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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.snb.2004.12.104>

Sensors and Actuators B: Chemical, 108, July, pp. 102-112, 2005

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Hydrocarbon sensing with thick and thin film p-type conducting perovskite materials

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Received 14 July 2004; received in revised form 20 November 2004; accepted 20 December 2004

Available online 17 February 2005

Abstract

The members of the p-type semiconducting $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ family of perovskites have been studied as novel materials for hydrocarbon sensor applications. Screen-printed thick film devices are contrasted to thin films prepared by pulsed laser deposition (PLD). In order to enhance sensor specificity towards hydrocarbons, the influence of iron content, x , film thickness and operating temperature in the range from 300 to 500 °C has been investigated. In addition, the use of a catalytically active cover layer made of a platinum-doped zeolite has been successfully studied to reduce the influence of species with cross-interference. An initial model explaining the underlying sensing mechanism is proposed.

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Keywords: p-type semiconductor; PLD; Zeolite; Hydrocarbon sensor; Perovskite; $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

1. Introduction

Due to the introduction of more stringent regulations governing air-pollution, it becomes important to focus research on the development of low-cost gas sensors in order to access applications where the use of conventional analytical systems is prohibitively expensive, e.g. in harsh environments such as in automobile exhaust. Much previous research effort has focused on n-type conducting oxide ceramics such as SnO_2 (cf. review articles, e.g. [1,2]). Although p-type conducting oxide ceramics may present an excellent alternative due to their higher catalytic activity [3], they are considerably less investigated. Some exceptions include the commercially available ammonia gas sensors, $\text{Cr}_{2-x}\text{Ti}_x\text{O}_3$ [4–6] and NO_x sensors based on perovskite rare-earth metal oxides of the LnFeO_3 family, where Ln is La, Nd, Sm, Gd and Dy [7].

This contribution focuses on sensor characteristics of a p-type conducting semiconductor formulation with the perovskite structure, $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ with $x=0.2\text{--}0.5$ (annotated in the following as STF x with x as a percentage). Originally, this material was introduced for oxygen sensing at temperatures between 700 and 900 °C. For the STF35 composition, in particular, a temperature independent resistance over this temperature range has been reported in the literature [8].

The oxygen stoichiometry of oxide ceramics like STF x depends on the oxygen partial pressure of the ambient gas phase as well as on temperature. At lower temperatures, i.e. in the range between 350 and 450 °C, the bulk equilibration with oxygen, which leads to oxygen sensitivity of the material, is kinetically hindered and, therefore, a very slow process. However, a stable and reversible response towards hydrocarbons in the analyte atmosphere has been observed in preliminary studies [9,10].

In this contribution, results of systematic investigations on hydrocarbon sensitivity are presented. In addition to studies on sensor response towards saturated and unsaturated hydro-

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carbons, i.e. propane and propene, measurements of cross-sensitivity and temperature dependency were conducted. Work has focused on STF40, with an iron content close to the temperature independent composition, which enables the detection of hydrocarbons and oxygen with a single sensor device by simply changing its operating temperature.

In order to develop a highly selective and sensitive hydrocarbon sensor, different deposition techniques for STF have been tested. Sensor films have been fabricated using thin and thick film processing techniques and their corresponding sensor functionality has been compared and contrasted. Response characteristics, cross-sensitivity and temperature dependency of screen-printed thick film devices are compared to thin films that were grown using a pulsed laser deposition (PLD) technique. The different behaviour of both sensor types is discussed. Furthermore, a reactive cover layer has been studied in order to enhance selectivity of the sensors.

2. Experimental

Ball-milled powders of different $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ compositions ($x=0.2\text{--}0.5$) were prepared via a mixed oxide route using SrCO_3 , TiO_2 and Fe_2O_3 as precursor materials. Phase purity of the samples was assured by XRD measurements, and the average particle diameter was determined by laser diffraction. In Fig. 1, typical XRD patterns of STF x powders are presented, which can be indexed as single phase on the pseudo-cubic perovskite lattice. Particle size of the powders varied between 1.6 and 2.1 μm .

To prepare thick film samples, initially a SrAl_2O_4 underlayer was deposited to serve as a diffusion barrier in order to avoid interactions with the alumina substrate. Then, the STF film was deposited on top using a screen-printing technique, as described in Ref. [11]. In a second step, printable pastes of STF powders were applied and sintered at 1100 °C. Film thicknesses of 15–25 μm were obtained.

For preparation of thin film samples, cylindrical pellets of the same STF powders were sintered, and these served as targets for PLD technique. The substrate used was sap-

phire (1 $\bar{1}$ 0 2) single crystal squares of 1 cm $\times$ 1 cm and of 0.5 mm thickness, and these were heated to 700 °C under vacuum conditions (4×10^{-4} Pa) prior to deposition. Films were then deposited under 13 Pa of oxygen partial pressure for 15 min using a Lambda-Physik LPX305i excimer laser operating with Kr/F ($\lambda = 248$ nm). With a pulse rate of 8 Hz and an energy density of 1.5 J/cm², the film thickness, from earlier calibration measurements, was estimated to be approximately 200–300 nm. Gold electrodes were evaporated onto the film surface to serve as electrodes for conductivity measurements.

The films were characterised using X-ray diffraction with Cu-K α radiation in the range $10^\circ \leq 2\theta \leq 80^\circ$ on a Bruker D8 diffractometer. The diffractometer is equipped with Göbel mirrors, which effectively filter the Cu-K β radiation with parallel-beam geometry. For the microstructural analysis, images were obtained by scanning electron microscopy on a Hitachi S4800 FEG-SEM with an accelerating voltage of 0.5 kV.

Measurements of sensor performance were conducted in a tube furnace, where the specimens were exposed to different gas compositions. The total test gas flow was adjusted between 300 and 600 ml/min. Before each measurement, samples were kept in a reference composition of 20% oxygen in nitrogen for at least 20 min to allow equilibration.

To this baseline gas composition, propane and propene as well as a hydrocarbon mixture (containing ethane, ethene, acetylene and propene in equal proportions, denoted as HC4) were then added to test the sensitivity of the material towards hydrocarbons. Concentrations for the analyte gases ranged from 0 to 3000 ppm. In order to study response to interference gases, similar measurements were conducted with CO, NO and H₂.

The furnace temperature was adjusted in the range between 300 and 500 °C, and the dc-sensor resistance was measured with a Keithley 2700 digital multimeter. Additionally recorded ac-impedance spectra and in some cases I–V-plots indicated an ohmic behaviour of STF films. These findings are in accordance with other published data which predict the presence of conductive grain boundaries for compositions with high iron content [12], although the presence of

Fig. 1. XRD spectra of STF x powders.

depletion layers and highly resistive grain boundaries was observed for slightly Fe-doped SrTiO_3 with an iron content up to 0.15% [13].

3. Results

3.1. Microstructure of sensor films

3.1.1. Thick films

An SEM micrograph of an STF40 thick film deposited on an alumina substrate is shown in Fig. 2. A very porous structure is found, with particle sizes of approximately $2\ \mu\text{m}$. The powder particles have almost conserved the size of their “green state” before sintering. The high porosity and the absence of pronounced sinter necks indicate that only a slight sintering had occurred at 1100°C , which is in accordance with sinter experiments that predict a required sinter temper-

atures of at least 1430°C for STF x . Contrary to bulk ceramics, where one tries to achieve very dense structures, the observed porosity is favorable in the case of thick film sensors, because the analyte gas can penetrate the sensor structure more easily. A larger reaction surface for the sensor response is thereby provided.

3.1.2. Thin films

Fig. 3 shows a set of X-ray diffraction patterns obtained at room temperature for the films deposited at 700°C . In the 2θ range examined, only one reflection at $2\theta \sim 32.3^\circ$ is observed which is due to the sample film. The two high intensity reflections are assigned to the sapphire substrate. Based on the pseudo-cubic perovskite lattice, the reflection for STF x is indexed (1 1 0), and the films are therefore considered to be microcrystalline with partial texturing and with an orientation (1 1 0) dominant. Inset in Fig. 3 are details in the (1 1 0) region of three STF compositions for $x=0.3, 0.4$ and 0.5 .

Fig. 2. Scanning electron micrograph of an STF40 screen-printed thick film.

Fig. 3. XRD pattern of STF40 measured at room temperature. Inset shows the enlarged portion of the (1 1 0) region as a function of changing Fe content x . Sapphire (*) peaks are (1 $\bar{1}$ 0 2) and (2 $\bar{2}$ 0 4).

Fig. 4. Scanning electron micrograph of an STF40 thin film deposited by PLD.

There is a trend to higher 2θ (1 1 0) with increasing x which indicates a decreasing unit cell volume with increasing Fe content. Again, this is in accordance with published results [14].

Fig. 4 shows the FEG-SEM image of an STF40 thin film, which was deposited by PLD at 700°C . The image was obtained with an accelerating voltage of 0.5 kV and a magnification of 100×10^3 .

When compared to the microstructure of the thick film (Fig. 2), the grains are more homogeneously distributed and

present a considerably reduced porosity. The grain sizes also are comparatively small with an average dimension of around 10–20 nm, indicating a dense film with a relatively smooth surface.

3.2. Comparison of different STF compositions

Fig. 5 presents typical resistance response measurements for STF40 thick and thin film sensors when exposed to propane. The sensor devices show a fast, stable and reversible

Fig. 5. Resistance response of an STF40 thick film (left) and thin film (right) to propane in dry air.

Fig. 6. Arrhenius plots of normalized sensor resistance ρ' of thick film samples (in air).

response over a wide concentration range. As resistance is reciprocally proportional to film thickness, the thin film shows a higher base resistance than the thick film.

In order to study base features of the STF x series, Arrhenius measurements of normalized resistance $\rho' = R \frac{wd}{T}$ were conducted on thick-film specimens with a film width w of 1.2 mm and an electrode spacing l of 1.5 mm; film thickness d being about 20 μm for all samples. For calculation of plotted resistivity values, film porosity has not been taken into account. Therefore, the obtained values ρ' are approximately one order of magnitude higher than bulk resistivity values. In addition, it becomes clear that the sensor resistance decreases rapidly with increasing iron content (Fig. 6).

A strong temperature dependency of resistance is observed. This dependency is a drawback for practical applications and will need to be addressed in such devices, as an exact control of the operating temperature T is required.

In order to identify the most suitable STF composition for studying in more detail, the response towards 500 ppm propane of samples with different iron content from $x=0.2$ to 0.5 was surveyed.

In Table 1, the resistance responses towards propane of thick film and thin film samples at 400 °C are summarised.

Table 1
Influence of STF composition, x , on hydrocarbon sensitivity of thick and thin film sensors with platinum electrodes

Composition	Sensitivity (500 ppm propane, 400 °C) (%)	
	Thick films	Thin films
STF20	59	141
STF30	43	118
STF40	42	112
STF50	48	113

Table 2

Sensitivity of thick film sensors towards saturated and unsaturated hydrocarbons

T (°C)	S_{propane} (%)	S_{propene} (%)	S_{HC4} (%)
STF40			
375	80	195	110
400	50	79	62
425	40	37	33
450	18	8.8	7.3

For definition of S , see text.

Here, sensitivity S is defined as

$$S_{\text{gas}} = \frac{R_{\text{gas}} - R_0}{R_0} \times 100\% \quad (1)$$

where R_0 is the resistance in air and R_{gas} is the resistance in presence of the gas component.

In both the cases, sensitivity in the presence of propane is almost invariant for samples with higher iron content. However, a pronounced increase in sensitivity is observed for thin film samples, thus indicating that this effect should rather be related to the sample microstructure than to the iron content.

3.3. Saturated and unsaturated hydrocarbons

Fig. 7 shows results of a temperature dependency conducted on STF40 thick films and thin films. Propane was chosen as the saturated hydrocarbon species, whereas propene served as the unsaturated hydrocarbon. A double-logarithmic representation of sensor resistance as a function of analyte concentration is chosen in order to define slopes which are a measure of sensitivity.

In particular, in the case of thick film devices, comparison between saturated and unsaturated hydrocarbons indicates a different apparent thermal activation of sensitivity for these gases. At high temperatures of 450 °C, propane response is much more pronounced. However, as sensitivity towards propene increases more rapidly with decreasing temperature, it is observed that at temperatures below 400 °C, propene response becomes much more prominent. Hence, an appropriate choice of operating temperature may enable distinguishing between different hydrocarbons using STF thick films.

Furthermore, response measurements were conducted with a hydrocarbon mixture containing ethane, ethene, acetylene and propene in equal proportions (HC4). Sensitivities towards propane, propene and HC4 at different operating temperatures are summarized in Table 2. The total concentration in C-atoms, which has also been verified using an FID device, is kept constant, i.e. 500 ppm C_3H_8 , 500 ppm C_3H_6 and 682 ppm HC4. Although actual concentration of the latter is even higher, one observes that response towards this HC4 mixture that contains mostly unsaturated and therefore very reactive hydrocarbons decrease more rapidly with increasing temperature than in the case of propane or propene.

Fig. 7. Temperature dependency of the resistance response towards propane (left) and propene (right) of an STF40 thin film sensor (upper part) and of an STF40 thick film sensor (lower part) in double-logarithmic representation. Balance: dry air, sensor temperature as indicated. R_0 indicates the baseline resistance.

3.4. Temperature dependency and cross-sensitivity

Cross-sensitivity towards other gaseous species that might be present in the ambient is another crucial aspect in sensor applications. In order to evaluate a new gas sensitive material, it is important to test its response to a variety of gases.

In Figs. 8 and 9, cross-sensitivity tests of STF40 thick film and thin film sensors towards a variety of analyte gases is plotted as a function of operating temperature in the range from 350 to 500 °C. Different gaseous species were added to a dry air flow as indicated in Figs. 8 and 9.

It is observed that the response characteristics of the thick and thin film samples are different. In the case of the porous screen-printed thick film with platinum electrodes, the sensor resistance varies negligibly when hydrogen or CO is added. The thin film sample, however, responds towards each tested gas over almost the entire temperature range.

These findings indicate that thick film sensors present greater selectivity for certain hydrocarbons and are potentially more favourable than thin film devices. However, the pronounced cross-sensitivity towards NO in the thick film is a drawback that requires further attention.

As a first strategy, the use of a cover layer on top of the thick film has been studied. This method is well known in the literature, where different groups have recently investigated

different kinds of catalytically active layers for selectivity enhancement [15–17].

In the present case, a Pt-doped zeolite (ZSM5) has been chosen as a catalytic filter layer. The material has been prepared using an ion exchange process as described elsewhere [18]. For initial measurements, a paste of this powder has

Fig. 8. Cross-sensitivity of a thick film sensor (composition: STF40) at different temperatures. Balance: dry air, other gas concentrations as indicated.

Fig. 9. Cross-sensitivity of a thin film sensor (composition: STF40) at different temperatures. Balance: dry air, other gas concentrations as indicated.

been applied on top of thick film STF20 sensors and fired at 450 °C. Fig. 10 shows an SEM cross-section of such a device, from which the zeolite layer thickness was determined to be approximately 100 μm . Impedance spectra of the covered devices do not show any pronounced deviation from those of the original sensor elements, which indicates that the zeolite does not contribute to the overall sensor resistance.

In Fig. 11, cross-sensitivity of sensor devices with and without a zeolite layer are compared and contrasted. Clearly, the zeolite covered sensor films are very selective towards saturated hydrocarbons, i.e. propane. In particular, the response towards NO is reduced without either CO or hydrogen cross-sensitivity being enhanced. Hence, a very selective propane sensor element is obtained.

4. Discussion

In sensitivity measurements towards propane (Fig. 5), the STF compositions show the expected behaviour of a p-type

Fig. 10. SEM cross-section of a thick film sensor covered with a zeolite layer.

Fig. 11. Cross-sensitivity of thick film sensors with and without the zeolite cover layer.

conductor in presence of reducing gases [9,10], such that when propane is added to the ambient, the resistance of the sensor increases. This is in accordance with the understanding of n-type materials, where the inverse effect is observed.

In the following, an initial mechanistic model for these p-type semiconductor sensors is proposed which is based on work by several research groups describing the sensing mechanism of n-type metal oxide sensors [1,19,20]. In oxygen containing atmospheres, an oxygen adsorption layer is always present on the sensor surface surrounding the grain boundaries, and each adsorbed oxygen species is expected to act as an electron acceptor state. This state traps electrons and is therefore negatively charged, which is written formally as $O_{2,ads}^-$, O_{ads}^- or O_{ads}^{2-} . In the considered temperature range, O_{ads}^{2-} is expected to be the predominant adsorbed species [1]. From heterogeneous catalysis studies, it is known that a p-type semiconductor oxide surface tends to be covered completely with chemisorbed oxygen, even at temperatures up to 500 °C and at low oxygen content in the ambient [3].

When reducing agents, i.e. hydrocarbons C_nH_m , arrive on the catalytically active sensor surface, they react with the adsorbed oxygen or with labile oxygen in the bulk material (i.e. for $SrTi_{1-x}Fe_xO_{3-\delta}$, there is an increase in δ). This process may be described by the following reaction, assuming complete hydrocarbon oxidation to be occurring on these p-type semiconductors [3].

where h^+ denotes defect electrons or holes.

For this reaction, charge carriers h^+ are consumed, which leads to an increase in resistance. However, the redox-reaction is not the only process responsible for a high sensitivity. To cause a notable resistance change, the gas components need to penetrate deeply into the film structure in order to react with the total film bulk. Depending upon the average pore size of the film, this penetration is governed either by Knudsen diffusion or by classical gas diffusion.

Thus, in order to study the film response towards different gaseous species, it is necessary to consider the competition which occurs between a diffusion and a reaction step, as described by the following differential equation:

$$\frac{\partial c}{\partial t} = D_{eff} \frac{\partial^2 c}{\partial z^2} - kc^n \quad (2)$$

In Eq. (2), c denotes the concentration of the gas component, D_{eff} the effective diffusion coefficient, k the reaction constant and z is the penetration depth from the surface into the film.

For first calculations, one assumes steady state conditions, i.e. $d/dt=0$, and a first-order reaction, i.e. $n=1$, which is generally valid in the case of excess oxygen [3]. The reaction can either follow a Langmuir–Hinshelwood mechanism, where both reaction species have to chemisorb on the surface, or an Eley–Rideal mechanism, where only one gas species is adsorbed on the surface. Given the general behaviour of p-type oxides in excess oxygen, the second is more likely.

Furthermore, a parameter $\gamma = (k/D_{eff})^{0.5}$ describing the ratio between reaction kinetics and diffusion constant is introduced. Solving the differential equation using appropriate boundary conditions leads to a concentration profile $c(z)$ that depends strongly on γ as well as on film thickness d .

In the case of thin films, all gases should penetrate the film completely, so that each gas species reacting with adsorbed oxygen is also detected. For the thick film case, however, $c(z)$ cannot be expected to be almost constant throughout the film volume. If γ is prominent, i.e. the gas is highly reactive, it is expected that the entire incoming gas is already oxidised at the upper surface of the sensor. Consequently, total sensitivity (i.e. an integral value over the entire layer thickness) towards such gases (e.g. hydrogen or CO) should be very small in the case of thick film sensors. If γ is small, i.e. the gas is not very reactive (e.g. propane), the gas can penetrate the entire thick film volume, so that these gases are more likely to cause a pronounced response.

The initial model has been further developed to fit experimental data for thick film sensors. Given that conductivity, σ , of STF increases with the amount of adsorbed oxygen, and hence, depends on the reaction rate of the redox reaction, the following equation (Eq. (3)) is proposed as a first approximation:

$$\sigma \approx \sigma_0 \theta \quad (3)$$

Here σ_0 denotes film resistivity in air and θ is the degree of oxygen occupation of the surface. Surface occupation, θ , in the presence of a reducing gas is governed by an adsorption–desorption equilibrium of oxygen and consumption of adsorbed oxygen according to the following equation [21]:

$$\theta = \frac{k_{ads}\sqrt{pO_2}}{k_{des} + k_{ads}\sqrt{pO_2} + k_{red}p_{red}} \stackrel{k_{ads}\sqrt{pO_2} \gg k_{des}}{\approx} \frac{1}{1 + \beta p_{red}} \quad (4)$$

where k_{ads} and k_{des} are the rate constants of dissociative oxygen adsorption and desorption, k_{red} the rate constant of redox reaction, p_{red} the partial pressure of reducing gas and β is a temperature dependent constant, which combines the rate constants for adsorption, desorption and redox reaction and oxygen partial pressure.

In Eq. (4), a Langmuir adsorption process involving oxygen dissociation has been assumed. The assumption that $k_{ads}\sqrt{pO_2} \gg k_{des}$ is justified by the fact that p-type semiconductors tend to be covered completely with an oxygen layer.

Using the dependency between partial pressure, p_{red} , and concentration, c , of reducing gas species and introducing the constant α , Eq. (4) can be rearranged to the following form:

$$\sigma \approx \frac{\sigma_0}{1 + \alpha c(z)} \quad (5)$$

with $c(z)$ denoting the gas concentration profile and α being a thermally activated factor.

Table 3
Fitting parameters of Fig. 12

	M (g/mol)	ε/k_B (K) ^a	κ (nm) ^a	k_0 (10 ¹⁰ /s) ^c	$E_{a,k}$ (eV) ^c	α_0 (ppm ⁻¹) ^b	$E_{a,\alpha}$ (eV) ^b
Propane	44.097	237.1	0.5118	70	0.83	27000	0.093
Propene	42.081	298.9	0.4678	500	0.81	400000	0.073
H ₂	2.016	59.7	0.2827	90	0.52	3000	0.052

^a From Ref. [22].

^b Fit parameter.

^c Estimated according to [3].

It is now possible to calculate sensitivity towards specific gases as a function of temperature using this dependency between conductivity, σ , and concentration profile, $c(z)$, which is calculated by solving Eq. (2).

$$R_0 = A_{\text{geo}} \frac{1}{\int_0^d \sigma_0 dz} \quad \text{and} \quad R_{\text{gas}} = A_{\text{geo}} \frac{1}{\int_0^d \sigma(z) dz} \quad (6)$$

$$S_{\text{gas}} = \frac{R_{\text{gas}} - R_0}{R_0} \times 100\% = \left(\frac{d}{\int_0^d \frac{1}{1+\alpha c(z)} dz} - 1 \right) \times 100\% \quad (7)$$

In Eq. (6), d is the film thickness and A_{geo} is a factor describing film geometry, which is present in both resistance terms and can thus be eliminated.

The experimental data of Fig. 8 has been fitted according to above hypothesis and Fig. 12 shows the fitted curves. In Table 3, the fitting parameters are summarized. Parameters in the first three columns serve for calculating gas diffusion coefficients after Reid and Sherwood as described in [22]. M is the molecular weight of each gas, k_B is the Boltzmann constant, κ describes the distance between the centers of colliding gas molecules and ε is a gas specific Lennard–Jones “force constant”. Assuming a porosity ξ of 0.5 and a diversion factor ν of 2, the effective diffusion constant $D_{\text{eff}} = \xi D / \nu$ is calculated. Parameters in columns 4–6 of Table 3 are used

for calculating k (cf. Eq. (2)) and α (cf. Eq. (5)) according to the following Arrhenius laws:

$$k = k_0 \exp\left(-\frac{E_{a,k}}{k_B T}\right) \quad \text{and} \quad \alpha = \alpha_0 \exp\left(-\frac{E_{a,\alpha}}{k_B T}\right) \quad (8)$$

Wherever possible, modeling parameters were collected from literature (cf. footnotes in Table 3). The remaining free parameters k_0 and α were obtained by curve fitting.

It is apparent that the different thermal activation of sensitivity towards saturated and unsaturated, i.e. more reactive, hydrocarbons is also included in the model. Although the order of magnitude of chosen parameters are quite probable, deviations of measured and calculated data, especially in the case of propene, indicate that the model has to be further refined. In particular, evaluating the parameter α , that describes the combined adsorption–reaction process, requires more experimental data. However, the model does adequately describe the film response towards propane and insensitivity towards H₂. An increase in sensitivity towards propene at low temperatures is also included in the model, but a lack of accuracy becomes evident at these temperatures.

Noteworthy with zeolite covered thick films (Fig. 11) is the selectivity towards saturated hydrocarbons, i.e. propane. By using a Pt-ZSM5 filter, one obtains a fast and highly selective propane sensor. Cross-sensitivity towards NO is effectively reduced. It is assumed that this is due to an oxidation process, while diffusing through the zeolite cover layer, NO is oxidised to NO₂ on the platinum clusters of the zeolite, so that it does not reach the actual gas sensitive STF layer.

In addition, further preliminary studies indicate that thickness of the filter layer is an important variable that has to be optimized carefully. The zeolite acts as a diffusion barrier that leads to a longer response time of the sensor if the cover becomes too thick. However, a very thin filter is not sufficient for eliminating NO sensitivity completely. Future studies will be addressing optimisation of zeolite layer thickness.

5. Conclusions

Different p-type conducting SrTi_{1-x}Fe_xO_{3-δ} compositions as thick and thin films have been investigated for hydrocarbon sensor applications. In order to enhance sensor specificity towards hydrocarbons, the influence of film thickness, operating temperature and iron content x have been investi-

Fig. 12. Fitted sensitivity curves assuming a diffusion-reaction model.

gated. In addition, the use of a catalytically active cover layer has been shown to be effective as a selectivity enhancer.

For thick film sensors, an optimum range for operating temperatures has been identified. Between 400 and 450 °C, hydrocarbons can be detected with sufficient sensitivity. Sensor response is stable, reversible and fast. At higher temperatures, hydrocarbon response decreases rapidly, whereas at lower temperatures, response towards NO becomes more prominent and sensor response is slow.

Thin film sensors present a more pronounced cross-sensitivity towards a variety of gases than thick film devices. In order to explain this behavior, a diffusion-reaction model for STF_x similar to the one reported for n-type tin oxide sensors has been proposed.

Noteworthy with the present perovskite formulation is the pronounced NO response, in either thick or thin film sensors. Application of a catalytically active cover layer made of a platinum-doped zeolite on top of thick film devices reduces this cross-sensitivity. A very selective propane sensor device can thus be obtained.

Acknowledgements

The authors thank Hans-Jürgen Deerberg for SEM micrographs, Monika Wickles for sample preparation, Andreas Dubbe and Gunter Hagen (all from University of Bayreuth) for zeolite preparation, Xiaomei Du (ICPET-NRC) for assistance with PLD and Jim Margeson (Institute for Research in Construction, NRC) for FEG-SEM images.

Financial support of this project is provided through a joint international program of the National Research Council of Canada, the Helmholtz Gemeinschaft and German Federal Ministry of Education and Research (BMBF) and is gratefully acknowledged (project NRCC-21-CRP-02 and 01SF0201 9.2).

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