and the optical transmission properties (12). Shown in Figure 5 are the resistance changes which occur for oxygen rich (*ie* high x) and oxygen deficient (*ie* low x) films with temperature. These compositions are maintained during the measurement by having the film under O_2 and Ar, respectively. Clearly, there exists a resistance "space" of about 2.5 orders of magnitude which can be exploited for sensor transduction purposes. Also apparent is that at low temperatures the BM films are insulators. At higher temperatures ($T > 180°C$) the BM and CP films are both semiconducting. The optical transmission properties also show distinct variation with oxygen content. Films with composition $SrFeO_{\sim 3}$ are brown-black in colour and reflective, while films with composition $SrFeO_{\sim 2.5}$ are light yellow and transparent. These optical properties are particularly evident uv-vis spectra, where for example, at a wavelength $\lambda = 400$ nm, there is about a 2 order of magnitude variation in optical transmission between the oxygen deficient and oxygen rich compositions. Both electrical and optical properties, therefore, can be used as transduction modes for the sensor, whereby a chemical effect with the sensor film is converted to a measurable output response. The changes in the resistance of the semiconductor properties of $SrFeO_{2.5+x}$ and related materials are used exclusively here. Some other work has been previously reported for the optical dependencies (12).

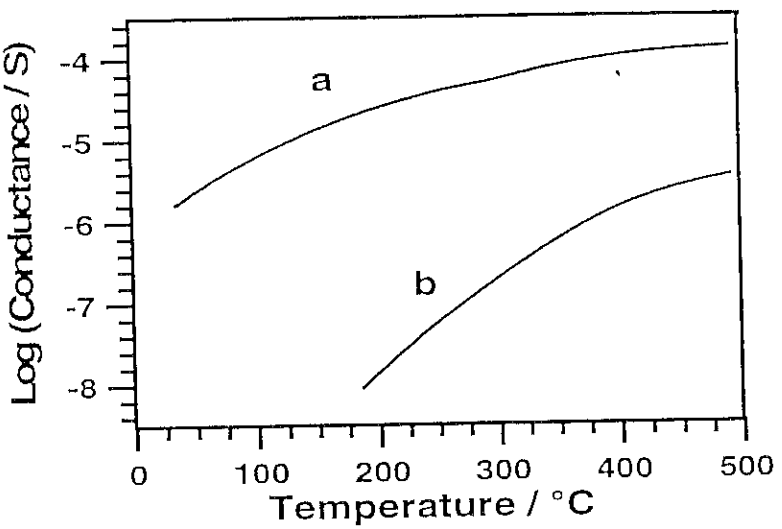

Figure 5 — Thin Film $SrFeO_{2.5+x}$: Dependence of Conductivity upon Temperature and Oxygen Stoichiometry. (a) CP: $x \approx 0.45$; (b) BM: $x = 0$

$SrFeO_{2.5+x}$ and Oxygen Sensing

The variation of conductivity of $SrFeO_{2.5+x}$ thin films with temperature upon oxygen exposure is shown in Figure 6. Again the wide range of resistance response is evident. Also evident is that the conductivity of the films increases with increasing oxygen concentration in O_2/N_2 gas mixtures, so that the films are behaving as *p*-type semiconductors (8). Plots of the Arrhenius type shown in Figure 6 also permit the extraction of experimental activation energies of conduction from the slope of the relationship. These values range typically from 0.2 eV to 0.5 eV for the films studied here.

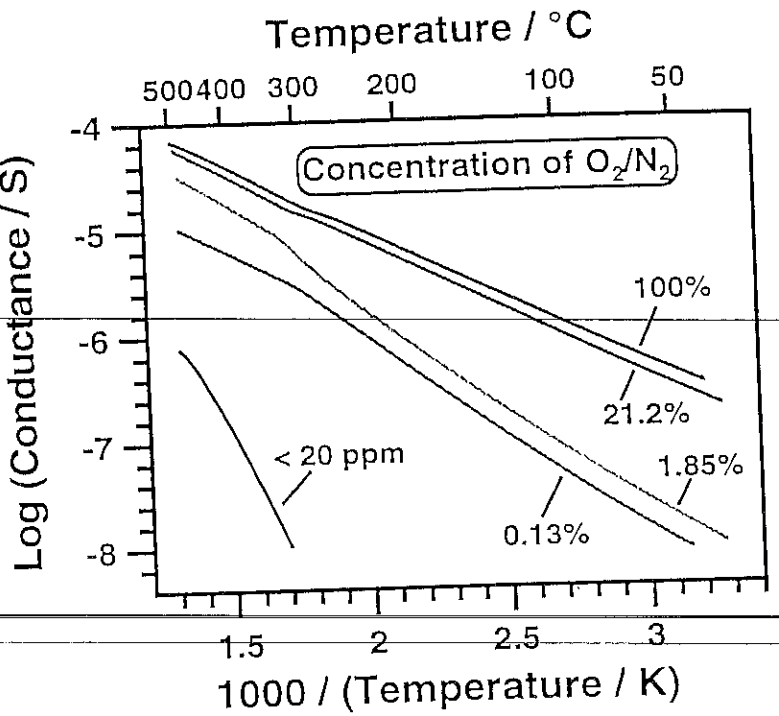

Figure 6 — $SrFeO_{2.5+x}$. Arrhenius Plot of Dependence of Conductance on Oxygen Concentration in O_2/N_2 Mixtures and Temperature

Conductivity data obtained for a stepwise variation of O_2 concentration under isothermal conditions is shown in Figure 7. This is a typical data set for the films of perovskite and related compositions, and in this case is for $SrFeCo_{0.5}O_x$ at $T = 500°C$ and for the O_2 concentration range 0.2% to 100% in O_2/N_2 mixtures. Three significant features relevant to sensor film functionality are evident in this data. The first is that the film conductivity increases with increasing $p(O_2)$ and with a magnitude which is dependant on $p(O_2)$. It is, therefore, possible to determine sensitivity and calibration factors for the sensor with respect to the level of oxygen exposure. Secondly, the rate of sensor response is fast when gas phase composition changes. The time to 80% of maximum response, a bench mark quantity commonly used in sensor studies, is less than

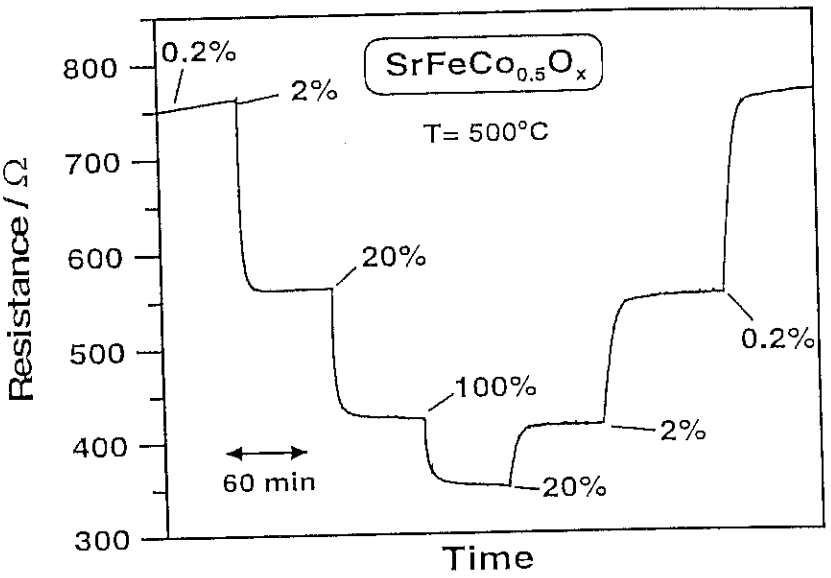

Figure 7 — $SrFeCo_{0.5}O_x$. Sensor Response at $T = 500°C$ upon Exposure to Changing Concentration of Oxygen in O_2/N_2 Mixtures

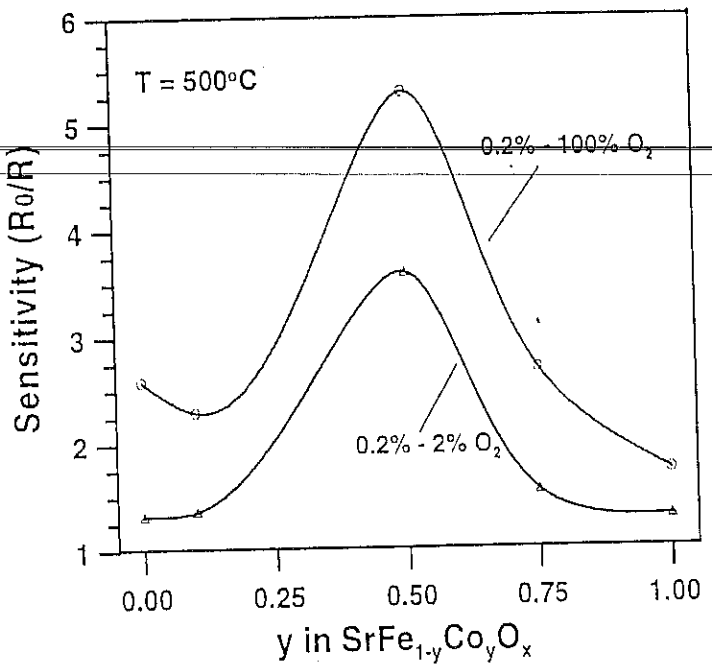

Figure 8 — Cobalt Substituted $SrFeO_{2.5+x}$. Dependence of Sensitivity at $T = 500°C$ upon Cobalt Substitution Level, y, for Oxygen Exposure in O_2/N_2 Mixtures

5 minutes. Thirdly, the sensor response is reversible, as is evident when the O_2 concentration returns to a previously set level, the sensor film conductivity also returns to its previous value at that level of O_2 exposure. All these physico-chemico features and qualities are attributes of a superior sensor material.

The tunability of the sensor response can be controlled by using judiciously selected modifications to the elemental composition of the parent perovskite. This can be demonstrated with the series of perovskite materials where Fe is partially or fully substituted by Co. The series has the generic formulation $SrFe_{1-y}Co_yO_x$. The sensor films for this series have sensitivity of response upon oxygen exposure which vary with Co content, and this is shown in Figure 8. The sensor sensitivity, as defined by the ratio of initial resistance R_o to final R exhibits a maximum ratio for Co/Fe with y ~ 0.5. This is this case for both low and high oxygen level exposure, and enhancement of sensitivity by factors between 3 and 5, respectively, are evident. The effect of ternary and quarternary metallic element substitution on the crystallographic structure and the phase relationships is evident in preliminary studies which are currently ongoing (13).

$SrFeO_{2.5+x}$ and Carbon Monoxide Sensing

The conductivity of $SrFeO_{2.5+x}$ films decreases when exposed to increasing concentrations of reducing gases such as CO and H_2. This would be expected because, upon reduction of the sensor film, x decreases and a more resistive phase composition of $SrFeO_{2.5+x}$ is being produced. As has been shown above, it has also been demonstrated

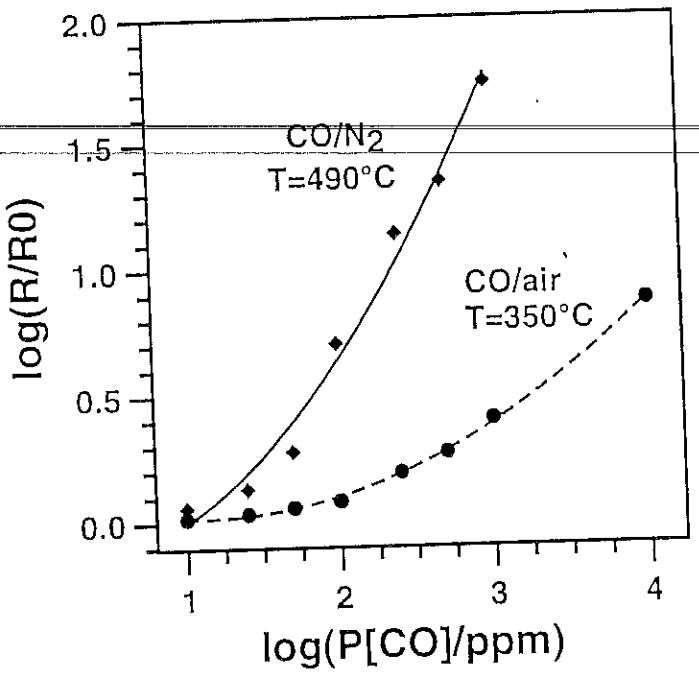

Figure 9 — Thin film $SrFeO_{2.5+x}$. Response and Sensitivity to Carbon Monoxide in Nitrogen and Air Mixtures

that relationships between conductivity and gas concentration can be determined for these and other reducing gases (14). The sensitivity and magnitude of sensor response is strongly dependent on the redox character of the analyte gas and its ambient, or carrier, gas. These characteristics are clearly shown in Figure 9, where data for $SrFeO_{2.5+x}$ films under exposure to CO mixtures of concentration 10 to 1000 ppm in air and in nitrogen are reported. The temperatures used for the sensor film for CO/air and CO/N_2 mixtures were selected to obtain maximal response for these two carrier gas ambients. The magnitude of the sensor response to CO in each carrier gas is different, with the sensitivity to CO being greater in N_2 than in air by a factor of about 5 for 1000 ppm CO. For gas mixtures such as these, the ambient gas with lower redox potential will result in larger sensor signal response from the analyte. This issue is significant when considering the optimal sensor applications and ambient environments.

Integration of Gas Sensor Thin Films with Devices

For the functionality and testing studies above, the perovskite thin films were fabricated into sensor prototypes which were based on a macroscopic platform, a substrate of sapphire. Typical substrate size was 10 x 10 x 0.5 mm^3 and, to provide heating to the temperatures required for adequate speed of sensor response, an independent heated surface was used. For sensor studies which are of a more fundamental and development nature, this type of prototype fabrication is suitable; it facilitates many aspects of sensor studies at the laboratory bench, and the ease of handling permits the measurements to be made routinely. However, in a sensor device, particularly one which has commercial potential, a more compact design with integrated heater and other control functions is desirable. Additionally, the smaller size facilitates integration into other platforms, decreases heater power requirements and increases battery life if the sensor is so powered. A number of strategies in microfabrication of sensors have been reported (4,15,16). One device presently under development is based

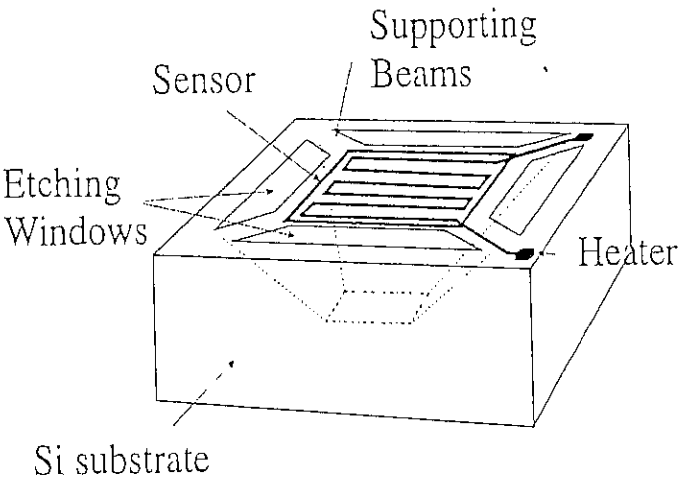

Figure 10 — Schematic View of the Silicon Microhotplate Sensor (MHP) Design with Suspended Diaphragm Above an Etched Cavity,

on CMOS microfabrication technology with a micromachined membrane to support the sensor thin film. The membrane is heated by means of an imbedded polysilicon layer which serves as a resistive electrical heater. The device shown schematically in Figure 10 is known as a microhotplate sensor (MHP). In this device, the perovskite sensor film is deposited by PLD onto the membrane using a shadow mask. The CMOS fabrication and silicon substrate permits the integration of sensor electrodes, heater power supply and signal data acquisition and processing on one chip of area less than 0.5 cm^2. Each MHP in the structure has dimensions of approximately 100 x 100 μm^2, and an array of MHP membranes are fabricated to permit inclusion of multiple sensor films in one compact device. This type of fabrication strategy permits the creation of electronic nose sensors which are under development for applications involving gas sensing in multi-component gas mixtures.

CONCLUSIONS

The use of chemical sensors for real time monitoring and detection of gases is appropriate in many environmental, industrial and manufacturing applications. They provide compact, robust and low cost devices which can be effectively deployed in multi-point locations to satisfy a broad range of monitoring requirements related to environmental, regulatory, industrial and manufacturing concerns. Chemical sensors can augment or replace the considerably more expensive analytical equipment that is currently employed in many monitoring applications. The gas phase components which are present in an actual application should be evaluated to ensure that no significant cross-interferences exist that could compromise sensor reliability. Much of the research effort in chemical sensor development is directed toward improving the functionality of the sensor material and eliminating problems related to chemical selectivity and cross-interferences.

The research and development activities reported here demonstrate that chemical sensors based on materials selected from the family of non-stoichiometric perovskite compounds, particularly those of $SrFeO_{2.5+x}$, hold high potential in providing a key technology in the creation of reliable sensor devices. The exposure of these perovskite materials to analyte gases is accompanied by large changes in the semiconductor properties which are then correlated with the gas concentration. The solid state chemistry of these perovskite compounds can be modified by judiciously chosen elemental substitution and, consequently, the sensor functionality can be altered in a controlled fashion to improve selectivity to specific analyte species. These chemical sensor materials also exhibit a rapid response and in most cases have a large dynamic range of gas concentrations over which reliable monitoring is possible. The perovskite sensor materials studied here produce excellent quality thin films by the PLD technique. The thin films have been integrated with a variety of sensor substrates in order to fabricate sensor devices and prototypes. By integrating the films with platforms based on silicon

chip technology and applying micromachining techniques, a versatile sensor array can be created which has sensor function, control circuitry and signal processing electronics on one chip. A device of this fabrication type can be considered an electronic nose, which offers potential in providing a more versatile sensor device and one which is capable of monitoring individual components in a complex gas mixture.

REFERENCES

1. D. Malloy and A. Crull, Eds., Air Pollution and the Market for Monitors and Sensors: Report E-409, Business Communications Co. Inc., Norwalk, CT, USA, 1989.

2. J.P. Lodge Jr., Ed., Methods of Air Sampling and Analysis, Third Edition, Lewis Publishers Inc., Chelsea, MI, USA, 1989.

3. N. Eror, Ed., Expanding the Vision of Sensor Materials, National Research Council, National Academy Press, Washington, DC, USA, 1995.

4. W. Göpel, J.Hesse and J.N. Zemel, Eds., Sensors: A Comprehensive Survey, Vols.1-3, VCH Publishing, Weinheim, Germany, 1989.

5. M.L. Post, B.W. Sanders and P. Kennepohl, "Thin Films of Nonstoichiometric Perovskites as Potential Oxygen Sensors", Sensors and Actuators B, Vol. 13-14, 1993, 272-275.

6. M.L. Post and J.J. Murray, "Mg_2Ni Hydride: In-situ Heat Conduction Calorimetry of the Phase Transition near 510K", J. Less-Common Metals, Vol 134, 1987, 15-26.

7. B.W. Sanders and M.L. Post, "Deposition of Thin Film $SrFeO_{2.5+x}$ by Pulsed Laser Ablation," Mater. Res. Soc. Proc., Vol 285, 1993, 427-432.

8. J.J. Tunney and M.L. Post, "The Electrical Conductance of $SrFeO_{2.5+x}$ Thin Films", J. Electroceramics, In Press.

9. Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama and Y. Bando, "Phase Relation in the Oxygen Nonstoichiometric System $SrFeO_x$ ($2.5 \leq x \leq 3.0$)", J. Solid State Chem., Vol. 63, 1986, 237-249.

10. J. Mizusaki, M. Okayasu, S. Yamauchi and K. Fueki, "Nonstoichiometry and Phase Relationship of the $SrFeO_{2.5}$ - $SrFeO_3$ System at High Temperature", J.Solid State Chem., Vol. 99, 1992, 166-172.

11. A. Wattiaux, L. Fournès, A. Demourgues, N. Bernaben, J-C. Grenier and M. Pouchard, "A Novel Preparation Method of the $SrFeO_3$ Cubic Perovskite by Electrochemical Means", Solid State Communications, Vol. 77, 1991, 489-493.

12. M.L. Post and J. Yao, "The Optical Transmittance Properties of $SrFeO_{2.5+x}$ Thin Films for Oxygen Sensing", Proc. 8th Intl. Conf. Sensors and Actuators, Stockholm, Sweden, 1995, 804-806.

13. M.L. Post, "The Effect on Sensor Properties of Substitution by Other Transition Metal Elements for Fe in $SrFeO_{2.5+x}$", Manuscript in preparation.

14. M.L. Post, J.J. Tunney, D. Yang and X. Du, "Detection of Carbon Monoxide and Hydrogen with Non-Stoichiometric Perovskites and Variation in Transduction Modes", Electrochem Soc. Symp. Proc., Vol. 99-23, 1999, 270-274.

15. S. Wessel, M. Parameswaran, S.R. Morrison and R.F. Frindt. "A CMOS Thermally Isolated Heater Structure as a Substrate for Semiconductor Gas Sensors". Proc. Canadian Conference on Very Large Scale Integration, Kingston, ON, Canada, 1991, 1.6.1 - 1.6.8.

16. N.R. Swart and A. Nathan. "Design Optimization of Integrated Microhotplates", Sensors and Actuators A, Vol. 43, 1994, 3-10.