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DETECTION OF CARBON MONOXIDE AND HYDROGEN WITH NON-STOICHIOMETRIC PEROVSKITES, AND VARIATION IN TRANSDUCTION MODES

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Thin films of the non-stoichiometric perovskite $\text{SrFeO}_{2.5-x}$ were grown by pulsed laser deposition on sapphire substrates and investigated as the sensor material for detecting CO and H_2 at concentration levels less than 1%. The variation in the electrical resistance of these semiconductor films was used as the transduction mechanism. Studies were done with CO and H_2 in air or nitrogen mixtures, with the sensor films in the temperature range $100 < T < 490$ °C. The concentration of oxygen in the gas mixture and the operation temperature of the sensor films were significant parameters in determining the magnitude of response of the films to variations in CO and H_2 concentrations. When air was used as the carrier gas, the $\text{SrFeO}_{2.5-x}$ films showed minimal response to both CO and H_2 up to 1000 ppm at $T \geq 450$ °C. At lower temperatures the sensitivities increased, but the response times were slower. When high purity N_2 was used as the carrier gas the $\text{SrFeO}_{2.5+x}$ film sensitivities to both CO and H_2 at $T \geq 400$ °C increased by close to two orders of magnitude. Over the temperature range studied, the sensor films exhibited different activation energies for CO and H_2 in N_2 so that, for these mixtures, appropriately selected temperature programming could be used to distinguish the gas species present.

INTRODUCTION

The gas-solid chemistry of non-stoichiometric perovskites can be exploited to provide the basis for chemical sensors for certain species in the gas phase (1). The structural features of these compounds (2), based on the general formula $\text{ABO}_{2.5+x}$ where A and B are each metallic elements, are highlighted by there being a large, and thermodynamically reversible, range of oxygen composition. For some $\text{ABO}_{2.5+x}$ compounds the oxygen stoichiometry ranges from $0 < x < 0.5$. The chemistry defining this range in composition is redox in character, thus the B element must exist in at least two stable oxidation states. In addition, it is found for some compounds that within the composition limits (*ie* as x changes) order-disorder phase transitions occur as a consequence of longer range interactions in the oxygen sub-lattice. For example (3), the perovskite $\text{SrFeO}_{2.5-x}$ exhibits four phases in the range $\text{SrFeO}_{2.5}$ to SrFeO_3 . The combination of reversible chemical composition and structure is accompanied by large and reversible changes in physical properties, such as electrical and optical (4,5), which

can be used in sensor applications. Previously, $\text{SrFeO}_{2.5+x}$ thin films have been shown to behave as p-type semiconductors with respect to variations in oxygen concentration (4). The present work describes the conductance response of $\text{SrFeO}_{2.5+x}$ thin films with respect to variations in either CO or H_2 concentrations in gas mixtures which have both low and high partial pressures of oxygen.

EXPERIMENTAL

$\text{SrFeO}_{2.5+x}$ pellets were prepared from stoichiometric mixtures of SrCO_3 and Fe_2O_3 using standard sintering methods, and thin films ($d \sim 200$ nm) of $\text{SrFeO}_{2.5+x}$ on (1102) sapphire substrates were grown by the pulsed laser deposition technique as described elsewhere (1,6). Electrical contact to the films was achieved by thermally evaporating two gold pads ($d \sim 200$ nm) directly onto the ends of the film followed by the bonding of gold wires to these pads. The films were then mounted onto a heater assembly within a stainless steel 1 liter chamber where flowing gas mixtures could be delivered, and the temperature could be controlled within the range $20 < T < 490^\circ\text{C}$. A gas chromatograph (MTI 200D) in parallel with a gas manifold equipped with mass flow controllers provided independent measurements of the gas phase composition. Construction details of this system are provided elsewhere (4,7). The subject gases were each delivered at a flow rate of $250 \text{ cm}^3/\text{min}$ in a binary mixture with either ultra high purity N_2 (with $[\text{O}_2] < 40$ ppm; $[\text{H}_2\text{O}] < 10$ ppm) or air (Matheson, "zero" grade, $[\text{H}_2\text{O}] < 10$ ppm) at CO or H_2 concentrations ranging from $10 \text{ ppm} \leq [C] \leq 1\%$. The resistance of the $\text{SrFeO}_{2.5+x}$ film immediately prior to changing the concentration of a gas mixture was taken to be R_0 , and after a time period which allowed for the film to equilibrate in the new gas environment, a final value, R , was recorded to determine the relative sensitivity R/R_0 . The equilibration time varied from about 5 minutes at the higher temperatures, to periods exceeding 1 hour at lower temperatures where the reaction kinetics were found to be very slow.

Initial screening experiments were conducted on the $\text{SrFeO}_{2.5+x}$ thin films, where the resistance was measured isothermally in the range $100 < T < 490^\circ\text{C}$. The composition of the gas phase was incremented from 0 to 1000 ppm of the target gas in the carrier gas, and then back to 0 ppm. Subsequent, more detailed measurements were made for exposure to CO at a selected temperature in both air and N_2 , where the gas concentration was varied from $10 \text{ ppm} \leq [C] \leq 1000$ ppm.

To determine the dependence of sensor response on temperature, dynamic temperature ramping experiments were performed for sensor films exposed to both CO and H_2 at 1000 ppm in N_2 . The temperature was cycled at a rate of $\pm 50^\circ\text{C}/\text{min}$ between $350 < T < 490^\circ\text{C}$ four consecutive times to confirm reproducibility and reversibility.

RESULTS AND DISCUSSION

Figure 1 represents an overview of the data obtained for a series of experiments with CO and H_2 at $[C] = 1000$ ppm in air and N_2 . In all cases under the conditions examined, p-type behaviour was observed, where an increase in either CO or H_2 concentration resulted in an increase in resistance. The data show two distinct regions of response, with resistance changes obtained for the subject gases in N_2 mixtures being close to two orders of magnitude larger than those for air mixtures. From the phase relationships for $\text{SrFeO}_{2.5+x}$ at low O_2 partial pressures (1,3), it is clear that larger sensitivity and resistance response is found for the sensor film which has a composition

close to $\text{SrFeO}_{2.5}$, *ie.* has the brownmillerite structure. When air is the carrier gas, there is a temperature dependence on the sensitivity of the film to both 1000 ppm CO and H_2 , with maximum sensitivities $R/R_0 = 1.7$ at 300 °C for CO and $R/R_0 = 1.45$ at 350 °C for H_2 . When N_2 was the carrier gas and for $T > 350$ °C, the sensor response (R/R_0) to CO was greater than that for H_2 as was observed when air was the carrier gas. However for N_2 mixtures with the sensor film at $T < 350$ °C, no resistance data was obtained because the films are essentially insulators in this lower temperature range and exhibit a resistance greater than the 120 M Ω instrumental limit.

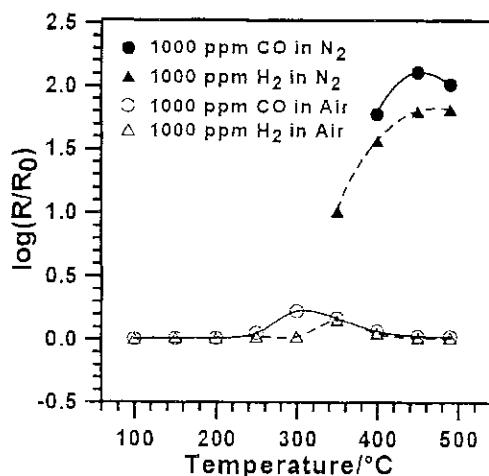


Figure 1. changes in relative resistance, R/R_0 , (sensitivity response) for $\text{SrFeO}_{2.5-x}$ thin-films when exposed to CO and H_2 in air and ultra high purity N_2 mixtures.

The rates of response for films at $T > 350$ °C were relatively rapid, with time to 80% of resistance change of about 5-10 min. In many cases, the response to a change in gas composition resulted in a very fast initial change in conductance (30-100 seconds for an 80% of resistance change) followed by a much more gradual conductance response. For temperatures $T < 350$ °C, the response rates were significantly slower, exceeding 60 minutes, indicating that lower temperature operation of $\text{SrFeO}_{2.5-x}$ thin-films for CO and H_2 sensing is probably not appropriate. It was found that the rate of response of the films with respect to exposure to H_2 was slower than that for CO.

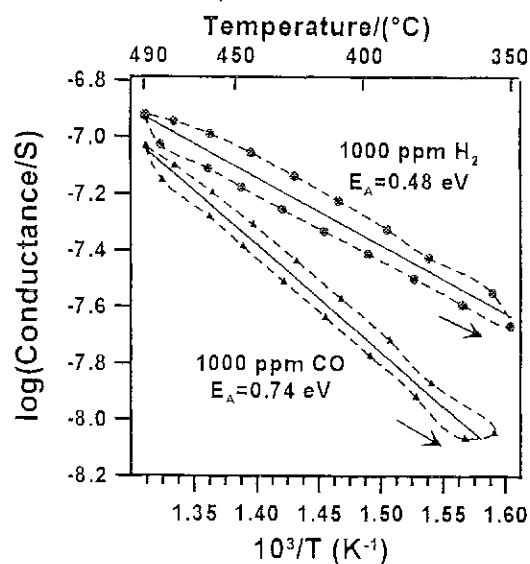


Figure 2. Arrhenius plot showing the dynamic temperature response for $\text{SrFeO}_{2.5-x}$ thin films to thermal cycling between $350 < T < 490$ °C at rates ± 50 °C/min: (\blacktriangle) CO and (\bullet) H_2 , each at 1000 ppm in N_2 . Hysteresis is a result of non-equilibrium at these temperature ramp rates.

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Shown in Figure 2 are data obtained during programmed temperature ramps over the range $350 < T < 490$ °C for films exposed to 1000 ppm CO and H₂ in N₂. The sensor films did not achieve equilibrium during the rapid temperature ramps, thus the curves exhibit the hysteresis form shown. The data show a distinct difference in thermal response between the two gases, as evidenced by the slope variation. From the slope, the experimental activation energy of conduction can be calculated as 0.74 eV and 0.48 eV for CO and H₂, respectively. In contrast, the same film thermally cycled in N₂ alone has a significantly smaller experimental activation energy of conduction of 0.27 eV. For SrFeO_{2.5+x} thin films higher activation energy values usually indicate that the film is in a more reduced state (4). This latter observation, along with the faster kinetics for exposure to CO compared to H₂, and the slightly greater sensitivity response of the film to CO than to H₂ (Figure 1) indicates that CO is more effective at reducing the film. This offers the potential to exploit the difference in reactivity in order to discriminate between these two gases by, for example, a dynamic method employing thermal cycling techniques (8).

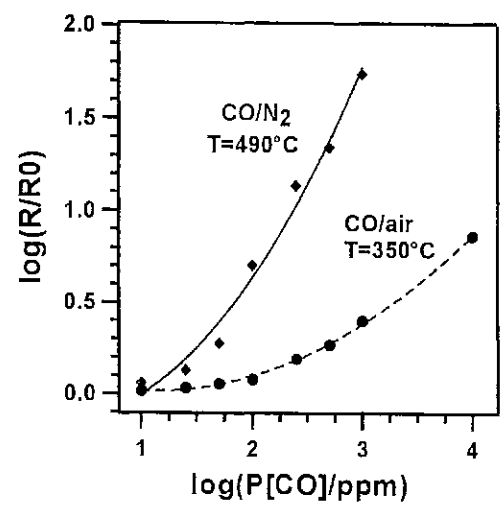


Figure 3. Dependence of the sensitivity response for SrFeO_{2.5+x} thin films on the concentration of CO in: (●) air and (◆) N₂ mixtures at the selected optimum operational temperatures.

Figure 3 shows the relationship between the concentration of CO and the sensitivity response of the SrFeO_{2.5+x} film for each carrier gas at the selected optimum temperature of operation. The magnitude of the sensor film response to CO in each carrier gas is different, indicative of different mechanisms of transduction. Clearly, the sensitivity to CO as shown in Figure 3 is much greater in the low partial pressure oxygen environment of the N₂ carrier gas.

Two transduction mechanisms which are proposed to account for the change in thin-film conductance are based on the following different redox processes: (i) a reduction of the SrFeO_{2.5+x} thin-film bulk with a consequent change in *x*; and (ii) oxidation of CO (or H₂) at the SrFeO_{2.5+x} surface by reaction with O₂ in the gas phase and/or adsorbed/chemisorbed state without a change in *x*. The former would be expected to dominate for CO (or H₂) in N₂ mixtures, and the latter for air mixtures. When a change in *x* occurs, which is a bulk, structural change, it is accompanied by larger changes in physical properties of the sensor film than is the case for surface reaction alone. Which of these mechanisms predominates is dependent upon the redox chemical potential of the gas mixture and the reaction kinetics at the gas-surface-bulk interfaces. Although there is complex chemistry taking place at the SrFeO_{2.5+x}-gas interface, this qualitative

transduction model explains the relative sensitivity responses of SrFeO_{2.5-x} thin-films to CO and H₂ in environments with both high and low oxygen partial pressures

CONCLUSIONS

The optimum conditions for application of SrFeO_{2.5-x} thin-films in detecting CO and H₂ at levels lower than 1000 ppm in air and in an atmosphere with very low oxygen partial pressure have been determined. The SrFeO_{2.5-x} sensor films exhibited the best combination of magnitude of response, speed of response and sensitivity under conditions with moderately high temperatures, $T > 450^{\circ}\text{C}$, and in an environment with low oxygen partial pressure: as provide in this case by N₂ ($C[\text{O}_2] < 40 \text{ ppm O}_2$). The higher and lower sensitivity of the sensor films when exposed to the target gases in N₂ and air, respectively, is rationalised in terms of two competing mechanistic processes, where CO or H₂ is oxidized either by oxygen in the SrFeO_{2.5-x} thin-film bulk or by a surface reaction with oxygen in the carrier gas. Under the conditions studied, CO is a stronger reducing agent for SrFeO_{2.5-x} thin films than is H₂. This difference in relative reactivities can be utilized to discriminate between the two gases by using programmed thermal operation of the SrFeO_{2.5-x} films.

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