The electrical conductance properties of SrFeO2.5+x thin-films and applications to gas sensing

Post, Michael L.; Tunney, James J.; Yao, Jianhua

Publisher's version / la version de l'éditeur:

Proceedings of the Symposium on Chemical and Biological Sensors and Analytical Electrochemical Methods, 97-19, pp. 889-895, 1997

THE ELECTRICAL CONDUCTANCE PROPERTIES OF $SrFeO_{2.5+x}$ THIN-FILMS AND APPLICATIONS TO GAS SENSING

Michael L. Post, James J. Tunney and Jianhua Yao
Institute for Chemical Process and Environmental Technology,
National Research Council of Canada,
Montreal Road, Ottawa, Ontario, K1A 0R6, Canada.

The electrical conduction properties of $SrFeO_{2.5+x}$ thin-films when exposed to oxygen/nitrogen atmospheres have been investigated under isothermal and non-isothermal conditions. The ranges of oxygen partial pressure and temperature were $0.05 < p(O_2) < 101$kPa and $40 < T < 480$°C, respectively. Over these ranges *p*-type semiconduction is exhibited. Isothermally, and at $T > 350$°C where the kinetics of oxygen exchange in the bulk $SrFeO_{2.5+x}$ is rapid, there is a logarithmic relationship of conductance with $p(O_2)$. At lower temperatures, a combination of mechanisms contribute to conductivity. These include intrinsic temperature dependencies of electronic conduction, surface oxygen reactivity and film annealing effects. A series of programmed temperature changes has been used to help determine the dominant conduction mechanism at different temperatures.

INTRODUCTION

The non-stoichiometric perovskite $SrFeO_{2.5+x}$ has an oxygen existence range of $0 \leq x < 0.5$ with a total of four phases, three related to the perovskite structure by distortions of the cubic lattice, and the lower composition limit being the brownmillerite form [1,2]. This perovskite material has been studied for its potential application in gas sensing [3]. Unlike most other metal oxides which have received attention in chemical sensor studies, [4-6] these non-stoichiometric materials, by virtue of the large variation in oxygen composition which can occur, offer transduction mechanisms based on bulk structural changes in addition to changes based on surface chemistry. To facilitate the integration of these materials into prototype sensor platforms, these materials have been deposited as thin-films onto substrates of several types by the technique of pulsed laser deposition [7].

There are some physical properties of the thin-films which change over 2 to 3 orders of magnitude when the oxygen composition varies over the full phase range. Both dc-electrical conductivity [8], and optical transmittance [9], have been the subjects of study in this laboratory, primarily to determine the dependence of these physical properties upon oxygen partial pressure, $p(O_2)$. Much of the earlier data was collected under isothermal conditions at elevated temperatures ($T > 350°C$), where the kinetics of oxygen exchange are rapid. The present work has been done with $SrFeO_{2.5+x}$ films, again *in-situ* in flowing O_2/N_2 mixtures at elevated temperatures, but also under non-isothermal conditions. This has been done in order to determine some other relationships of electrical conductance with temperature and with oxygen exposure which could be relevant when these materials are in use in prototype sensor applications. In many commercial sensors a thermal program or profile, often involving significantly large temperature variations, is commonly used during sensor operation and signal transduction [4].

EXPERIMENTAL

The $SrFeO_{2.5+x}$ parent powder materials were prepared by a standard sintering process using stoichiometric mixtures of $SrCO_3$ and Fe_2O_3 at temperatures up to 1150°C. Pellets of these materials were fabricated by isostatic pressing and sintering, and these were used as targets for pulsed excimer laser ablation / deposition. By this technique thin-films, (d~300nm), were deposited onto substrates of ($1\bar{1}02$) sapphire. Experimental details of each of these procedures can be found elsewhere [3,7].

For electrical conductance measurements, ohmic contact to the films was achieved by first evaporating a gold layer at each end of the film, and then bonding gold wire to the gold covered areas. These wires then served as electrodes for the conductance measurements. The substrate/film samples were mounted upon a heater within a chamber where flowing gas mixtures could be delivered from a gas manifold equipped with mass flow controllers. A gas chromatograph (MTI 200D) in parallel to the manifold permitted an independent measurement of the gas phase composition. The apparatus was under PC-DOS control of temperature and data acquisition *via* interfaces in order to automate the collection of data during multiple temperature *vs* time profiles (ramps). The maximum ramp rate for the heater system is about $60°C(min)^{-1}$, however, during the series of measurements reported here, the programmed ramp rate was selected as $10\ °C(min)^{-1}$.

Conductance data was obtained in a number of separate experiments, with the films exposed to a selected O_2/N_2 gas mixture flowing at about $240cm^3(min)^{-1}$. Initially, using a 4-wire method, the ohmic quality of the film contacts was ascertained under isothermal conditions, in several steps through the range $150 < T < 450°C$. This was achieved by collecting voltage *vs* current data, (V/I), over the range $-50 < V < 50$Vdc (and, typically, $-3 < I < 3$mA). The subsequent experiments used 2-wire measurements over the temperature range $40 < T < 480°C$. The conductance was measured at constant applied current, ($I_{film} \leq 5\mu A$), and again with a range of oxygen composition in the O_2/N_2 gas mixture. The temperature programs included both positive and negative ramps. The selected profiles were of two types, either a continuous ramp over a wide temperature range or a stepped ramp. The latter temperature profile consisted of a series of ramp components separated by periods under isothermal conditions.

RESULTS AND DISCUSSION

The $SrFeO_{2.5+x}$ system has conductivity properties which vary significantly depending upon temperature and oxygen stoichiometry. $SrFeO_{2.5}$ is essentially an insulator under ambient conditions, but does exhibit a very low conductance at temperatures $T > 350°C$. However, with only a small increase in x, the material exhibits semiconductor characteristics even at relatively low temperatures, $T > 50°C$, and an increasing conductance with increasing temperature. When exposed to oxygen containing atmospheres with $p(O_2) > 500$ppm, the conductance of the film increases with increasing oxygen composition in the gas phase, and thus behaves as a p-type semiconductor in this region. Reversibility of oxygen uptake and conductance of the film with changing gas phase compositions is also observed, and the kinetics are rapid provided that the temperature is sufficiently high, generally for $T > 350°C$. For $SrFeO_{2.5+x}$ films under isothermal conditions and $350 < T < 480°C$, a linear relationship of ln{conductance} *vs* ln{ $p(O_2)$} has been shown to exist [8]. Data are shown in Fig.1 for both $SrFeO_{2.5+x}$ and a substitutionally related material $La_{0.1}Sr_{0.9}FeO_{2.5+x}$ for which the slopes of the logarithmic relationship lie in the range 1/4 to 1/6. The conductance data which are presented for each of the materials (Fig.1) have been normalised to permit illustration of all the data sets on one graph. The normalised conductance (σ_{norm}) is defined by the ratio of the film conductance when exposed to the indicated O_2 compositions to the conductance which is measured when the film is under an O_2/N_2 mixture containing 0.2% O_2. The linear logarithmic relationship of σ_{norm} with $p(O_2)$ is shown to hold for O_2 compositions which range from approximately 0.6% through to 100%. It is apparent from the intercepts of these curves, however, that a deviation from this linear relationship occurs as the O_2 composition decreases from 0.6%.

The films behave ohmically over wide voltage ranges. As shown in Fig. 2, there is a linear relationship in (V,I) over the full range of applied voltage ($-50 < V < 50$Vdc). Data is presented for a film held isothermally at each of two temperatures when exposed to 0.2% (Fig. 2a) and 100% O_2 (Fig. 2b), and the corresponding calculated resistance can be correlated with the isothermal data. Shown in Fig. 3 is an example of conductance data obtained during temperature ramps for a film exposed to several O_2/N_2 mixtures. The curve shown for an oxygen composition of approximately 20ppm indicates the extremely low conductance exhibited at the lower limit of oxygen stoichiometry, *ie*. for a composition of $SrFeO_{2.5}$. Experimental activation energies of conduction (E_a) have been extracted from data of this type for films maintained in an oxygen environment over wide temperature ranges. Here E_a is defined as the slope of the ln{conductance} *vs* 1/*T* curves, given by the Arrhenius form:

$$\sigma = \sigma_0.\exp(-E_a/kT)$$

Overall, values ranging between $E_a \approx 0.2$eV to $E_a \approx 0.4$eV have been measured for samples exposed to 100% and 0.2% O_2, respectively. The values for the films are comparable to those reported for sintered powders [10]. Of interest in the E_a data is the possibility of distinguishing where phase boundaries of the $SrFeO_{2.5+x}$ system exist, particularly in the higher temperature regions where the kinetics of oxygen exchange are more rapid. For instance, in Fig. 3 for $1.7 < 1000/T < 1.9$ there is clear evidence for a change in E_a *vs* 1000/*T* for all $p(O_2) \geq 0.13\%$. This region corresponds to the temperature range through which a eutectoidal transition occurs between the orthorhombic and cubic perovskite phases of $SrFeO_{2.5+x}$ [3]. Further studies are, however, required to confirm this interpretation.

Resistance data obtained for $SrFeO_{2.5+x}$ during combined ramp/isothermal temperature programs are shown in Fig. 4. These were obtained over different ranges, and for Fig. 4a shows data for a temperature program of 480-450-400-450°C with ramps in between each of the isothermal segments. Each temperature decrease results in a resistance increase, the opposite being the case for a temperature increase. This is as expected for the *p*-type semiconductor properties. At each ramp termination, as the isothermal segment is entered, the resistance continues to change, but with opposite sign to that observed during the ramp. Since the kinetics of bulk oxygen exchange are not instantaneous, these observations can be explained by the effects of a continuation of oxygen absorption (or desorption) as the $SrFeO_{2.5+x}$ system approaches equilibrium with the gas phase. The thermodynamics for the $SrFeO_{2.5+x}+O_2$ system dictate a decrease in $p(O_2)$ with decreasing *T* and, in consequence, an incremental increase in *x*. Thus, during a decreasing temperature ramp oxygen uptake will be occurring and this will continue as the ramp ends. The opposite will be the case during an increasing temperature ramp, and as noted above, an increase in oxygen composition results in a decrease in resistance, and *vice versa*. Similar data are presented in Fig 4b, but for a lower temperature region than that just described, *ie.* 400-350-400°C. Some features of this data correspond to that shown in Fig. 4a. There is a large decrease in resistance with increasing temperature, (and *vice versa*), followed by a resistance change in the opposite sense attributable to oxygen equilibration with the bulk phase. However, during the isothermal period there is an additional, slow change, where the trend is toward decreasing resistance following a temperature increase (and *vice versa*). This is possibly a consequence of the thermal treatment which the film has previously experienced, (*eg.* annealing effects upon film morphology and conductivity), although other potential mechanisms such as phase conversion, stress/strain effects and surface oxygen compositional changes cannot be eliminated at this stage.

ıtained in an
s the slope of

neasured for
the films are
he E_a data is
system exist,
;en exchange
evidence for
ɔonds to the
between the
studies are,

p/isothermal
erent ranges,
)-450°C with
rease results
crease. This
mination, as
vith opposite
exchange are
continuation
equilibrium
em dictate a
ncrease in x.
ring and this
n increasing
n results in a
4b, but for a
ome features
in resistance
hange in the
e. However,
the trend is
versa). This
is previously
ty), although
and surface

CONCLUSIONS

The conductance of $SrFeO_{2.5+x}$ thin-films over the phase limits, ($0 < x < 0.5$), and wide temperature ranges ($40 < T < 480$°C) includes components which result from bulk-compositional, surface-morphological and intrinsic electronic mechanisms. There are temperature regions within this range where one or other of these components becomes a significant contributor to the observed changes in conductivity. Overall, the dependence of conductance upon temperature and $p(O_2)$ indicates $SrFeO_{2.5+x}$ to be a p-type semiconductor for the present experimental conditions of temperature and $p(O_2)$. At temperatures where no oxygen exchange occurs because of very slow kinetics, (*ie.* for $T < 200$°C) intrinsic conduction mechanisms dominate. For $T > 350$°C, the dominant mechanism is reversible O_2 reactivity in the bulk material with a consequent contribution being due to ionic mobility as the anionic oxygen species enters the lattice. This is the region where a sensor response from the film would normally be measured, and where a linear relationship of ln{conductance} vs ln{p(O2)} has been shown to hold. At lower temperatures the conductance data indicate that thermal history plays a role, and that morphology and/or film stress relaxation can cause longer term, slow changes in conductance.

REFERENCES

1. Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama and Y Bando, *J. Solid State Chem.* 63, 237-249, (1986).
2. S.E. Dann, D.B. Currie, M.T. Weller, M.F. Thomas and A.D. Al-Rawwas, *J. Solid State Chem.*, 109, 134-144, (1994).
3. M.L. Post, B.W. Sanders and P. Kennepohl, *Sensors and Actuators* B13-14, 272-275, (1993).
4. J. Watson, K. Ihokura and G.S.V. Coles, *Meas. Sci. Technol.*, 4, 711-719, (1993).
5. *Techniques and Mechanisms in Gas Sensing*, P.T. Moseley, J.O.W. Norris and D.E. Williams, Eds., Adam Hilger, New York, (1991).
6. *Chemical Sensor Technology*, S. Yamauchi, Ed., Kodansha Ltd, Tokyo, vol 4, (1992).
7. B.W. Sanders and M.L. Post, *Mater. Res. Soc. Symp. Proc.* 285, 427-432, (1993).
8. M.L. Post, J. Yao and B.W. Sanders, *Proc 5th Int. Meeting Chem. Sensors,* v1, 446-449, (1994).
9. M.L. Post and J. Yao, *Mater. Res. Soc. Symp. Proc.* 403, 533-537, (1996).
10. J. Hombo, Y. Matsumoto and T. Kawano, *J. Solid State Chem.*, 84, 138-143, (1990).

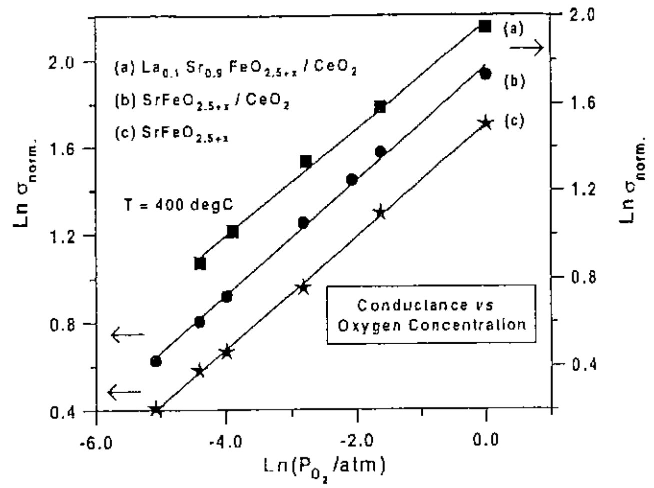


Figure 1. Dependence of conductance upon oxygen partial pressure in O_2/N_2 mixtures for three thin-film perovskite compounds at T = 400°C. Conductance has been normalised to that measured for 0.2% O_2 and is defined as σ_{norm}. For (a) and (b), the perovskite films were deposited upon an intervening layer of CeO_2 to enhance film texture with preferential orientation (110).

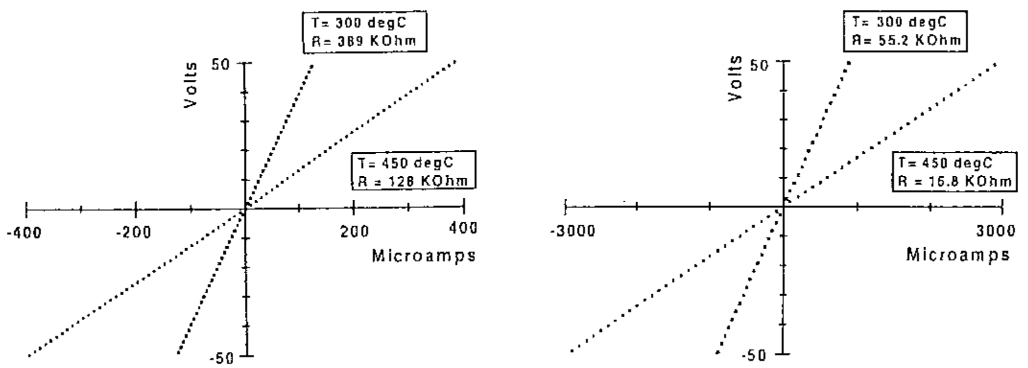
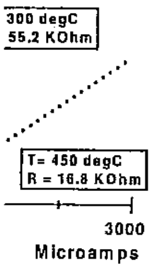


Figure 2. Data showing ohmic voltage *vs* current (*V,I*) behaviour for $SrFeO_{2.5+x}$ thin-films at two selected elevated temperatures under 0.2% O_2 (left figure), and 100% O_2 (right figure). The data were collected for each gas composition and temperature using a 4-wire method within the limits -50 < V < +50 Vdc.

/N_2 mixtures
ıce has been
) and (b), the
enhance film



$FeO_{2.5+x}$ thin-
ınd 100% O_2
erature using

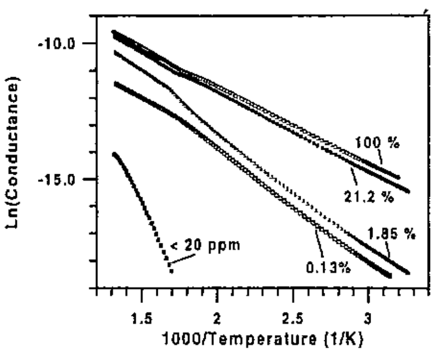


Figure 3. Arrhenius plots of the dependence of conductance upon reciprocal temperature for thin-film $SrFeO_{2.5+x}$ when exposed to flowing O_2/N_2 mixtures with the compositions indicated. For each composition, data was obtained for a temperature program (ramp) of $+10^{o}C/(min)^{-1}$. The curve for <20ppm O_2 shows the very low conductance exhibited by the $SrFeO_{2.5}$ phase.

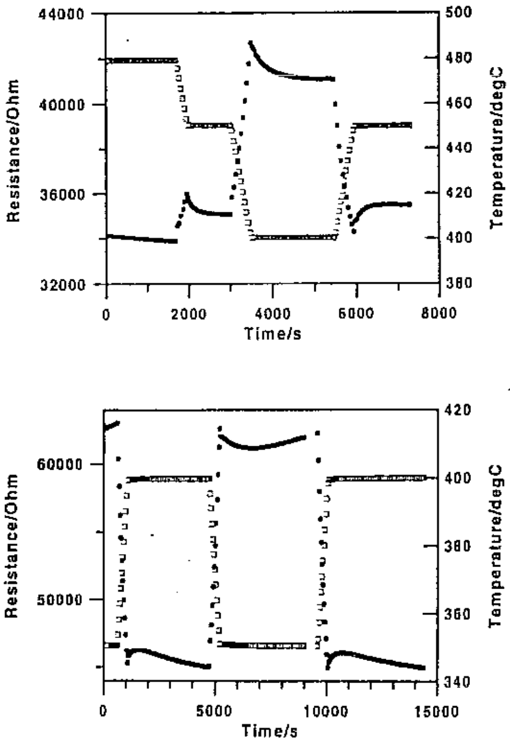


Figure 4(a&b). The dependence of electrical resistance upon temperature for thin-film $SrFeO_{2.5+x}$ when exposed to 1.9% O_2. The data were collected in a series of programmed temperature ramps with rates of $\pm 10^{o}C(min)^{-1}$ with intervening isothermal segments, and plotted as resistance (●) and temperature (□) *vs* time. Two data sets are shown. The upper fig.4a, and lower fig4.b, sets are for temperature programs of 480-450-400-450°C and 400-350-400°C, respectively.

PROCEEDINGS OF THE SYMPOSIUM ON

CHEMICAL AND BIOLOGICAL SENSORS AND ANALYTICAL ELECTROCHEMICAL METHODS

Editor

A. J. Ricco
Sandia National Laboratories
Albuquerque, New Mexico

M. A. Butler
Sandia National Laboratories
Albuquerque, New Mexico

P. Vanysek
Northern Illinois University
DeKalb, Illinois

G. Horvai
Technical University of Budapest
Budapest, Hungary

A. F. Silva
Pr Gomes Teixera
Porto, Portugal

SENSOR AND PHYSICAL ELECTROCHEMISTRY DIVISIONS

Proceedings Volume 97-19

THE ELECTROCHEMICAL SOCIETY, INC.,
10 South Main St., Pennington, NJ 08534-2896