Universität Bayreuth
Lehrstuhl für Funktionsmaterialien
Fakultät für Angewandte Naturwissenschaften

Selective Hydrocarbon Sensors based on Nano-engineered *p*-type Oxide Films

Project partners

R. Waser, Forschungszentrum Jülich, Institut für Elektrokeramische Materialien

R. Moos, University of Bayreuth, Lehrstuhl für Funktionsmaterialien

M. Post, National Research Council of Canada, Institute for Chemical Process and Environmental Technology

Final report

Objectives

The focus of the sensor development is on the non-stoichiometric perovskite family of materials $SrTi_{1-x}Fe_xO_{3-y}$ (designated STFx with *x* as a percentage) and engineering the chemical and morphological structure with respect to refining the sensor response to gaseous hydrocarbon species. Propane was selected as the initial target gas. The STFx materials are *p*-type semiconductors, which exhibit large and reversible changes in conductivity when exposed to redox gases at elevated temperatures (eg $T > 350\ ^{\circ}C$). It is this property which is exploited with STFx to produce functional conductometric sensors.

The principal objectives of the project:

- Development of preparation techniques for bulk STFx
- Optimize methods of thick and thin film growth for STFx
- Determine sensor film response to propane and dependence on *x* (in STFx), temperature, film thickness & morphology
- Integrate the films with heater substrates for initial sensor prototypes
- Perform measurements of interference gases (eg H_2, NO, CO, … propene)
- Perform dc and ac impedance measurements and develop an initial defect chemical model for the STFx films at various oxygen partial pressure p_{O2}
- Identify methods to enhance hydrocarbon (propane or propene) selectivity with respect to film morphology and nanostructure.

Progress and achievements

The objectives of the project have been addressed in a strongly interactive series of collaborative research activities which have been closely coordinated between the 3 partnering institutions. There has been a very effective and mutual exchange of samples, data and personnel between the 3 labs to maximize the synergistic application of the unique techniques and skills resident in each. In general, STFx preparative work has been done at UBT and NRC, with a focus at these two laboratories on thick and thin film techniques, respectively. This work has involved: (a) developing effective methods of STFx synthesis, and, (b) optimizing processing parameters for the growth of high quality thin films by a laser ablation technique and thick films by screen printing. At FZJ, a preparation method for dense STFx bulk ceramics has been developed. Comprehensive materials characterization of the chemistry and morphology of the products has also been conducted. These film materials behave as *p*-type semiconductors in the temperature range of interest for sensor applications ($350 < T < 500^{o}C$). At these temperatures, oxygen non-stoichiometry plays a significant role, in addition to grain boundary and bulk effects, in defining chemical and physical properties. Thus, the fundamental electrical impedance properties of STFx in oxygen have been determined at the FZJ, and the initial modelisation for the STFx system and its defect chemistry have been initiated. For actual gas sensor studies, hydrocarbon sensor

functionality of all STFx film types has been determined at both UBT and NRC, using custom built gas delivery systems. A series of more comprehensive studies of sensor specificity and interferences with other gaseous species has been done at UBT.

Overview of successes and achievements

- High temperature thermal preparation of bulk STFx
- Sol precipitation of nanoscaled STFx powders
- Pulsed laser deposition (PLD) for thin-film STFx
- Screen printed thick films of STFx (nano- and microscaled)
- Integrated sensor/heater modules fabricated
- Demonstrated propane sensitivity and sensor functionality
- Application of hybrid zeolite layers to enhance sensor specificity
- AC impedance studies for defect chemistry
- Determination of dependency between temperature, film morphology, film thickness, or iron content and sensor functionality
- Model of transport and reaction to explain sensor functionality

Some specific details of the research achievements are highlighted in the following:
A large number of STFx compositions (x = 0,10,20,30,40,50%) have been prepared using two techniques. These bulk powders served as a base for: (a) screen-printable pastes for thick film samples, (b) precursors for sintered pellets for pulsed laser deposition (PLD) targets and, (c) producing densely sintered ceramics for impedance studies. Besides a conventional mixed oxide route, a sol-gel process has also been developed as an alternative approach for both powder synthesis and film preparation. Film deposition conditions by PLD have been refined to the stage where now it is routine to grow high quality STFx thin films with well controlled stoichiometry on a number of different substrate types, with both smooth and rough surfaces with a thickness of 200 – 300 nm. Thin films by PLD have been deposited onto sintered alumina principally for sensor functionality measurements and onto polished sapphire to facilitate additional fundamental studies of surface morphology. It was found that a preferential crystallographic orientation of STF could be obtained, (110) and (200), and that this texturing of the nano-morphology, which is a parameter relevant to sensor response, is controllable.
Sensor response characteristics of both film types (thin / thick) have been investigated concerning sensitivity towards various hydrocarbons, temperature dependency, and selectivity of different STFx compositions. For thick and thin film sensors optimum operating temperatures with respect to response time and sensitivity were identified – and found to be in the range ($300 < T < 500$ °C). Because of higher sensitivity, STF20 and STF40 compositions have been focused upon in subsequent studies.
However, during selectivity tests, a considerable difference between thick and thin film devices was observed with each composition: whereas both sensor types respond to unsaturated hydrocarbons, only the thick films present a response towards saturated hydrocarbons. Hydrocarbon sensitivity of the thick films was found to increase with either the chain length or the reactivity of the target hydrocarbon gas. Sensor functionality of screen-printed thick film devices was improved considerably by passing from conventional microscaled precursor powders to nanoscaled, sol-precipitated materials.
Additionally and unexpectedly, it was found that the choice of electrode material (eg Pt, Au, Ag) influenced the sensor response characteristics, and a considerable contribution of electrodes to the overall sensitivity of the semiconductor has been identified. This electrode effect was mainly attributed to the different catalytic activity of the metals.

The component of the project that identifies the key chemical-physical features of the film structure is based upon developing a mechanistic model of the conductometric properties of the films. To explain the observations made during sensor optimization in a quantitative way, a novel sensor model was proposed. In this context, the mechanism responsible for gas sensitivity was divided into a “macroscopic” and a “microscopic” part. Under steady state conditions, a macroscopic concentration profile of the analyte gas develops in the gas sensitive layer. The geometry of this profile essentially depends on the diffusion coefficient, gas reactivity, film thickness, and film morphology. The corresponding morphology parameters needed for the macroscopic model were obtained by SEM studies. In addition, catalytic performance of $SrTi_{1-x}Fe_xO_{3-\delta}$ formulations was investigated with respect to different analyte gases.
At the microscopic scale, the local gas concentration affects local conductivity of the gas sensitive material. Two cases were discussed:

The first approach was based on the model reported in the literature for *n*-type semiconductors, i.e., sensors of the Taguchi type. Due to adsorption processes, a near-surface space charge layer forms on semiconducting materials. In analogy to the depletion layer, which develops on *n*-type surfaces due to oxygen adsorption, corresponding equations describing charge accumulation and its impact on conductivity were derived during this study for the present *p*-type system. If the charged oxygen adsorbates interact with surrounding gases, for example in a redox reaction, the conductance of the sensor film changes and the gas is detected.
However, according to observations reported for *p*-type semiconducting oxidation catalysts, it is more likely that lattice oxygen instead of adsorbed oxygen is exchanged during reaction with reducing gases. Hence, in the second approach, a reduction process affecting the entire bulk was assumed to govern gas sensitivity of $SrTi_{1-x}Fe_xO_{3-\delta}$ films. Although very few variables needed to be assumed or fitted, the present bulk-type model was found to represent well sensor functionality of *p*-type conducting STF20 films. In addition to temperature dependency of sensor response, hydrocarbon sensitivity, *m*, was predicted with good accuracy. The different sensor response towards hydrocarbons with a different chemical reactivity (e.g. as provided by propane and propene) and other cross-interfering species, such as NO, was explained as well as the dependency on film thickness for screen printed films. In addition, the impact of the surface-to-volume ratio observed for nanoscaled, sol-precipitated precursors was explained with the sensor model.
As an additional validation of the bulk-type sensor model, thermogravimetric analysis was conducted at FZJ. It has been shown that $SrTi_{1-x}Fe_xO_{3-\delta}$ materials display significant weight gain on cooling under oxidizing conditions and weight loss in the presence of reducing gases in the temperature range of interest (400-500 °C). Furthermore, impedance measurements were performed under synthetic air at temperatures between 50 °C and 600 °C. In contrast to slightly Fe-doped polycrystalline strontium titanate, the STF40 did not reveal a resistive grain boundary contribution to the overall resistance or to gas sensitivity.
Having thus described the sensor mechanism with focus on the semiconducting material, the final part of the present work was dedicated to development and fabrication methods used to create the complete sensor device. Cross-interference towards NO, one major deficiency of the $SrTi_{1-x}Fe_xO_{3-\delta}$ sensor films, was successfully addressed using a reactive filter layer. By applying a Pt-doped zeolite layer, which was optimized with respect to thickness and noble metal content, a very selective hydrocarbon sensor thick film with NO cross interference eliminated was prepared. The effectiveness of the zeolite layer was attributed to a catalytic conversion of cross-interfering species. This process was included in the diffusion-reaction model.
To meet the demand for compact, low-power consumption sensor devices with multiple integrated functionalities, strontium aluminate was tested as a novel tape material, which enabled a sensor design in HTCC technology. An extremely versatile sensor construction was thus possible, which permits co-firing of sensor multi-components in a single step and miniaturization of the sensor system. Hot-plate sensor prototypes with an integrated heater were thus manufactured.

Overall accomplishments: both thin and thick film formulations of STFx have been fabricated into sensor prototypes which exhibit a reversible conductometric hydrocarbon sensor response. The measured dependence upon composition (*x*), temperature, electrode material and overlayers allows for designed improvements of the sensor to be made. Cross sensitivity to other interfering gases has been observed, the magnitude of which can be controlled with film type (nano-morphology), electrode material, and designed overlayers. A sensor prototype with a hot-plate and an integrated heater was manufactured.
A novel sensor model has been proposed to explain the hydrocarbon sensitivity of the *p*-type STFx system as a base for material modeling and judicious design of the STFx formulations and nano-morphology. In contrast to conventional models describing the sensor mechanism of *p*-type semiconducting sensor films, this model considers the entire material bulk to participate in gas sensing.

Contact

email: Ralf.Moos@Uni-Bayreuth.de
phone: +49 921 55 7400