Strontium Aluminate: A Novel Tape Material for HTCC Gas Sensors

K. Sahner*, M. Wickles*, D. Schönauer*, F. Rettig*, A. Roosen**, R. Moos*

*Functional Materials, University of Bayreuth
**Department of Materials Science, Glass and Ceramics, Friedrich-Alexander-University of Erlangen-Nuremberg

received: 23.06.2005, revised: 14.07.2005, accepted: 18.07.2005

Keywords: tape technology, strontium titanate ferrate, multilayer, stontium spinel

Abstract

In this contribution, gas sensors prepared by HTCC technology (High Temperature Co-fired Ceramics) are investigated. Strontium aluminate is used as a substrate material instead of commonly used alumina or zirconia. The base material was prepared via a mixed-oxide route. After tape casting, characteristic parameters such as thermal expansion and sintering behavior were determined. The multilayer transducers were equipped with a screen-printed heater as well as with a buried temperature sensor. An additional buried metal grid provides electromagnetic decoupling, thus enabling undisturbed a.c. impedance spectroscopy of the sensor layer. Functionality of the multilayer transducer was probed using a hydrocarbon sensor material, strontium titanate ferrate ($SrTi_{0,8}Fe_{0.2}O_{3-\delta}$). In contrast to conventional transducers on alumina substrates, the use of strontium aluminate prevents interactions between the gas sensitive thick film and the substrate. As a consequence, the application of additional diffusion barrier layers can be avoided. The promising results obtained with the novel multilayer devices can be expanded to other transducer designs. Miniaturization and consequent reduction of power-consumption are subject to further studies.

1 Introduction

The development of low-cost gas sensors is very important due to the introduction of more stringent regulations governing air-pollution. Semiconducting metal oxides, which can withstand even harsh environments such as automobile exhaust, form a promising material class for this purpose [1-2]. In most cases, however, the operating temperature of these devices needs to be monitored and controlled precisely due to the pronounced temperature-dependency of the sensor signal. Hence, the sensor devices are commonly equipped with a heater as well as with a temperature sensing unit. Both elements need to be integrated on the sensor substrate, implying the need for an extremely flexible substrate design.
In combination with a cost-effective screen-printing (i.e., thick film) technique, ceramic tape technology meets the requirements of preparing miniaturized, low power-consuming transducer structures [3-4]. After printing the functional structures on the flexible green tapes in separate steps, the tapes are punched or cut, laminated, and sintered in one single process. Depending on the firing temperatures, the technology is called Low/High Temperature Co-fired Ceramics (LTCC or HTCC), respectively. In a final step, the gas sensitive metal oxide thick film then is deposited on the transducer.
However, not all semiconductors used for gas sensors are compatible with the commonly available ceramic tapes, which are mainly based on alumina, zirconia or silica. For example, thick films prepared from perovskite formulation $SrTi_{0,8}Fe_{0,2}O_{3-\delta}$ (denoted in the following as STF20), a very promising p-type conducting material for hydrocarbon sensing in the temperature range from 350 to 450 °C [5], [6] are known to deteriorate at high temperatures when in contact with alumina. In order to prevent these interactions, the use of a screen-printed strontium aluminate $SrAl_2O_4$ underlayer between the STF20 film and the alumina substrate was reported in the literature [7].
The present contribution investigates the suitability of green tapes prepared from strontium aluminate for STF20 sensors. The novel tape material is characterized with respect to sintering behavior and thermal properties, both crucial parameters for the preparation of miniaturized transducers with low power consumption. Then, the work focuses on optimizing of the transducer design as well as on testing the functionality of the complete sensor device. A very selective hydrocarbon sensor was successfully prepared.

2 Experimental

From the precursor materials $SrCO_3$ (Technipur, *Merck*, Germany) and Al_2O_3 (APA-0.4, *SASOL North America, Inc.*, USA), the strontium aluminate $SrAl_2O_4$ powders were prepared in a solid-state reaction. After calcination at 1200°C, the powders were ball-milled until yielding a medium particle size of 1,9 µm determined by laser diffraction. Phase purity of the samples was assured by XRD measurements.
The dried powder was transferred to a tape casting slurry [8]. For complete deagglomeration of the powder in the organic solvent (MEK-ethanol mixture), the suspension was homogenized in a ball mill in the presence of a suitable dispersing agent (Hypermer,

Contact: K. Sahner, Functional Materials, University of Bayreuth, Universitätsstr. 30, D-95447 Bayreuth, E-mail: funktionsmaterialien @uni-bayreuth.de

Uniqerma, Belgium). After 24 h, the binder polyvinyl butyral (Butvar, *Solutia*, USA) and the plasticizer butyl benzyl phthalate (Santicizer, *Ferro*, USA) were added and the mixture was homogenized for another 24 h. After degassing, the viscosity of the slurry was determined (UDS rheometer, *Physica*, Austria) as 2 Pa·s at a shear rate of 50 s^{-1}.

The high loaded slurry exhibited the desired pseudo plastic behavior. Then the slurry was cast on a tape casting machine of 4 m length with a fixed, double chamber casting head (Doctor-blade) onto a moving silicon coated PET polymer film at a velocity of 10 cm/min. After drying, the green tape had a thickness of 250 µm. The tape was removed from the tape carrier and cut to the desired shapes.

After characterising the relevant properties of the strontium aluminate tapes, multilayer sensors were prepared by tape technology. For technology improvement, investigation was aimed at developing a heatable sensor element with an integrated temperature sensor. Moreover, it should be suitable for impedance spectroscopy. In order to meet this last requirement, a shielding layer has to be applied between heater, temperature sensor, and measuring probes. In Fig. 1, the exploded view of such a device is presented schematically.

The multilayer set-up combines three separate layers. The bottommost layer features two functionalities. On the backside, a conventional Pt heater is screen-printed. On the other side, a metallic Pt grid is printed for electromagnetically decoupling the controlled heater and the sensor electrodes. In contrast to a full Pt layer, thermal strain between metal and ceramic, which occurs during sintering and might lead to cracks, can be balanced better with the grid. On the middle layer, a simple coiled Pt structure is deposited, which serves as a resistive temperature sensor. The topmost tape is equiped with interdigitated Pt electrodes (Interdigital capacitor, IDC) for electrically contacting the gas sensitive layer.

After the corresponding screen-printing steps, the tapes are cut and laminated in an isostatic press at 85°C. An isostatic pressure of 30 MPa is applied for 10 min. Then, the laminate is sintered at 1400°C with heating and cooling rates of 3 K/min. Subsequently, the gas sensitive STF20 layer is applied by screen-printing, followed by an additional firing step at 1100 °C.

For measurements on sensor performance, the specimens were heated to the corresponding operating temperature in the range of 370 to 400 °C in a measurement chamber. To a reference nitrogen flow containing 20 vol% of oxygen, different test gas species were added as described below using mass flow controllers. The total gas flow was adjusted to 600 ml/min. In addition to the actual values of the mass flow controllers, the gas composition was verified analytically. Prior to each measurement, samples were kept in the reference composition of 20 % oxygen in nitrogen for at least 20 minutes to allow equilibration. Hydrocarbon sensitivity was tested for saturated aliphatic species, i.e., propane (C_3H_8), and for unsaturated hydrocarbons, such as propene as well as a hydrocarbon mixture (containing ethane, ethene, acetylene and propene in equal proportions, denoted as HC mix). The concentration of the analyte gases was adjusted to 500 ppm. In order to study response to interference gases, similar measurements were conducted with CO, NO (both 500 ppm), and H_2 (1000 ppm). In addition to the actual values of the mass flow controllers, the gas composition was verified analytically using an FTIR spectrometer. The d.c.-sensor resistance was measured with a *Keithley* 2700 digital multimeter. For ac measurements with an impedance analyzer (*Novocontrol*, α-analyzer), a measurement frequency of 1 kHz was used. A former impedance spectroscopic study ensured an ohmic behavior of the STF20 sensor material.

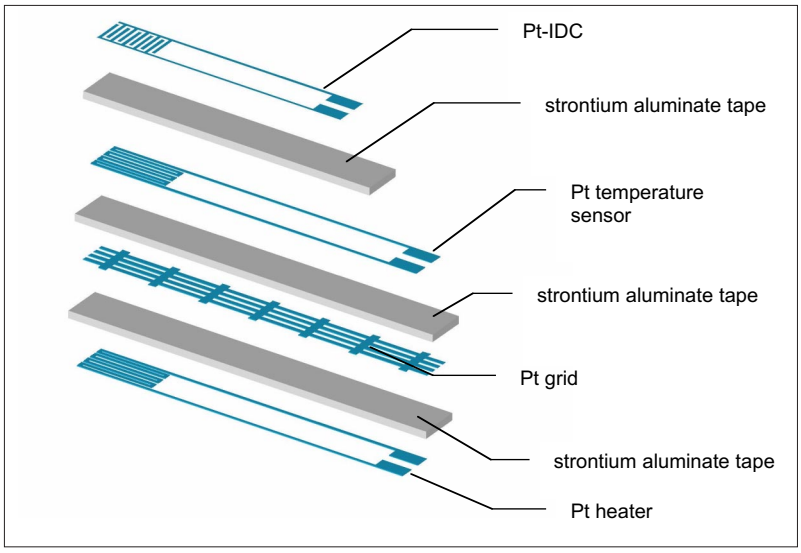

Fig. 1 Schematic exploded view of the multilayer transducer device. It should be mentioned that in this schematic sketch, the heater and the temperature sensor present identical structures for the sake of simplicity. In reality, the controllable heater structure has a more sophisticated four-probe set-up.

3 Results & Discussion

3.1 Characterization of the Novel Tape Material

In the preliminary stages of the study, processability of the novel tape material was investigated. Fig. 2 shows the results of a dilatometer measurement on densely sintered bulk specimens prepared from the strontium aluminate powders.

The ceramic presents a thermal expansion coefficient of 7,8 ppm/K (75 to 626 °C) and 10,3 ppm/K (626 °C

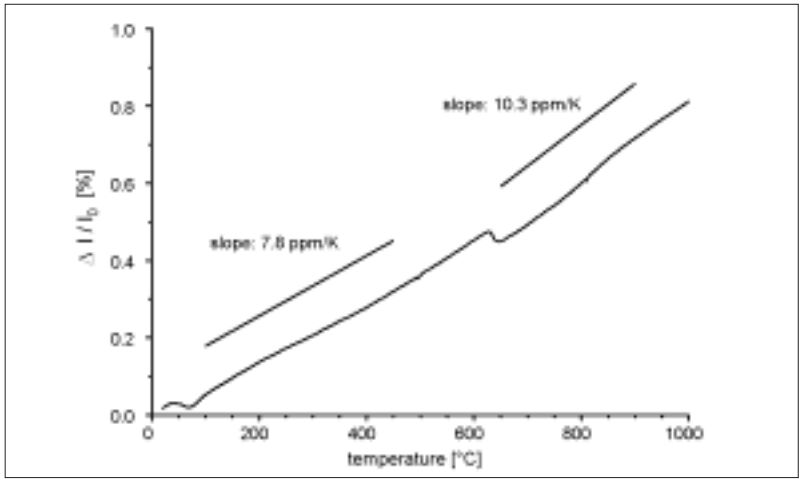

Fig. 2 Thermal expansion measurement on a densely sintered strontium aluminate sample in the temperature range from room temperature to 1000 °C. Noteworthy is the phase transition occurring at 650 °C

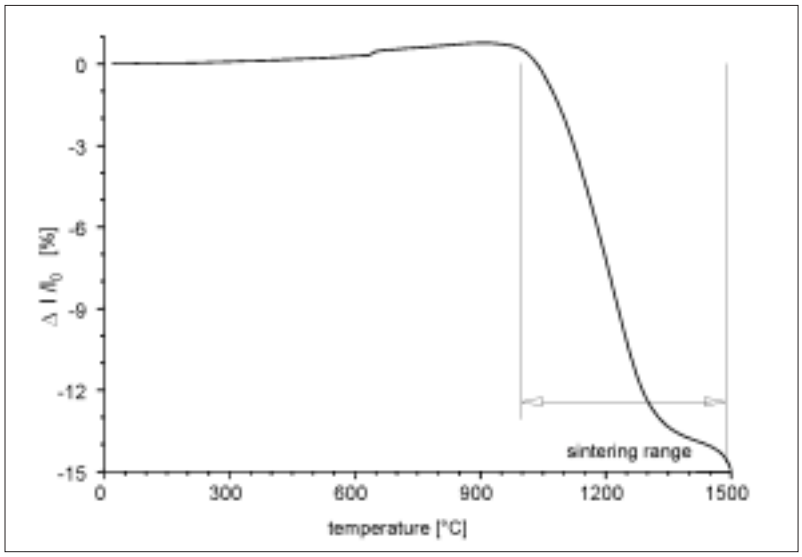

Fig. 3 Sintering profile of a bulk strontium aluminate specimen. Sintering occurs in the range from 1000 to 1500 °C

to 1000 °C), respectively. Noteworthy with the strontium spinel is the phase transition observed at approximately 650 °C. In the literature, a transformation of strontium aluminate from monoclinic at low temperatures (a = 10,2 Å, b = 20,26 Å, c = 8,42 Å) to hexagonal (HT-phase P6322, a = 5,13 Å, c=8,44 Å) has been reported [9]. As thermal stress between hot and cold substrate regions might lead to cracking, this phase transition prevents the use of strontium aluminate at operating temperatures above 650 °C. In the case of the present hydrocarbon sensors with a maximum operating temperature of 450 °C, the transition is of minor importance.

A sintering profile was also measured with pressed green ceramic samples (Fig. 3) and laminated tapes. Sintering occurs in the temperature range from 1000 to 1400 °C. In order to obtain densely sintered substrates, a sintering temperature of 1400 °C was chosen.

The sintered laminates are very smooth with average roughness values (CLA) R_a of 0,13 µm. In comparison to commercially available alumina substrates, this ranks between thick film qualities (R_a: 0,2 µm) and thin film qualities (R_a: 0,05 µm). In addition, compatibility to the platinum screen-printing paste was verified, thus ensuring the possibility of co-firing at 1400 °C. Sintering shrinkage was found to yield values of approximately 15 %.

In conclusion, strontium aluminate results to be an appropriate material for preparing substrate tapes.

Sensor Functionality

After calibrating the heater and the temperature sensor of the devices, initial measurements on sensor functionality were conducted. In particular, the study focused on the consistance of a.c. and d.c. measurements as well as on the compatibility between the substrate and the gas sensitive material.

In Fig. 4 a) and b), the sensitivity traces of a multilayer STF20 sensor in d.c. and a.c. (1 kHz) measuring mode are compared. Sensitivity S is calculated according to Eq. (1)

$$S(t) = \frac{R(t) - R_o}{R_o} \qquad (1)$$

with R_0: base resistance in dry air at t = 0 s
R(t): resistance

In this case, the base resistance R_0 was found to be 54,3 kΩ (d.c.) and 53,4 kΩ (a.c.). The sensor response is fast, stable, and reversible wihout baseline drift. The a.c. curve does not present any interference commonly observed for unshielded sensors equipped with an active heater. Clearly, both measurement techniques are in good accordance, also with respect to the base resistance R_0.

The temperature of the device is calculated from the resistance signal of the buried platinum temperature sensor using the above mentioned calibration results. According to this signal, shown in the upper part of Fig. 4, the sensor heating in the gas stream was found to be very stable.

The standard behavior of STF20 sensors when exposed to different gases could be reproduced. Although responding well to hydrocarbons (resistance

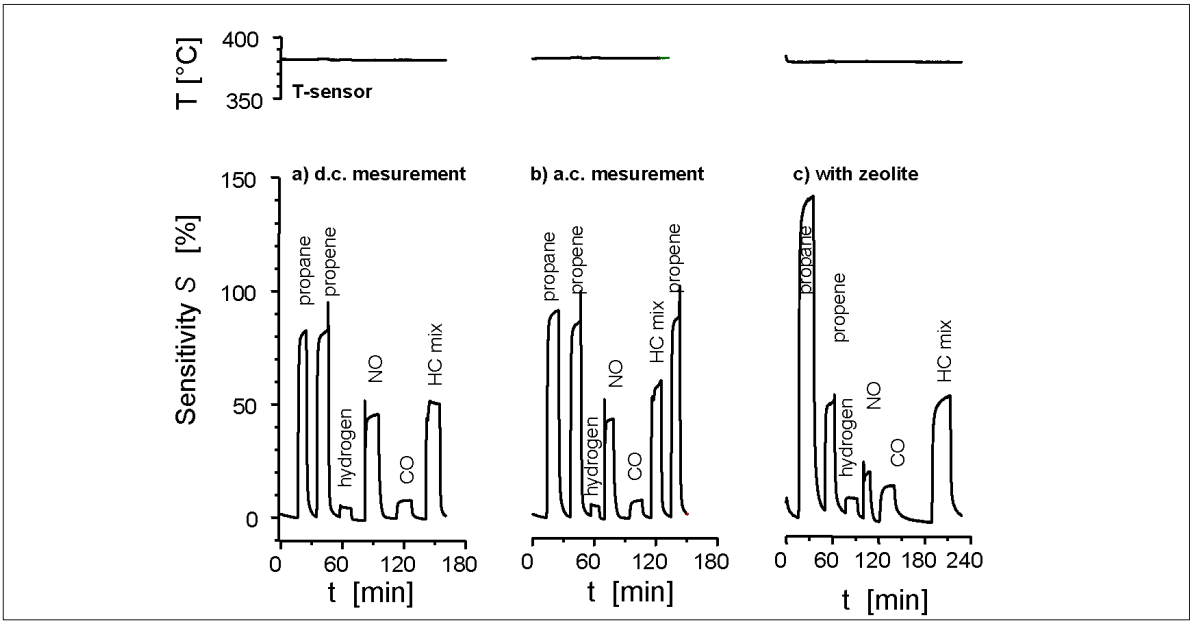

Fig. 4
Sensor response of the multilayer devices with STF20 as gas-sensitive material. Upper part: operating temperature as calculated from the resistance data of the temperature sensor. Gases as indicated, balance: dry air.
a) d.c. measurement, b) a.c. measurement, frequency: 1 kHz, c) d.c. measurement on a zeolite covered sensor

increase), the sensor shows a pronounced cross sensitivity towards NO. This cross interference has already been subject to previous studies [6]. As one possibility for sensor improvement, the application of a zeolite cover layer has been discussed [10].
Fig. 4c) shows the result of a measurement that tests the compatibility of a zeolite cover layer with the present novel substrate material. The selectivity of the thus covered sensor towards saturated hydrocarbons, i.e., propane, was strongly enhanced. The reduced cross interference of NO and unsaturated hydrocarbons (i.e., propene) as well as the increased propane sensitivity are in accordance with former findings [10].
To summarize, the functionality of the multilayer hydrocarbon sensor was not diminished by the use of the novel tape material. Moreover, the use of strontium aluminate prevents interactions between the gas sensitive thick film and the substrate and allows a co-firing process, thereby facilitating sensor preparation. The additionally inserted metal grid provides electromagnetic decoupling, thus enabling undisturbed a.c. impedance spectroscopy of the sensor layer.

4 Conclusion

The application of strontium aluminate tapes as a novel substrate material for gas sensors offers an extremely flexible transducer design. It allows to integrate further functionalities such as a separate temperature control or electromagnetic decoupling. In contrast to commonly used alumina substrates, this material is entirely compatible to thick film sensors based on strontium titanate ferrate.
Future studies are aiming at further miniaturizing the transducer structure, thus leading to low power consuming hot-plate configurations. The poor thermal conductivity of strontium aluminate, which guarantees low heat transfer losses, presents an interesting feature for this purpose.

Acknowledgements

The authors express their thanks to *Mr Scheeler*, University of Bayreuth, for the dilatometric studies.
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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