



The Electrical Conductance of $\text{SrFeO}_{2.5+x}$ Thin Films

JAMES J. TUNNEY & MICHAEL L. POST

Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Montreal Road, Ottawa, Ontario, K1A 0R6, Canada

Submitted June 29, 1999; Revised December 2, 1999; Accepted December 21, 1999

Abstract. Thin films of the non-stoichiometric perovskite $\text{SrFeO}_{2.5+x}$ have been grown by the pulsed excimer laser deposition technique onto sapphire substrates. The electrical conductance properties of the thin films have been determined in a series of experiments done both isothermally and with programmed temperature changes from ambient to 490°C and under O_2/N_2 atmospheres with oxygen concentrations in the range from 100 ppm to 100%. Over these ranges of temperature and oxygen partial pressure a wide range of oxygen stoichiometry in $\text{SrFeO}_{2.5+x}$ occurs (approximately $0 < x < 0.5$), which includes all four known phases in the $\text{SrFeO}_{2.5+x} + \text{O}_2$ system. The experimentally measured values for the activation energy of conduction, ε_A , for $\text{SrFeO}_{2.5+x}$ films at temperatures $100 < T < 200^\circ\text{C}$ are in the range $0.30 < \varepsilon_A < 0.47$ eV under oxygen at partial pressures $0.001 < P_{(\text{O}_2)} < 0.05$ atm and $0.18 < \varepsilon_A < 0.28$ eV for $0.2 < P_{(\text{O}_2)} < 1$ atm. These values for ε_A are typical for compositions of $\text{SrFeO}_{2.5+x}$ with stoichiometries in the range $0.25 < x < 0.45$. For $T < 300^\circ\text{C}$ and for $P_{(\text{O}_2)} < 0.001$ atm the films were essentially insulators. For $T > 250^\circ\text{C}$ and $P_{(\text{O}_2)} > 0.001$ atm, the oxygen stoichiometries of the films change during the programmed temperature ramps. For these conditions, the values $\delta\varepsilon_A/\delta T$ exhibit minima/maxima in the temperature range $250 < T < 320^\circ\text{C}$ which are interpreted as being due to the onset of the order-disorder phase transition from the cubic to the tetragonal and orthorhombic ordered phases of $\text{SrFeO}_{2.5+x}$ with oxygen stoichiometry in the range $0.08 < x < 0.38$. The $\text{SrFeO}_{2.5+x}$ thin films have application as oxygen sensing materials, and a relationship between conductance and oxygen sensitivity, S_{O_2} , has been derived. The values of S_{O_2} for $\text{SrFeO}_{2.5+x}$ thin films increases by more than an order of magnitude for compositions close to the lower stoichiometric limit where the principal phase conversion is between the cubic perovskite and the brownmillerite forms.

Keywords: perovskite, brownmillerite, $\text{SrFeO}_{2.5+x}$, thin film, oxygen sensor

1. Introduction

The $\text{SrFeO}_{2.5+x}$ system has a wide range of oxygen stoichiometry ($0.0 \leq x \leq 0.5$) and four phases, the structures of which are based primarily on long range ordering of the oxygen sub-lattice [1–3]. Two of the phases are related to the cubic perovskite (CP) structure of the oxygen rich material and exhibit tetragonal and orthorhombic distortions to the cubic lattice; these are denoted as the TP and OP forms, respectively. The fourth phase, which exists at low x , has the perovskite-like brownmillerite (BM) structure. The phase relationships between these forms in the

$\text{SrFeO}_{2.5+x} + \text{O}_2$ system is complex, and a representation of the reduced phase diagram is shown in Fig. 1, where a combination of data from previous work [1–3] has been used to show the phase relationships. Some structural and thermodynamic properties of the phase interrelationships as a function of temperature and oxygen partial pressure, $P_{(\text{O}_2)}$, have been investigated in the bulk powder state. For example, in an earlier study [3] using gas titration techniques to determine oxygen-pressure vs composition isotherms, the coexistence regions for the TP + CP and OP + TP phases have been identified. Takeda et al. [1] have shown by differential thermal analysis and

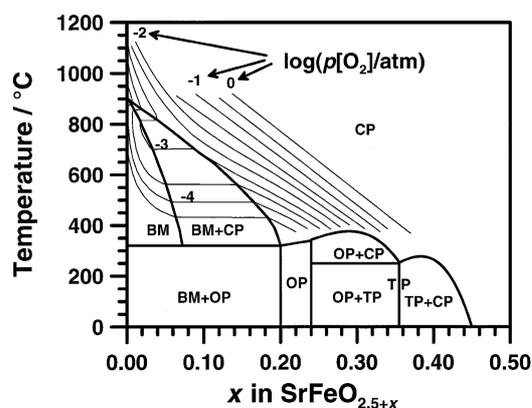


Fig. 1. Reduced phase diagram for the $\text{SrFeO}_{2.5+x} + \text{O}_2$ system (adapted from Mizusaki et al. [2]). Reaction isobars are also shown for the oxygen partial pressure range $-4.5 \leq \log\{P_{(\text{O}_2)}\} \leq 0$.

thermogravimetric analysis that phase transitions are readily identified by scanning the temperature of $\text{SrFeO}_{2.5+x}$ at constant $P_{(\text{O}_2)}$. In this manner, the $\text{CP} \rightarrow \text{BM}$, $\text{CP} \rightarrow \text{OP}$ and $\text{CP} \rightarrow \text{TP}$ phase transitions and their coexistence ranges have been identified. Wissman and Becker [4] identified by using Mössbauer spectroscopy, the $\text{CP} \rightarrow \text{BM}$ phase transition which resulted at $T = 500^\circ\text{C}$ when the oxygen partial pressure in O_2/N_2 mixtures was varied through the range from $1 > P_{(\text{O}_2)} > 10^{-5}$ atm. Hombo et al. [5] demonstrated that the bulk electrical conductivity of the $\text{SrFeO}_{2.5+x}$ system was dependent on the equilibrium $P_{(\text{O}_2)}$ and that the material was a *p*-type semiconductor in the $\{T, P_{(\text{O}_2)}\}$ domain studied, with the conductivity of $\text{SrFeO}_{2.5+x}$ increasing with increasing $P_{(\text{O}_2)}$.

Earlier studies [3, 6–13] have shown that, by exploiting the non-stoichiometric properties of $\text{SrFeO}_{2.5+x}$ and structurally related materials, there is considerable potential for their use in gas sensor applications. When exploited for this purpose, the chemical change which occurs as a result of interaction between the gas and sensor material is accompanied by a large change in a physical property. The physical property which has been used as a transduction signal from sensor films of ceramic type such as $\text{SrFeO}_{2.5+x}$ has primarily been electrical conductance. $\text{SrFeO}_{2.5+x}$, in the form of thin films, enables integration with platforms such as those provided by silicon microfabrication techniques [14–16] thus providing possibilities for versatile gas sensor fabrication. In the present work, pulsed laser

deposition has been used to deposit high quality $\text{SrFeO}_{2.5+x}$ thin ceramic films onto sapphire substrates which served as gas sensor prototypes. The goal of the study was to systematically investigate the dependence of the electrical conductivity, (σ), of $\text{SrFeO}_{2.5+x}$ thin films on temperature and oxygen composition and to determine relationships existing between σ , x and film sensitivity, S_{O_2} , to oxygen over ranges of pressure and temperature, $10^{-5} < P_{(\text{O}_2)} < 1$ atm and $25 < T < 490^\circ\text{C}$, respectively.

2. Experimental

$\text{SrFeO}_{2.5+x}$ powders were prepared by a standard ceramic process using as precursors stoichiometric mixtures of SrCO_3 and Fe_2O_3 , and thermal treatments in flowing oxygen at temperatures up to $T = 1150^\circ\text{C}$ [3,6]. Pellets ($\phi = 12$ mm) of these materials were then fabricated by isostatic pressing to 4 Tonnes followed by sintering at $T = 1050^\circ\text{C}$. These were used as targets for pulsed excimer laser ablation/deposition (PLD). Thin films of $\text{SrFeO}_{2.5+x}$ were deposited by PLD onto (1102) single crystal alumina (sapphire) using a laser (Lambda-Physik LPX305i) operating at $\lambda = 248$ nm. Typical deposition conditions included an energy density at the target of $1.5 \text{ J}\cdot\text{cm}^{-2}$, pulse rate of 10 Hz, substrate temperature 650°C and deposition time of 600 s; other details of the process are described elsewhere [3,6]. These conditions produce a film with a thickness of approximately 200 nm. The deposition parameters were selected and a duplicate series of thin films were produced under conditions where films with both oxygen rich and oxygen deficient compositions were prepared. All four samples were subjected to subsequent study to ensure that the data presented below was representative of the $\text{SrFeO}_{2.5+x}$ system. X-ray spectra for both the initially prepared $\text{SrFeO}_{2.5+x}$ and the thin films were collected with a Scintag D2000 diffractometer over the range $20 \leq 2\theta \leq 80^\circ$ using graphite monochromated $\text{Cu-K}\alpha$ radiation. To facilitate electrical conductance measurements, ohmic contact to the films was achieved by bonding gold wires to thin gold layers (~ 150 – 200 nm) which had been evaporated onto each end of the film such that there was a 10 mm gap between the electrodes thus permitting resistance measurements over approximately 1 cm^2 of film surface. The substrate/film samples were then

mounted onto a heater and inside a chamber equipped with gas-flow manifold and mass flow controllers. The gases used were ultra high purity O₂ (Central Oxygen Ltd. UHP grade with [N₂] < 10 ppm; [H₂O] < 10 ppm) and ultra high purity N₂ (Matheson UHP grade with [O₂] < 10 ppm; [H₂O] < 10 ppm). A gas chromatograph (MTI 200D) connected in parallel to the gas delivery manifold provided an independent measurement of gas composition. The apparatus facilitated automated (PC-DOS) control of temperature and data acquisition of thin film resistance using a 2-wire method with a Hewlett Packard 34401A digital voltmeter which permitted resistance measurements in the range $0 < R < 120 \text{ M}\Omega$. Resistance data for the SrFeO_{2.5+x} films were collected either isothermally ($T = 490^\circ\text{C}$) or in programmed temperature ramps with nominal rates of $\pm 10^\circ\text{C} \cdot \text{min}^{-1}$ within the temperature range $25 < T < 490^\circ\text{C}$. The O₂/N₂ mixtures to which the SrFeO_{2.5+x} thin films were exposed varied in oxygen partial pressure over the range $10^{-5} < P_{(\text{O}_2)} < 1 \text{ atm}$ and were delivered to the sample chamber at a flow rate of $240 \text{ cm}^3 \cdot \text{min}^{-1}$.

In a typical data collection sequence, the SrFeO_{2.5+x} thin film was first thermally pretreated by temperature cycling in oxygen over the range $490 \rightarrow 40 \rightarrow 490^\circ\text{C}$ at a rate of approximately $\pm 10^\circ\text{C}/\text{minute}$. This treatment resulted in a stable and reproducible film resistance for any given $\{P_{(\text{O}_2)}, T\}$ condition. One consequence of the pre-treatment process is to partially relieve the tensile stress which would develop in the film as a result of thermal expansion differences between film and substrate, when cooled from its deposition condition at $T \sim 650^\circ\text{C}$ to ambient temperature. Separate studies [17] are being pursued regarding the morphological and structural effects which accompany short and long term exposure of SrFeO_{2.5+x} thin films at temperatures in the range $500 < T < 800^\circ\text{C}$. For isothermal ($T = 490^\circ\text{C}$) investigation of the conductance of SrFeO_{2.5+x} thin films with respect to variations in oxygen partial pressures, the O₂ concentration of the O₂/N₂ mixture was then decreased from 100% in a stepwise manner within the range $100\% > [\text{O}_2] > 100 \text{ ppm}$ to provide the $P_{(\text{O}_2)}$ range stated above. Reversibility of the conductance response of the film with changing oxygen concentration was confirmed in a subsequent series of exposures to O₂/N₂ mixtures with increasing $P_{(\text{O}_2)}$. For resistance data collected during temperature

ramps, the SrFeO_{2.5+x} thin films were exposed to a constant $P_{(\text{O}_2)}$ throughout a complete temperature cycle from 490°C to ambient and back to 490°C . Prior to a subsequent temperature cycle, $P_{(\text{O}_2)}$ was set to the new value and the film re-equilibrated at 490°C . The film conductance was recorded, typically, once each 30 s during the continuous temperature ramps, and no curve fitting was done with the data sets.

3. Film Preparation and Characterization

The SrFeO_{2.5+x} bulk powder samples prepared by sintering were shown by XRD to be single phase. The Sr/Fe stoichiometric ratio in SrFeO_{2.5+x} films has been shown to be 1:1 in earlier work by RBS spectroscopy [8] and elemental analysis by ICP-MS, thus confirming congruent transfer of material from the target pellet during PLD. The films were textured with a preferential orientation of (110) dominant, as shown by XRD. The adherence of the films to the sapphire was excellent, and no peeling or spalling of the film was observed. The XRD spectra of SrFeO_{2.5+x} thin films deposited under oxygen rich conditions were indexed as the cubic perovskite phase (CP) with a composition approximately SrFeO_{2.9}, whereas those deposited under oxygen deficient conditions were indexed to the brownmillerite SrFeO_{2.5} phase (BM) [6]. Interconversion and reversibility between these phases, such as would be achieved by cycling $P_{(\text{O}_2)}$ between low and high values, has been previously demonstrated [2–4]. It should be noted that the stoichiometric composition SrFeO₃ is produced only at oxygen pressures greater than 500 atm [1] or by anodic oxidation [18–20], and that the maximum oxygen stoichiometry achieved by slow cooling of SrFeO_{2.5+x} under $P_{(\text{O}_2)} = 1.5 \text{ atm}$ has $x \approx 0.47$ [3]. The XRD spectra in the region ($30 < 2\Theta < 35^\circ$) clearly show the difference in crystallographic symmetry between the CP and the BM phases as previously reported [3,6]. The thin films of CP and BM phases are also different in colour, with the CP phase being dark and opaque and the BM phase pale yellow and transparent [9,10]. The distinct difference in color provides an additional, visual means of identification of a film which has a composition in the BM form.

4. Electrical Conductance of SrFeO_{2.5+x} Thin Films and Temperature Relationships

4.1. Background

By measuring the electrical conductance of thin film SrFeO_{2.5+x} during exposure to various gas compositions at different temperatures, it is possible to determine relationships existing between conductivity, temperature and, as in the present case, oxygen partial pressure. In general, the conductivity of a semiconducting metal oxide in equilibrium with oxygen at partial pressure $P_{(O_2)}$, can be described with the following equation [21,22]:

$$\sigma = A \exp(-\varepsilon_A/kT) P_{(O_2)}^{1/N} \quad (1)$$

where σ is the electrical conductivity; ε_A is the activation energy of conduction; A is a constant; k is the Boltzmann constant and T is the temperature in degrees Kelvin. The range of values typical for $1/N$ are $\frac{1}{6} < |1/N| < \frac{1}{4}$, these values being positive for p -type and negative for n -type conduction. It follows from Eq. (1) that, at constant temperature, the relationship which defines sensor material sensitivity (i.e., change in conductivity) to changes in $P_{(O_2)}$ can be expressed as:

$$S_{ox} = d\{\log(\sigma)\}/d\{\log(P_{(O_2)})\} = 1/N \quad (2)$$

where ε_A is assumed to be invariant over the $P_{(O_2)}$ range considered. Much of the prior understanding and derivation of Eq. (1) is predicated on there being an incremental change in the oxygen composition in the metal oxide and the existence of only one phase. For the reaction of SrFeO_{2.5+x} with O₂, there is an additional complexity because changes in bulk oxygen stoichiometry, and phase changes, will occur provided that the process kinetics are sufficiently rapid [1–3]. During the higher temperature portion of programmed temperature ramps, the composition of the SrFeO_{2.5+x} thin films will be changing as a result of oxygen uptake (or loss) as determined by T , $P_{(O_2)}$ and the thermodynamics of the SrFeO_{2.5+x} + O₂ system. The equilibrium oxygen partial pressure for a given value of x increases with temperature, thus for a fixed $P_{(O_2)}$, the value x will decrease with increasing temperature. However, the kinetics of oxygen exchange between the gas phase and the SrFeO_{2.5+x} films become progressively slower with decreasing temperature so that for $T < 200^\circ\text{C}$ there is essentially

no further compositional change occurring under the conditions used for this study.

4.2. Conductance versus Temperature Data for SrFeO_{2.5+x} Thin Films

Shown in Fig. 2 is the Arrhenius plot obtained {c.f. Eq. (1)} for the variation of conductance with temperature of a typical SrFeO_{2.5+x} thin film during a series of exposures to different $P_{(O_2)}$ in O₂/N₂ mixtures. The large variation in conductance observed between SrFeO_{2.5+x} in the oxygen rich (CP) phase, Fig. 2(a), versus the oxygen deficient (BM) phase, Fig. 2(e), highlights one potential advantage of SrFeO_{2.5+x} for use in gas sensor applications when electrical resistance is used as a transduction signal. Over the temperature range, $300 < T < 500^\circ\text{C}$ the conductance difference between the CP and BM phases is greater than 2 orders of magnitude. Also evident in Fig. 2 is that for $T < 300^\circ\text{C}$, the BM form is essentially an insulator, with a sheet resistance, $R > 120\text{M}\Omega$. From the slopes of the family of curves in Fig. 2, activation energies of conduction, ε_A , can be extracted for the various $P_{(O_2)}$ over the temperature range studied. With the exception of the data for the BM form at $P_{(O_2)} = 2 \times 10^{-5}$ atm (i.e. for SrFeO_{2.5+ δ x}), which clearly shows the extremely low conductance expected for an insulating material, and

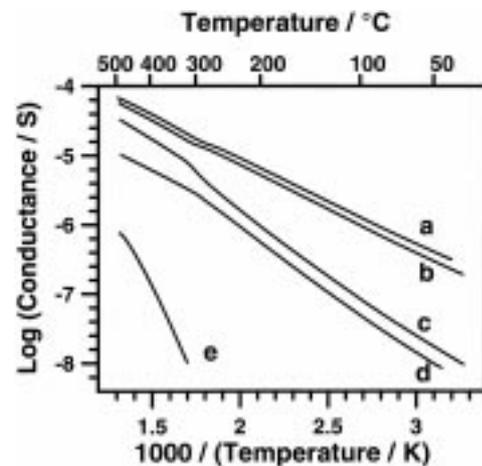


Fig. 2. Log(Conductance) versus $1/T$ relationship of thin film SrFeO_{2.5+x} and its variation with oxygen partial pressure. Data is shown for $P_{(O_2)}$ = (a) 1 atm, (b) 0.21 atm, (c) 4.4×10^{-2} atm, (d) 1.3×10^{-3} atm, (e) 2×10^{-5} atm.

which still retains a high resistance ($R \sim 1 \text{ M}\Omega$) even at 500°C , the other curves show some general trends. As would be expected for a semiconductor, for all $P_{(\text{O}_2)}$ the conductance increases with increasing temperature. In the high temperature region, $330 < T < 490^\circ\text{C}$, the relationship $\log(\sigma)$ versus $1/T$ is approximately linear. For temperatures $T < 200^\circ\text{C}$, the relationship $\log(\sigma)$ versus $1/T$ is approximately linear at the lower temperatures, and then exhibits a gradual change in slope up to $T \sim 250^\circ\text{C}$. Between these two regions, (i.e., for $250 < T < 330^\circ\text{C}$), is a temperature range over which some more rapidly changing values are observed. In this temperature range it has been previously demonstrated in TGA and DTA measurements [1], and thermodynamic studies [3], that both the rate of oxygen exchange between the gas and solid phase, and the rate of oxygen ion diffusion in the lattice, is still rapid. This ensures that the consequent phase conversions are occurring with no kinetic arrests in this temperature and composition range. The features evident around the points of inflection in the $250 < T < 330^\circ\text{C}$ region are shown more clearly by plotting the derivative of the slope, which is the experimental activation energy, ε_A , versus temperature. This data is shown in Fig. 3. The $\{P_{(\text{O}_2)}, T\}$ region where the temperatures of the maxima and minima occur correspond to an area in the phase diagram (Fig. 1) where phase changes involving the TP form would be expected. The phase relationships in this portion of the phase diagram have

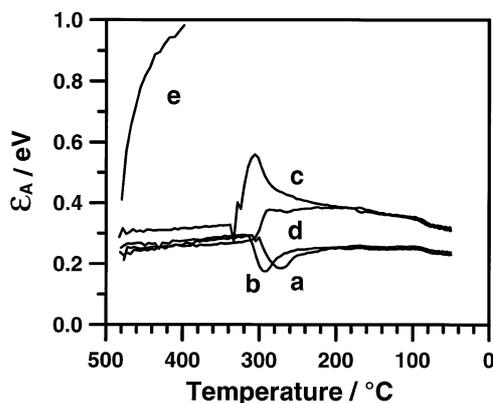


Fig. 3. Experimental activation energy of conduction (ε_A) vs. temperature for thin film $\text{SrFeO}_{2.5+x}$ and its variation with oxygen partial pressure. Data is shown for $P_{(\text{O}_2)}$ = (a) 1 atm, (b) 0.21 atm, (c) 4.4×10^{-2} atm, (d) 1.3×10^{-3} atm, (e) 2×10^{-5} atm.

not been previously determined with any precision, and although the TP phase with $x \sim 0.36$ is shown as a line compound below about 250°C , above this temperature precise (T, x) values at which the phase changes occur is not clear from the previously available data [1–3]. In the present case, by extrapolation of the $P_{(\text{O}_2)}$ isobars [2] shown in Fig. 1, the maxima/minima positions (T, x) in Fig. 3 correspond in the phase diagram to the area bounded by approximately $0.2 < x < 0.4$ and $250 < T < 375^\circ\text{C}$. The actual values of x associated with the maximum or minimum of each curve in Fig. 3 can be estimated by using an extrapolation of the $P_{(\text{O}_2)}$ relationship with temperature, assuming that no significant quenching occurs at the lower temperature range. With this approach, the x values in $\text{SrFeO}_{2.5+x}$ at which phase boundaries are crossed are estimated to be 0.42, 0.38, 0.31 and 0.27 for the data given in Fig. 3 as curves a, b, c and d, respectively. Without a detailed phase diagram, it is not possible to unequivocally associate specific phase transitions to the features in Fig. 3. However, some generalizations can be made. The compositions of the films under higher $P_{(\text{O}_2)}$ have $x > 0.36$, and are thus likely to be experiencing phase conversion from CP to TP during the temperature decrease. For the other two data sets, for which $x < 0.36$, the phase boundary being crossed is most probably from CP to OP. It may be significant to the conductivity properties of each of the phases involved that for the former pair of these transitions there is a corresponding minimum in the data of Fig. 3, whilst for the latter pair, there is a maximum.

5. Relationship of $\text{SrFeO}_{2.5+x}$ Thin Film Conductance versus $P_{(\text{O}_2)}$

Shown in Fig. 4 are conductance data for a typical $\text{SrFeO}_{2.5+x}$ thin film which have been obtained isothermally at $T = 490^\circ\text{C}$ by changing the oxygen partial pressure of the O_2/N_2 mixture with which the film is in contact. The concentration of O_2 in the mixture has been varied from 100% to approximately 100 ppm. The slope, S_{ox} , of the logarithmic relationship would be expected, (c.f. Eq. (2)), to lie in the range $\frac{1}{4} < S_{ox} < \frac{1}{6}$ for this p -type semiconductor. However, for the $\text{SrFeO}_{2.5+x} + \text{O}_2$ system, the relationship is more complex as a result of the effects upon chemical and physical properties of there being

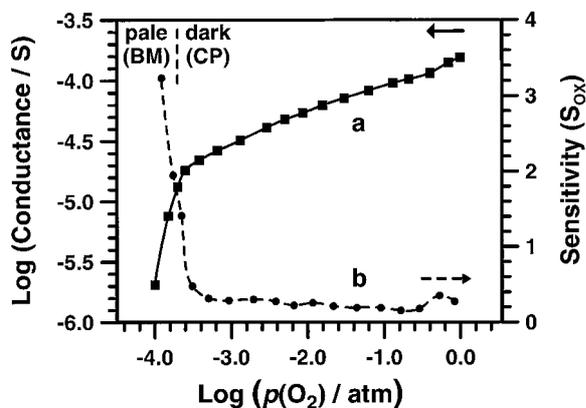


Fig. 4. Dependence upon oxygen partial pressure, $P_{(O_2)}$, of (a) Conductance, and (b) Sensitivity (S_{ox}) for thin film $SrFeO_{2.5+x}$. The vertical broken line indicates the approximate value of $P_{(O_2)}$ through which a color change occurs.

more than one phase present for certain ranges of oxygen composition as a consequence of the oxygen non-stoichiometric phase relationships. For $P_{(O_2)} > 10^{-3}$ atm, values in the range of $1/5 < S_{ox} < 1/4$ are found. For $P_{(O_2)} < 10^{-3}$ atm, the S_{ox} values increase substantially and, as shown in the data presented in Fig. 4, reach values of $S_{ox} > 3$ near 100 ppm. As defined in Eq. (2), the value of S_{ox} is considered a sensitivity factor which relates the change in film conductance with a variation in $P_{(O_2)}$. Thus, in the lower $P_{(O_2)}$ ranges the sensitivity of $SrFeO_{2.5+x}$ thin films increases by more than an order of magnitude. At $T = 490^\circ C$ and over the oxygen partial pressure range $10^{-4} < P_{(O_2)} < 10^{-3}$ atm, it is evident from the phase diagram (Fig. 1) that the $SrFeO_{2.5+x} + O_2$ system is undergoing phase conversion between the CP and BM forms. The rapid decrease in conductance and the increase in S_{ox} accompanies the formation of the BM form. Visually, the film is observed to change color through this range of $10^{-4} < P_{(O_2)} < 10^{-3}$ atm, and to become more transparent as $P_{(O_2)}$ decreases. These observations are in agreement with the existence of the BM phase as reported previously [9,10] for the optical transmittance of $SrFeO_{2.5+x}$ thin films. By inspection of Eq. (1,2) it is evident that a change in the quantity S_{ox} is dependent on any variation in the parameters $1/N$ or ϵ_A , either or both of which are likely to change during the phase transition from CP to BM. However, the data do not permit identifying which term will dominate. The phase interconversion of $BM \leftrightarrow CP$

requires cation (Fe) re-arrangement in addition to structural modification in the oxygen sublattice. A consequence of this more significant structural change is a slowing of the kinetics of oxygen exchange. This has a direct effect on the rate of sensor response, particularly when exposed to decreasing oxygen concentrations, where the phase transition is $CP \rightarrow BM$, in the $10^{-3.5} < P_{(O_2)} < 10^{-5}$ atm range. Although there is an immediate change in conductance upon changing $P_{(O_2)}$, the response times, measured as the time taken to reach 80% of the maximum resistance change, are typically longer than 20 min. However, for conditions where the oxygen concentration is increasing, (i.e., for $BM \rightarrow CP$), the response rate is significantly faster, as has been reported elsewhere [23], with typical response times of less than 5 min. These response rates can be compared to values of less than 2 min where other phase regions are being accessed in the $10^{-3.5} < P_{(O_2)} < 1$ atm range.

The enhanced oxygen sensitivity associated with the $CP \leftrightarrow BM$ phase conversion in $SrFeO_{2.5+x}$ thin films provides the physical basis for a highly sensitive chemical sensor for use in appropriate applications. Although the enhanced sensitivity is evident for a relatively narrow range of $P_{(O_2)}$ at a given temperature, it becomes possible to select other $P_{(O_2)}$ regions of high oxygen sensitivity by operating the sensor film at a different temperature. This is implicit in the phase diagram (Fig. 1) where different $P_{(O_2)}$ isobars intersect the sloping $(BM + CP) \rightarrow CP$ phase boundary at different temperatures. In this respect, chemical sensors based on the non-stoichiometric, multiphase family of perovskites, of which $SrFeO_{2.5+x}$ is a member, differ from sensors based on stoichiometric metal oxide materials. The additional structural and chemical complexity afforded by these non-stoichiometric materials provides potential advantages leading to enhanced sensitivity and chemical tunability in gas sensor applications.

6. Conclusions

Thin films of the non-stoichiometric perovskite $SrFeO_{2.5+x}$ grown onto sapphire substrates by pulsed laser deposition exhibit excellent structural quality and adherence whether grown under conditions which produce oxygen rich (high x) or oxygen deficient (low x) compositions. When the temperature

of the thin films is above 300°C, rapid and reversible exchange of oxygen occurs and this results in the SrFeO_{2.5+x} films displaying changes in conductivity of close to 2 orders of magnitude between compositions at the lower and upper phase limits. The SrFeO_{2.5+x} films are *p*-type semiconductors with conductivity dependent upon the oxygen partial pressure and temperature. This relationship permits the films to be exploited in oxygen sensing applications, and the highest sensitivity is found for SrFeO_{2.5+x} films where the phase transition between the cubic perovskite and brownmillerite forms is occurring as a consequence of the changing oxygen concentration in the analyte gas phase. The experimental activation energies of conduction, ϵ_A , for SrFeO_{2.5+x} films exhibit a dependence on oxygen partial pressure and temperature. The relationship of ϵ_A with temperature has been shown to provide evidence for the onset of order-disorder transitions in the oxygen sub-lattice, between the disordered cubic perovskite phase and the ordered tetragonal and orthorhombic forms of SrFeO_{2.5+x}.

References

1. Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama, and Y. Bando, *Journal of Solid State Chemistry*, **63**, 237 (1986).
2. J. Mizusaki, M. Okayasu, S. Yamauchi, and K. Fueki, *Journal of Solid State Chemistry*, **99**, 166 (1992).
3. M.L. Post, B.W. Sanders, and P. Kennepohl, *Sensors and Actuators B*, **13-14**, 272 (1993).
4. S. Wissman and K.D. Becker, *Solid State Ionics*, **85**, 279 (1996).
5. J. Hombo, Y. Matsumoto, and T. Kawano, *Journal of Solid State Chemistry*, **84**, 138 (1990).
6. B.W. Sanders and M.L. Post in *Laser Ablation in Materials Processing: Fundamentals and Applications* edited by B. Braren, J.J. Dubowski and D.P. Norton (Materials Research Society, Pittsburgh PA, Symposium Proceedings Vol. 285, 1993), p. 427.
7. M.L. Post and B.W. Sanders, in *Sensors VI: Technology, Systems and Applications*, edited by K.T.V. Grattan and A.T. Augousti (Institute of Physics Publishing, Bristol and Philadelphia, 1993) p. 33.
8. M.L. Post, J. Yao, and B.W. Sanders in *The Fifth International Meeting on Chemical Sensors: Technical Digest* Vol. 1 (Rome, 1994), p. 446.
9. M.L. Post and J. Yao, in *Polycrystalline Thin Films: Structure, Texture, Properties and Applications II*. Edited by H.J. Frost, M.A. Parker, C.A. Ross and E.A. Holm (Materials Research Society, Pittsburgh PA, Symposium Proceedings Vol. 403, 1996), p. 533.
10. M.L. Post and J. Yao, in *The 8th International Conference on Solid-State Sensors and Actuators and Eurosensors IX, Digest of Technical Papers*, Volume 2 (Stockholm, 1995), p. 804.
11. M.L. Post, J.J. Tunney, and J. Yao, in *Proceedings of the Symposium on Chemical and Biological Sensors and Analytical Electrochemical Methods*, edited by A.J. Ricco, M.A. Butler, P. Vanysek, G. Horvai and A.F. Silva (The Electrochemical Society, Pennington NJ, Proceedings Volume 97-19, 1997), p. 889.
12. T. Yu, Y.F. Chen, Z.G. Liu, L. Sun, S.B. Xiong, N.B. Ming, Z.M. Ji, and J. Zhou, *Applied Physics A*, **64**, 69 (1997).
13. J.S. Cauhape, C. Lucat, C. Bayle, F. M n il, and J. Portier, *Sensors and Actuators*, **15**, 399 (1988).
14. S. Wessel, M. Parameswaran, S.R. Morrison, and R.F. Frindt, in *Proceedings of the 1991 Canadian Conference on Very Large Scale Integration* (Kingston, Canada, 1991), p. 1.6.1.
15. S. Semancik and R. Cavicchi, *Accounts of Chemical Research*, **31**, 279 (1998).
16. S.V. Patel, K.D. Wise, J.L. Gland, M. Zanini-Fisher, and J.W. Schwank, *Sensors and Actuators B*, **42**, 205 (1997).
17. J.J. Tunney, S. Lealess, and M.L. Post, *manuscript in preparation*.
18. J-C. Grenier, J-M. Bassat, J-P. Doumerc, J. Etourneau, Z. Fang, L. Fourn s, S. Petit, M. Pouchard, and A. Wattiaux, *Journal of Materials Chemistry*, **9**, 25 (1999).
19. A. Wattiaux, L. Fourn s, A. Demourgues, N. Bernaben, J-C. Grenier, and M. Pouchard, *Solid State Communications*, **77**, 489 (1991).
20. A. Nemudry, M. Weiss, I. Gainutdinov, V. Boldyrev, and R. Sch llhorn, *Chemistry of Materials*, **10**, 2403 (1998).
21. P.T. Moseley and A.J. Crocker, *Sensor Materials* (Institute of Physics Publishing, Bristol and Philadelphia, 1996), Chapter 4.
22. P.T. Moseley, *Measurement Science and Technology*, **8**, 223 (1997).
23. D.M. Smyth, E.K. Chang, and D.H. Liu, *Phase Transitions*, **58**, 57 (1996).