Nanostructured SnO$_2$ thick films for gas sensor application: analysis of structural and electronic properties

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Nanostructured SnO₂ thick films for gas sensor application: analysis of structural and electronic properties

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Abstract. This research is focused on structural and electrical characterisation of tin oxide (SnO₂) applied as a thick film and investigation of its properties as gas sensitive material. Micron sized SnO₂ powder was milled in an agate mill for six hours to fabricate SnO₂ nanopowder, which was afterwards sieved by 325 mesh sieve and characterized by XRD and SEM. This powder was used as functional part in the production of thick film tin oxide paste containing a resin vehicle with 4 wt. % nanosize glass frits acting as permanent binder. The glass frits where additionally milled for twelve hours in the agate mills to nanosized powder and sieved by a 325 mesh sieve as well. The achieved thick film paste was screen printed on alumina and fired at 850°C peak temperature for 10 minutes in air. After the sintering process, thick film samples where characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The reflectivity was measured on the same samples by UV-VIS spectrophotometer: the band gap was determined from the slope of reflectance. After that a matrix of different interdigitated electrode structure of PdAg paste was printed and sintered using the mentioned sintering conditions. The tin oxide thick film was printed over the interdigitated electrodes as a top layer and sintered again under the same conditions. The total electrical resistance was measured as a function of the electrode spacing and temperature. A negative temperature coefficient (NTC) was identified and measured in the range from room temperature (27°C) to 180°C in a climate chamber. Finally the samples were placed into a gas reactor with NOx and CO gas and the resistance was measured in the same temperature range (27°C-200°C).

1. Introduction

Solid state gas sensors are one of the most used and the most present type of gas sensors for commercial applications in auto industry, airplane industry, heavy industry, environmental monitoring etc. In particular gas sensors based on semiconducting sensitive materials, such as metal oxides (MOX), have attracted the attention of the scientific community for the last few decades [1]. However, not all materials are suitable for all kinds of gas detection and the right choice of a suitable and effective solid state sensor depends on analysis and correlation between various metal oxide parameters, such as electro-physical (band gap, conductivity etc.) and electronic, structural and other properties.

SnO_2-based gas sensors have been the subject of much research [2] due to the advantage of a relatively low operating temperature, long term stability and low cost. Thin and thick films of SnO_2 have been deposited using a variety of techniques [2-4]. Thick film gas sensors have a certain advantage such as low cost, simple construction and high sensitivity [5]. One of the factors affecting gas sensitivity is the microstructure [6, 7]. Nanostructured materials for gas sensor applications have been the subject of much research as the large surface to volume ratio of these materials enhances gas response characteristics thus having a great influence on the sensor performance.

In this work we have used milling as a simple, low cost method to reduce the grain size of the starting SnO_2 powder and also glass frit used in thick film paste. Structural and electronic properties of SnO_2 thick films were analyzed in view of application as inexpensive gas sensors.

2. Experimental

SnO_2 powder (Sigma Aldrich, 99.9% purity, 325 mesh) was milled in an agate mill for six hours in order to reduce grain size and obtain nanopowder. The milled powder was sieved through a 325 mesh sieve. XRD analysis was performed on a Philips PW1050 diffractometer with CuKα radiation step f 0.05s and hold time of 10 s, 2θ 10-90°. A SEM analysis was performed on a TESCAN Electron Microscope VEGA TS 5130MM device.

Thick film paste was prepared by mixing the milled powder with a resin vehicle and 4 wt.% nanosized glass frits acting as a permanent binder. The glass frit was additionally milled for twelve hours in an agate mill to reduce grain size and then sieved through a 325 mesh sieve. The prepared SnO_2 thick film paste was screen printed on an alumina substrate and sintered in a hybrid conveyor furnace at 850°C for 10 minutes in air. Thick film samples were characterized by XRD and SEM analysis.

Diffuse reflectance spectra of thick film samples were measured on an UV/Vis Shimadzu UV-2600 with an ISR2600-Plus integrating sphere attachment in the measuring range 220-1000 nm.

Interdigitated test matrices were made by screen printing an interdigitated electrode structure of PdAg paste with an electrode spacing of 0.25 μm and 0.35 μm. The tin oxide thick film was screen printed as a top layer and sintered in a hybrid conveyor furnace at 850°C for 10 minutes in air. The electrical resistance was measured as a function of the electrode spacing value and the input voltage. The DC resistance versus temperature was measured in a climate chamber in the temperature range of 27°C to 200°C enabling the determination of the material constant B characteristic for negative temperature coefficient (NTC) materials.

3. Results and Discussion

XRD patterns of the milled SnO_2 powder and thick film are shown in Fig. 1.
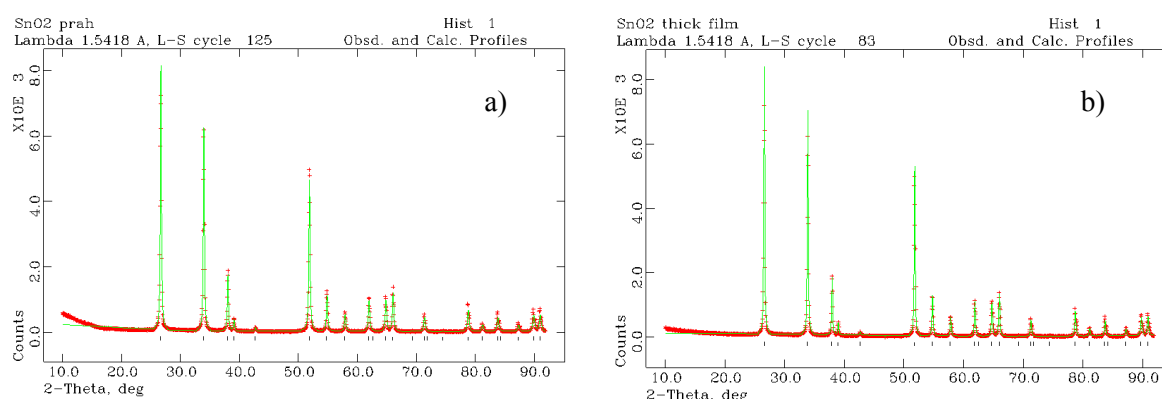

**Figure 1** XRD patterns of milled SnO_2 powder (a) and thick films (b)

Structural refinement was carried out by the Rietveld method using the GSAS [8] package with the EXPGUI graphical user interface [9]. SnO_2 (cassiterite) with a tetragonal structure (space group - $P4_2/mnm$) was determined. Starting values for tetragonal SnO_2 were taken from Bolzan et al [10]. The

lattice parameters determined were a=4.7364(3), c=3.1853(3), crystallite size 59.6 nm for milled SnO_2 powder and a=4.7419(2), c=3.1894(2), crystallite size 67.3 nm for SnO_2 thick film samples.

SEM micrographs of SnO_2 powder and thick film are shown in Fig 2 and Fig. 3, respectively, confirming the small grain size of both. The thick film is porous with a small relatively uniform grain size.
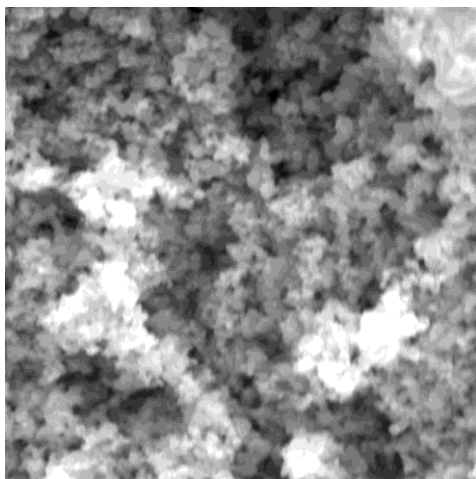
Figure 2. SEM micrograph of milled SnO_2 powder.
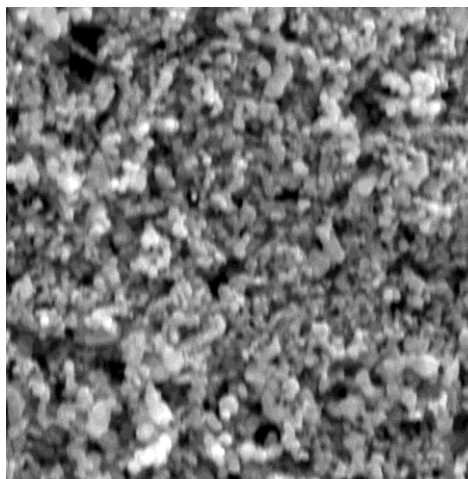
**Figure 3.** SEM micrograph of SnO_2 thick film sample.

The measured diffuse reflectance specter of a tin oxide thick film sample is shown in Fig. 4. It was converted to the Kubelka-Munk function that is proportional to the absorption coefficient using the UV-Probe software. The optical band gap was estimated using a Tauc plot relating the Kubelka-Munk function to the density of optically absorbing energy transitions using the relationship of Davis and Mott:

$$h\vartheta \cdot F(R_\infty) = A(h\vartheta - E_g)^m,$$

where *hv* is the absorbed photon energy, A is a constant related to the density of electronic states above and below the band gap, E_g is the optical band gap where *m*=1/2 is direct allowed transition and *m*=2 is indirect allowed transition. In case of SnO_2 the allowed transition is direct [11]. The band gap of the tin oxide thick film was determined as 3.95 eV (as shown in the inset in Fig. 4) that is in accordance with literature data where the optical band gap of SnO_2 varies in the range between 3.4 and 4.6 eV [5].
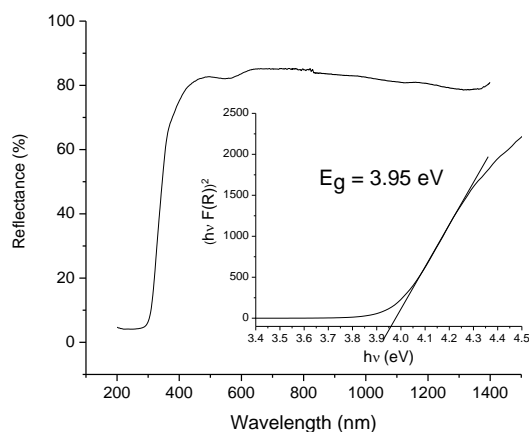
Figure 4. Diffuse reflectance spectra of SnO_2 thick film sample (inset: Tauc plot for the allowed direct transition).

The measured resistance in a climate chamber in the temperature range 27-180°C is shown in Fig. 5.
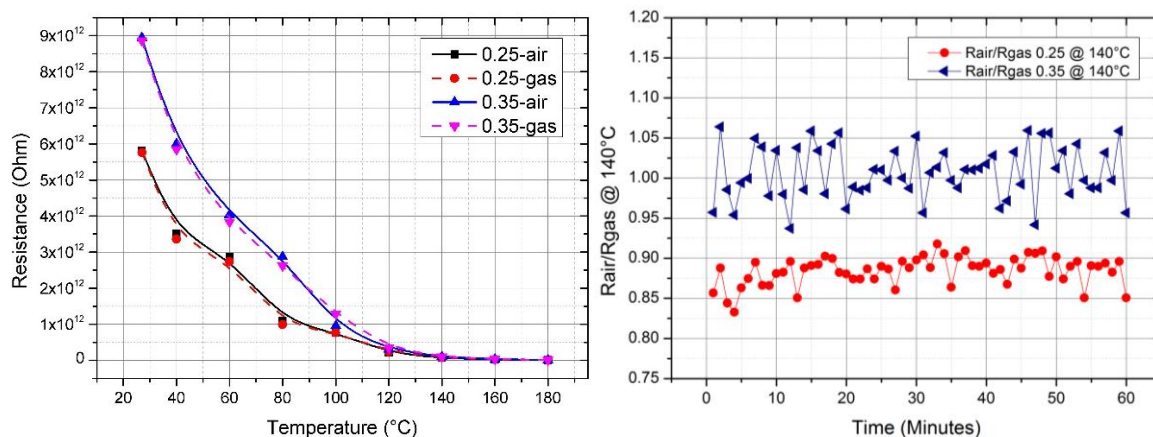
Figure 5. Resistance of SnO$_2$ thick film sample exposed to air and to 5% of CO measured in a climate chamber.

As Fig. 5 shows, the measured values are quite high. Up to 120°C the measured values were unstable so 100 measurements were made and the average value has been taken for further analysis. From 120°C the measured values are stable and 10 measurements were taken for averaging. Clearly samples with bigger spacing between electrodes (0.35mm) have higher values of resistance, but both types of samples exhibit the same temperature dependence. In both atmospheres a decrease in the resistance with increase in temperature can be noted. In case of air, the B-value (material constant) can be determined from the slope of the ln$R$-1000/T (in Kelvin) characteristic over the specified temperature range [12]. B$_{27/180}$ for both analysed electrode spacing values (0.25 and 0.35 mm) was determined as 5931 K and 8081 K, respectively. After exposing samples to 5% of CO gas, measurements were performed for 1 hour. As an example, the ratio Rair/Rgas at 140°C for both samples is given in Fig. 5. As it can be seen, there is a lack of reaction towards CO gas and similar values were obtained for other temperatures as well as for 5% of NO gas.

4. Conclusion

In this paper a complete analysis and characterisation of nanostructured SnO$_2$ thick film was made. Micron sized SnO$_2$ powder was milled in an agate mill to fabricate SnO$_2$ nanopowder, which was afterwards characterized by XRD and SEM. This powder was used as functional part in the production of thick film tin oxide paste. The achieved thick film paste was screen printed on alumina and fired at 850°C peak temperature for 10 minutes in air. After the sintering process, thick film samples where characterized by X-ray powder diffraction (XRD) and SnO$_2$ (cassiterite) with a tetragonal structure (space group - $P4_2/mnm$) was determined. Scanning electron microscopy (SEM) confirmed the small and relatively uniform grain size. The reflectivity was measured on the same samples by UV-VIS spectrophotometer: the band gap of SnO$_2$ was determined from the slope of reflectance as 3.95 eV. As for the response toward CO and NO, the samples exhibited a lack of sensitivity, which is explained with the low temperature needed for electro-chemical reactions. Plans for future work is to add catalytic dopants (Pt, Pd) and to perform measurements at higher temperatures.

5. Acknowledgement

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