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Gas sensing properties of volume-doped $CoTiO_3$ synthesized via polyol method

Maike Siemons, Ulrich Simon *

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, Aachen 52056, Germany

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Abstract

Volume-doped $CoTiO_3$ was synthesized via the polyol method. As volume dopants Gd, Ho, K, La, Li, Na, Pb, Sb, and Sm with a concentration of 2 at.% were applied. By X-ray diffraction (XRD) materials structure was confirmed, while the materials morphology was imaged using scanning electron microscopy (SEM). Thick films of the nanocrystalline material were applied with a laboratory robotic system to a 8 × 8 multielectrode substrate. We show that the p-type semiconducting material doped with various metals is applicable for the fast detection of ethanol and propylene. The volume dopants affect the sensing and response behavior of the base material.

Keywords: $CoTiO_3$; Volume-doping; Polyol method; Nanoparticles; Gas sensor; Impedance spectroscopy

1. Introduction

The development of sensitive and selective gas sensor layers is crucial for many industrial, environmental, medical and domestic applications. Metal oxide semiconductors are widely used as resistive sensing layers which change their resistances under gas exposure. Commonly used materials are for example SnO_2 or ZnO. A drawback of these materials is the sensitivity dependence on changes in the humidity and their lack of selectivity. Sensing capabilities are often improved by addition of surface dopants. However, also volume dopants are useful additives to change or improve the sensing behavior [1].

Ilmenite-type $CoTiO_3$ has earlier been studied for possible applications as catalysts [2–4] or as a high-κ dielectric [5]. The potential application of p-semiconducting $CoTiO_3$ as a gas sensing material is restricted on a few examples, indicating the suitability for ethanol detection [6]. However, the low conductivity together with the thermal stability suggests possible sensor applications only at higher temperatures.

An easy way to prepare nanoscaled metal oxide nanoparticles is the polyol mediated synthesis [7]. Low annealing temperatures in combination with the opportunity to tune the composition of the materials by mixing the initial components on the molecular level make the polyol method to a beneficial tool for many different material applications [7–10]. Particle size and porosity are important parameters for the performance of gas sensing layers. Porous layers of materials with smaller particle size are expected to show higher sensitivities because of the higher surface area in comparison to dense layers and/or large particles [11].

In the present study we report for the first time on different volume dopants in $CoTiO_3$. We applied high throughput impedance spectroscopy (HTIS) for the analysis of the gas sensing properties of nanometer-sized $CoTiO_3$, volume-doped with Gd, Ho, K, La, Li, Na, Pb, Sb, and Sm (2 at.% each). Partial substitution may lower the electrical resistivity and may enhance the sensitivity of the material. We applied the polyol method for the synthesis of volume-doped $CoTiO_3$ and we will show that the use of HTIS enables the analysis of the materials in order to find out the highest selectivity and sensitivity of the respective material composition.

2. Experimental

2.1. Synthesis of volume-doped $CoTiO_3$

According to the polyol process particles have been synthesized by precipitation from precursors dissolved in diethylene

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* Corresponding author. Tel.: +49 241 8094644; fax: +49 241 8099003.
E-mail address: ulrich.simon@ac.rwth-aachen.de (U. Simon).

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glycol (DEG). Materials and solvents were obtained from commercial suppliers and were used without further purification. Cobalt (II) acetate tetrahydrate (Merck, 99%), titanium (IV) isopropoxide (Aldrich, 97%) and the desired amount of volume dopant were dispersed in 10 mL of diethylene glycol (Merck, 99.99%). The dispersion containing the reactants was slowly heated up to T_1 under mechanical stirring at 700 RPM. 4 mL nitric acid (surplus of hydrolysis agent) was added to the mixture after salt dissolution. The emerging suspension was heated up to T_2 and maintained at this temperature during t h, and then it was cooled down to room temperature. The preparation results in a greenish black stable suspension. Standard concentration in all experiments was typically 1 wt.% (solid to DEG).

Different metal salts ($La(NO_3)_3\cdot 6H_2O$, $K(CH_3COO)$, $Sm(NO_3)_3\cdot 6H_2O$, $LiNO_3$, $Gd(CH_3COO)_3\cdot nH_2O$, $Ho(NO_3)_3\cdot 5H_2O$, $Sb(CH_3COO)_3$, $Pb(CH_3COO)_2\cdot 3H_2O$, $Na(CH_3COO)\cdot 3H_2O$) were introduced as volume dopants. K, Li, Na, Sm, La and Ho were inserted in the reaction with a smaller amount of Co, while Gd, Sb, Pb, La, Sm and Ho were inserted with less Ti. Indices A and B are used for dopants, which have been inserted into the base materials with less Co (A-position) and less Ti (B-position), respectively, although a direct assignment at which crystallographic position the dopand is located is not finally proven. A detailed description of the syntheses can be found in Table 1.

For further characterisation of the "as-synthesised" materials the solid products were separated from the suspensions via centrifugation in acetone and dried at 90 °C. The suspensions were transferred into the crystalline phase by annealing at 700 °C for 12 h, appearing as green fine powders. For structural characterisation we carried out powder XRD measurements (Cu Kα, λ = 1.54059 Å) on thin films with a Huber Image Plate in transmission. The powder diffraction patterns were analysed using Stoe WinXPow 1.06 Software (Stoe&CIE GmbH). Powder morphology was examined by SEM analysis using a Zeiss DSM 982 Gemini. For that purpose, all samples were coated with carbon.

2.2. Thick film preparation

The materials were well suited for thick layer preparation on interdigital electrode structures (interdigital capacitors; IDC). The thick film preparation method was described elsewhere [12]. The substrate was first dried for 48 h at room temperature in air. After that it was held for 12 h at 700 °C in air to remove the organic residues. Thick films were formed, having a thickness between 50 and 100 μm. To compensate possible gradients in gas concentration and temperature as well as single failures due to contact defects over the substrate, three statistically selected positions are equipped with the same material composition.

2.3. Electrical characterisation

Electrical measurements were performed using an impedance analyzer (Agilent 4192 A) in a frequency range from 10 to 10^7 Hz (15 measuring points per frequency decade) and an amplitude of 100 mV (rms). The measurements were taken in a temperature range between 500 and 325 °C in 25°-steps. Reference measurements were performed in synthetic air (air), which was also used as a carrier gas for the test gases of ethanol and propylene. For the gas sensing experiments, the test gases were mixed with synthetic air to reach a consistent volume flow of $100\,cm^2/min$ (standard cubic centimetre; sccm). Conditioning of the materials was carried out at 500 °C for 240 min in air and at the following temperatures for 90 min. The measuring sequence was air, ethanol (40 ppm), air, propylene (25 ppm), and air. The intermediate measurements in air ensure the recovery of the sensor material, before the next test gas is applied. Relative humidity of the gases was 45% at room temperature in order to perform the measurements in a typical humidity range representative for ambient conditions.

For sample conditioning a preliminary gas flow was applied over 30 min to reach adsorption equilibrium. The data were stored in a database, which has been developed for data mining and for comparison with complementary measuring methods [13].

In order to measure the response time of the individual samples, measurements at single frequency (100 Hz) were performed. 100 Hz was chosen to stay in any case in the quasi-dc plateau, i.e. the frequency independent part of the impedance spectra. Each measurement took 1.5 s, while the time interval between the measurements was 4 s.

3. Results and discussion

3.1. Material characterisation

Fig. 1 shows exemplary the X-ray diffraction pattern of La-doped $CoTiO_3$.

All "as-synthesised" samples were amorphous right after preparation. The XRD data of the calcined samples were in good agreement with those reported in ICSD file number 48107 for $CoTiO_3$. There were no indications of how and where the volume dopants were inserted into the $CoTiO_3$ lattice. All patterns showed the same structure as $CoTiO_3$, i.e. the amount of dopant

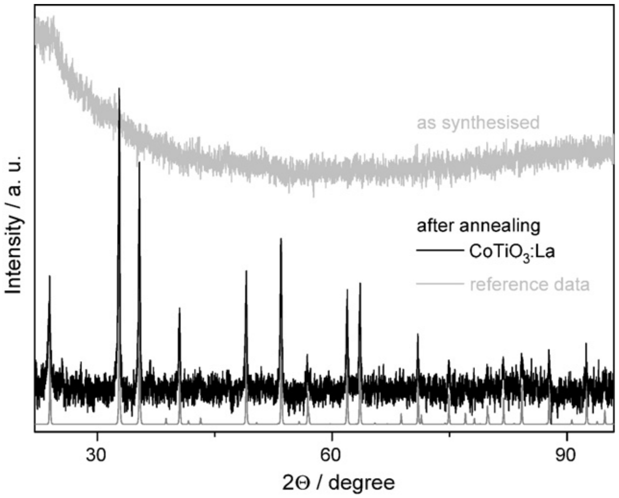

Fig. 1. X-ray diffraction pattern of $CoTiO_3$:La powder before and after annealing for 12 h at $T = 700\,°C$.