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Preparation of SrFeO3-X Thin Films by the Spin-Coating Method and its Gas Sensing Properties

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ABSTRACT

Nanostructured coatings have recently attracted increasing interest because of the possibilities of synthesizing materials with unique physical-chemical properties. In this report we describe our efforts at developing a methodology for the fabrication of $SrFeO_{3-X}$ based thin films using a modified Pechini method. Thin films of $SrFeO_{3-X}$ were fabricated using a spin coating and PLD method on Al_2O_3. The films annealed at 600 ^oC for one hour show a perovskite phase. The sensors based on $SrFeO_{3-X}$ thin films on alumina were fabricated using spin coating and PLD techniques. The sensing properties were determined using propane and propene as the probing gases. Response characteristics and temperature dependency of spin coated and PLD fabricated samples were compared. The effect of the electrode material, Au and/or Pt, on the gas detection sensitivity of the $SrFeO_{3-X}$ thin films was also investigated.

INTRODUCTION

The discovery that the adsorption of gas on the semiconductor surface causes a significant change in the electrical resistance of the material [1] initiated the development of commercial gas sensors based on semiconductors whose surface properties are very sensitive to changes in the gas atmosphere. Gas sensors based on thick-film semi-conducting metal oxide materials deposited on ceramic heater substrates are commercially available [2-4]. However, compared with thick films, the thin films have been shown to have the potential to improve upon sensor sensitivity and selectivity [5-7].

$SrFeO_x$ [8-11] and other perovskites based on the $SrFe_yCo_{1-y}O_x$ ($0 \le y \le 1.0$; $2.5 \le x \le 3.0$) system [12,13] are mixed ionic electronic conductors in which the reversible oxygen non-stoichiometry may be exploited for gas sensor applications. These materials undergo reversible phase transitions from the conductive cubic perovskite structure to the much less conductive brownmillerite structure. The phase transitions are very sensitive to temperature and gas composition [12, 13], thus providing the basis for a highly sensitive sensor material. It is important to tailor the micro and nano structure of metal oxide gas sensor materials in order to fully optimize their sensitivity, selectivity and response speed [14-17].

Our previous investigations [10-13] on the sensor applications of perovskite materials involved fabrication of thin films of these materials by pulsed laser deposition (PLD) method using materials synthesized by the solid-state reaction at high temperatures of the corresponding binary metal oxides or carbonates. Compared to more traditional coating methods, e.g., PLD, CVD, sputtering and evaporation, the solution based approach such as sol-gel technology is more flexible with respect to compositional limitations and substrate size/shape constraints. Perhaps more importantly, it permits micro-structural as well as compositional tailoring which is not possible by other coating methods. One advantage of wet coating techniques is, that molecular structures developed by chemical synthesis can be used to develop new properties, or to develop new desired molecular structures by heat-treatment and subsequent chemical reaction on the surface. An added advantage of solution methods is the capability of direct fabrication of thin films on various substrates using precursor solutions. Moreover, incorporation of dopants is easier in this technique. Thus the potential for solution derived coatings appears bright especially for coating large surfaces with complex shapes or topographies.

Among the different chemical routes, the sol-gel method based on the Pechini-type reaction has received considerable attention because of its relatively simple synthesis scheme. Although the Pechini process has been used in many studies to synthesize high surface area powders [18,19], there are only a few studies using the Pechini process to deposit thin films [20]. The Pechini process offers several advantages over other techniques for processing of ceramic thin films, including low cost, good compositional homogeneity, high purity, and relatively low processing temperatures [21,22]. In this study, a modified Pechini process has been used to prepare a thin, dense, conductive $SrFeO_{3-x}$ based film on alumina substrates to investigate its propane and propene gas sensing characteristics.

EXPERIMENTAL METHODS

The details regarding the fabrication and characterization of the thin films of $SrFeO_{3-x}$ by spin coating and a drop coating method were reported recently [23-24].

Film Deposition by PLD Method

For comparison purposes a few samples were also prepared using a *pulsed laser deposition* (PLD) method. The targets consisted of powders prepared by both the solid state method at 1100°C and sol-gel Pechini method at a calcinations temperature of 600°C. The used laser Lambda Physik LPX305i, KrF-248nm with 25ns pulse duration was set to a constant energy of 600 mJ and a repletion rate of 8 Hz. The substrate (either a 1cm x 1cm Rubalit 710 square or a substrate with screen-printed Pt-IDC provided by the Chair of Functional Materials, Bayreuth, Germany) was mounted onto the heater. In case of the IDC structure the part without interdigitated electrodes was masked with an alumina section to get a defined sensor area. The target movement was algined with help of low energy, visible laser beam, so that the actual laser beam would cover a selected area of the surface during the ablation process. For this task the target holder was rotated a few degrees clock- and counterclockwise, what resulted in up and down movement of the off-center mounted target. The initial procedure was carried out under high vacuum ($< 5*10^{-5}$ Torr). The substrate was slowly heated to 700 °C, before deposition, in order to avoid thermal stress.

The chamber was flushed with high purity oxygen to a constant pressure of 100 mTorr to ensure that no reduction of the material occurs. A high energetic laser beam was fired on the target, when a plume of evaporated material was deposited on the substrate. The heated substrate ensures the adhesion of the material and formation of a crystalline film. After a deposition time of 15 minutes an estimated film thickness of 300 nm was obtained. After deposition the oxygen gas pressure in the chamber was switched to 400 mTorr, to ensure that there is no depletion of oxygen in the crystal lattice. After holding the temperature for 30 minutes, the specimen was cooled down slowly to avoid quenching effects.

Electrodes

The electrodes for the measurement of conductivity included: gold, platinum and interdigitated capacitors (IDC), comp-like electrodes. Gold electrodes were obtained by thermally depositing 200 nm Au pads directly onto the film surface. Platinum electrodes were manually painted on the film or over the gold electrodes and annealed in a furnace at 600 °C for 3 hours. For IDC, the screen printing was employed using platinum prior to film fabrication.

Resistance Measurement

Electrical conductivity measurements of the films were taken using a two-wire method by mounting the substrate/film samples upon an aluminum heater in a controlled environment where the temperature could be varied between 20 and 600^{o}C and the composition of the flowing gas as required. High purity gas mixtures ([O2] + [N2] > 99.99 %) flowing at 200 cm^{3}/min in a 1 L volume chamber were used for all tests. The heating and cooling rate was set to 10 °C/min. To the baseline gas composition, propane and propene were added to test the response of the material towards hydrocarbons. Concentrations of the analyte gases ranged from 0 to 3000 ppm in dry air. The furnace and sensor temperature was adjusted in the range between 300 and 500 $^{\circ}$C, and the dc-sensor resistance of the sensor film was measured with a Keithley 2400 digital multimeter. Additionally recorded ac-impedance spectra and in some cases I–V-plots indicated an ohmic behaviour of $SFeO_{3-X}$ films.

RESULTS AND DISCUSSION

Sensor characterization

Solid-state samples – Au vs Pt electrodes

Fig. 1 summarises the propane and propene detection data carried out on ~ 300 nm thick thin films fabricated by the PLD method using a $SrFeO_{3-X}$ target prepared by the solid-state method at 1300^{o}C. Compared to the samples with Au electrodes on top of the sensor material the sample with Pt electrode at the bottom of the sensor material showed more than 2.5-fold increase for response to Propene at 350^{o}C. The selectivity for propene increased more than 4-fold at this temperature. However, the response at other temperatures was lower for both propene and propane for this sample compared with the sample with gold electrodes at top. When Pt-electrodes were placed on top of gold electrode the results were quite different. For this sample, the response for propene increased over 5-fold at all temperatures, compared with

response for sample with gold top electrodes. The selectivity for propene was also higher at all temperatures. Another interesting observation was the increase in response for propane relative to propene with increase in temperature. This was contrary to what was observed for all other samples, where response for propane declined at higher temperatures. These results indicate a catalytic conversion of the propane gas at the Pt electrodes, with a spill-over to the sensing area. This result would also confirm the previous findings regarding the role of 3-phase area of gas, sensor film and electrode for the sensing mechanism [25].

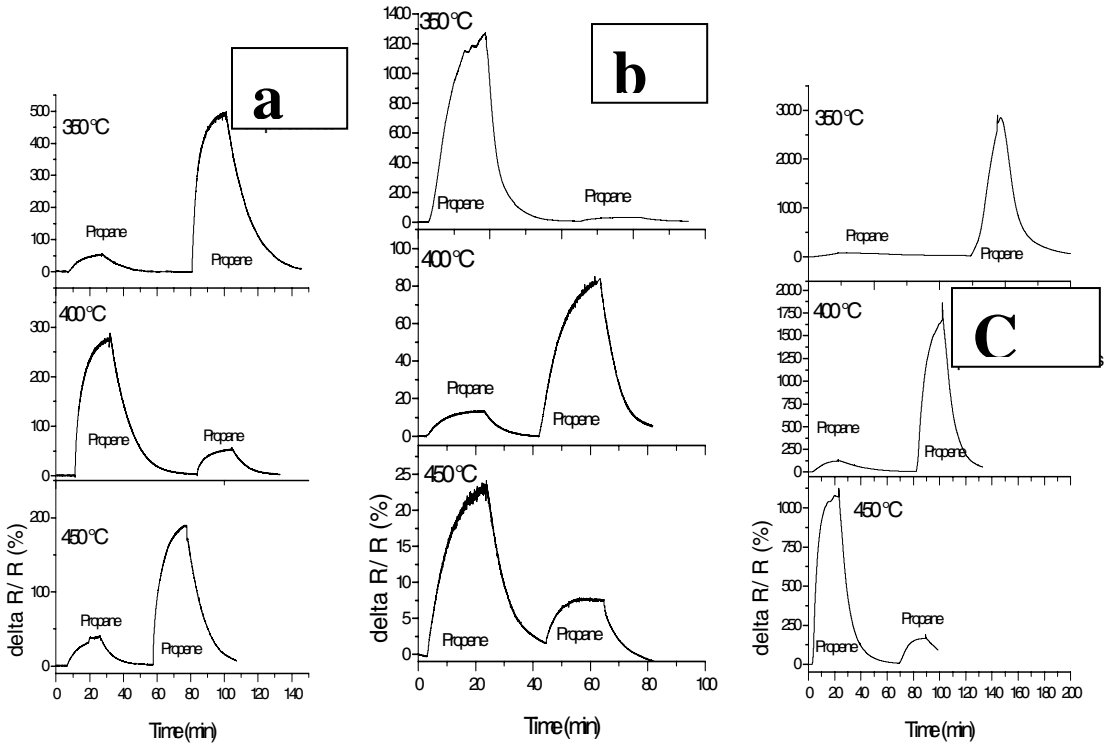

Fig. 1. The propane and propene gas response as a function of time, a). Au-top electrode; b). Pt-IDC; c). Pt- on top of Au

Solid-state vs Sol-gel - Propane & Propene gas Response at 350°C

Table I, lists preliminary data for the effect of target preparation on its sensor characteristics. The findings are not conclusive as there is a considerable variation in the data. This work is still in progress and the final results will be reported at a latter date. However, it appears that compared with the samples prepared using solid-state method; the samples prepared by sol-gel method gave higher response for both gases. This finding could be of considerable commercial importance because of the cost effectiveness of the low temperature sol-gel process that yields a product of good compositional homogeneity. In addition, the sol-gel process allows the modification of product characteristics such as size (nanometer to micrometers), porosity, surface area, refractive index, mechanical strength, wetting characteristics, and surface reactivity by controlling reaction parameters.

Table I. The effect of preparation method on the sensor characterizations of $SrFeO_{3-X}$.

Target Preparation Method	**ΔR/R (%) at 350°C**		**Selectivity**
	Propane	Propene	Propene/Propane
Solid-state – Au electrode	52	490	9
Solid-state- Pt-IDC	32	1252	39
Sol-gel – Au electrode	80	370	5
Sol-gel - Pt-IDC	160 ± 36	4017 ± 3247	23 ± 16
Sol-gel-Pt-top	305	1950	6

CONCLUSIONS

It has been demonstrated that the sol-gel Pechini process can be used to prepare $SrFeO_{3-X}$ based thin films for gas sensor applications. The thin films were fabricated by both spin coating and PLD techniques using $SrFeO_{3-X}$ samples prepared by solid-state as well as the sol-gel Pechini methods. The sensing properties of these films were determined using propane and propene as the probing gases. The results obtained with samples prepared by sol-gel Pechini method and PLD film deposition technique suggested much higher sensitivity for both gases compared with the samples obtained from the solid-state method. This has been ascribed to the smaller grain size of the sol-gel prepared samples compared with the sample prepared by the solid-state method. This is of potential commercial importance because of the cost effectiveness of the low temperature sol-gel process that yields a product of good compositional homogeneity.

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