

Gas sensing properties of nanosized tin oxide synthesised by mechanochemical processing

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Abstract

Tin oxide thin films have been prepared by mechanochemical processing and spin coating. Separated SnO₂ nanoparticles, averaging 24 nm, were produced by mechanochemical processing. The powder consisted primarily of tetragonal SnO₂, however, some orthorhombic SnO₂ was also found to be present. SnO₂ thin films were prepared by spin coating onto alumina transducers, followed by subsequent annealing. XPS analysis concluded the films were essentially stoichiometric with carbon being the main impurity. The average particle size of the SnO₂ film was found to be approximately 34 nm. The electrical response of the sensor to O₂, over the concentration range 1 ppm to 10%, was measured. The sensor was found to be extremely stable and repeatable, with a response and decay time of approximately 2 min. The response and decay times were found to decrease as the oxygen concentration increased. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tin oxide has been the most widely investigated metal oxide material for gas detection since gas sensors first appeared on the market in 1968 [1]. The sensing mechanism involves an electrical conductance change caused by gas adsorption on the semiconductor surface, which is highly dependent on surface stoichiometry [2]. In addition, the sensing properties are also influenced by the microstructural features, such as the grain size of semiconductor particles, the geometry and connectivity between particles [3].

Most previous fabrications of nanocrystalline thin sensing films have utilised a wet chemistry route or physical-vapour-deposition methods. In contrast, this article outlines the gas sensing properties of nanocrystalline thin films prepared by mechanochemical processing and spin coating.

Mechanochemical processing is a novel process used for the production of nanosized powders, with particle sizes as small as 5 nm reported [4]. The mechanochemical process uses a conventional ball mill in which the mechanical energy activates chemical reactions and induces structural changes. Repeated ball-powder collisions continually regenerate reacting interfaces, allowing chemical reactions to occur

at low temperatures. Suitable precursor powders are milled to form a nanocomposite structure of the starting materials, which react during milling or subsequent heat treatment. Nanoparticles of the desired material are obtained after washing away a soluble salt matrix. By controlling the milling conditions and relative volumes of product phases, separated nanoparticles can be formed [5]. A number of transition metals, including Fe [6]; ceramics, for example ZrO₂ [7]; and semiconductors such as ZnS [4], prepared by mechanochemical reactions have been reported.

2. Experimental

Nanosized SnO₂ particles were prepared by the mechanochemical reaction



in a Spex 8000 mixer/mill, with NaCl added as a diluent, under inert atmosphere. The milling was carried out with 12.7 mm chromium-steel balls for 3 h, with a pre-milling stage. Subsequent heat treatment to form SnO₂ was conducted at 700°C in an air atmosphere. The heat treated powder was washed in DI water to remove the NaCl by-product.

The structure of the powder was examined using a Siemens D5000 X-ray diffractometer with Cu K α radiation.

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The microstructure and the particle size were examined using a Philips 430 transmission electron microscope (TEM). The surface area of the powder was measured using a Micromeritics Gemini 2360 BET surface area analyser.

The slurry for film preparation was prepared in water with Darvan C used as a dispersant. After ultrasonic mixing, the slurry was roll milled prior to deposition to facilitate agglomerate removal. The thin films were deposited using the spin coating technique, at 3000 rpm for 40 s. Thin films were deposited onto single crystal silicon substrates for micro-characterisation. The microstructure of the thin film was examined using a JOEL 6300F field emission scanning electron microscope (FESEM).

The chemical state of the different elements of the films was analysed using an XPS system containing a hemispherical analyser (PHI 5600, Perkin-Elmer). The X-ray was generated by a non-monochromatic Mg source ($K\alpha$, 1253.6 eV), and the measurement was performed in an ultra high vacuum chamber at about 5×10^{-8} Pa. The spectrometer was calibrated from the binding energy of Au $4f_{7/2}$ (84.0 eV) with respect to the Fermi level. Survey scans were up to 1000 eV at 1 eV s^{-1} , and details were obtained at 0.1 eV s^{-1} .

Thin films for electrical characterisation were deposited onto alumina substrate transducers with interdigital electrodes on the front side and a heater element on the backside. The as-deposited films were annealed at 500°C for 1 h.

The sensor response to O_2 was examined using a 4-channel gas calibration system with a computerised multi-meter unit. The flow was set at 0.15 LPM, the ambient temperature was 20°C and RH 30%. The O_2 gas sensing properties were tested in the range from 1 ppm to 10%, with pure dry nitrogen used as the carrier gas. The operating temperature of the sensor was varied in the range of $200\text{--}400^\circ\text{C}$ by controlling the power applied to the transducer heater. The response times ($\tau_{\text{res}} = 0.9$), recovery times ($\tau_{\text{rec}} = 0.3$), stability, repeatability and sensitivity of the sensor were analysed.

3. Results and discussion

3.1. Micro analysis of the processed SnO_2 powder

A TEM micrograph showing the morphology of the SnO_2 nanoparticles after milling, heat treatment and washing is shown in Fig. 1. The SnO_2 particles, 5–40 nm in size, appear to be moderately aggregated by van der Waals forces. The measured BET surface area was $36.1 \text{ m}^2/\text{g}$, corresponding to an average particle size of 24 nm. This value is consistent with the particle size range observed in the TEM analysis and suggests that hard aggregates are not present.

An XRD pattern of the SnO_2 nanopowder is shown in Fig. 2. Two phases of SnO_2 are present, the rutile, or tetragonal phase, and the orthorhombic phase. By comparison of the integrated peak intensities, the powder contains

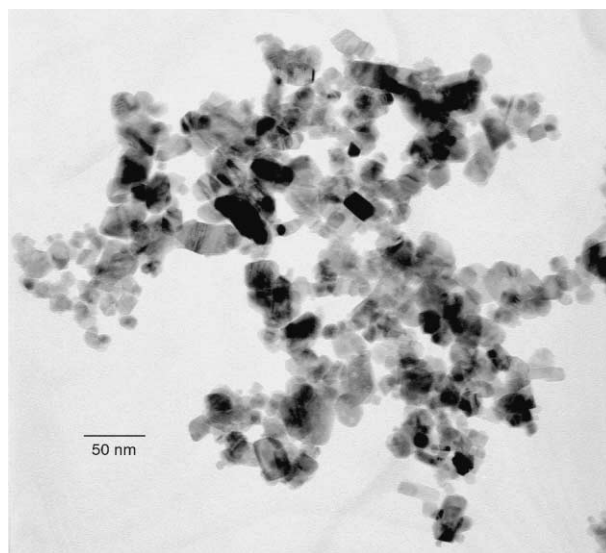


Fig. 1. TEM micrograph of the milled, heat treated and washed SnO_2 powder.

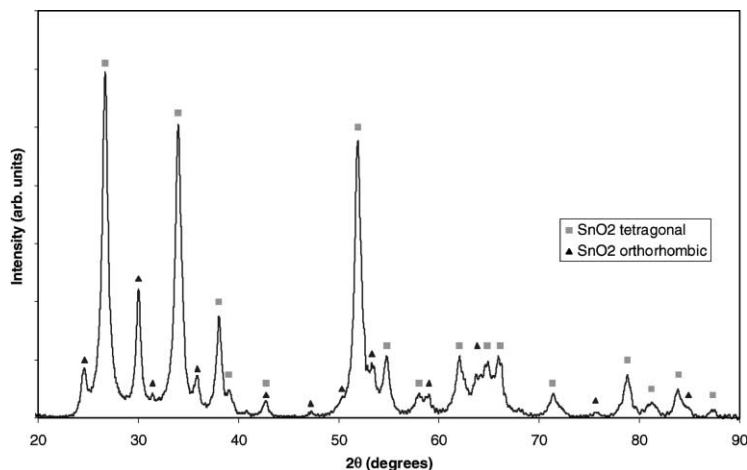


Fig. 2. XRD pattern of the milled, heat treated and washed SnO_2 powder showing the presence of the tetragonal phase and orthorhombic phase.

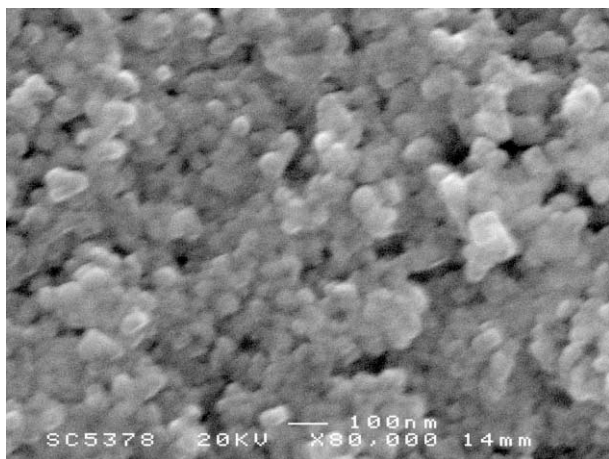


Fig. 3. FESEM micrograph of the spin coated SnO₂ thin film annealed at 500°C.

approximately 75% tetragonal and 25% orthorhombic SnO₂. The tetragonal phase is the stable phase under ambient conditions, whereas the orthorhombic phase is normally present under high pressure [8]. Previous studies have reported the presence of orthorhombic SnO₂, together with tetragonal SnO₂, in ultrafine 5–10 nm SnO₂ powders prepared by inert gas condensation [9]. The orthorhombic phase was also found in the production of SnO₂ thin films and it was suggested that the presence of SnO as a precursor was important in the transformation [10]. The stability of unstable phases in ultrafine particles can be explained by the Gibbs–Thomson effect. The ultrafine particles experience an increased effective internal pressure within the particles, which is due to the surface stress increase in surface energy. This internal pressure is inversely proportional to the particle radius, as given by the Laplace equation, and may be enough to stabilise a high pressure phase under ambient conditions [11].

Table 1
Chemical composition of the SnO₂ thin film surface

Peak	Position BE (eV)	FWHM (eV)	at.%
Sn 3p ₃	716.83	4.00	26.67
O 1s	530.73	1.80	57.82
C 1s	285.13	2.20	15.52

3.2. Micro analysis of the SnO₂ thin film

A FESEM picture of the spin coated film is shown in Fig. 3. The nanopowder annealed under similar conditions as the spin coated thin film was found to have an average particle size of 34 nm. This agrees with the average size observed from FESEM analysis and indicates that some particle growth occurred during annealing. The particle growth may be minimised by reducing the annealing temperature, depending on the operation temperature of the sensor. The relative amount of tetragonal and orthorhombic SnO₂ remained unchanged after annealing.

The chemical composition of the SnO₂ thin film is shown in Table 1, with the corresponding XPS spectrum shown in Fig. 4. The thin film is essentially stoichiometric. The main impurity element is carbon, which was introduced in the form of an organic dispersant in the suspension for spin coating.

3.3. Electrical response

Fig. 5 shows the dynamic response of the SnO₂ thin film, defined as $S(O_2) = (R_{O_2}/R_{1\text{ppm}})$. The response and recovery times ($t_{0-90\%}$) both decrease with higher O₂ concentrations. The response time of the sensor is approximately 2–3 min, occurring when the O₂ increases from 1 to 1000 ppm. The sensor exhibits a fast response throughout all oxygen concentration ranges when tested at an operating

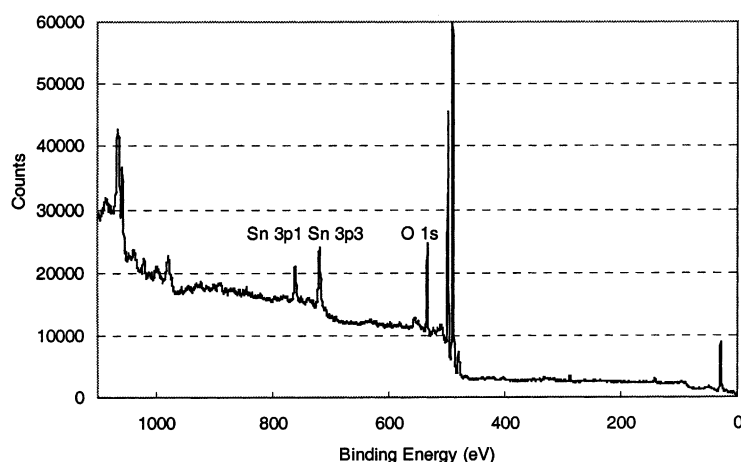


Fig. 4. XPS survey spectra of the SnO₂ thin film surface, annealed at 500°C.

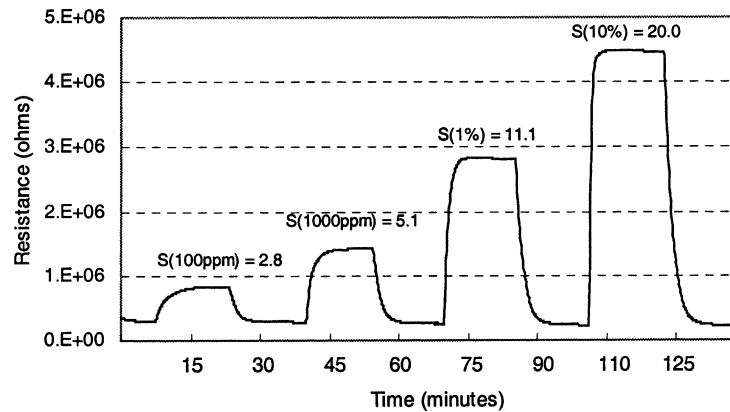


Fig. 5. Dynamic response of the SnO₂ thin film to O₂ operating at 400°C.

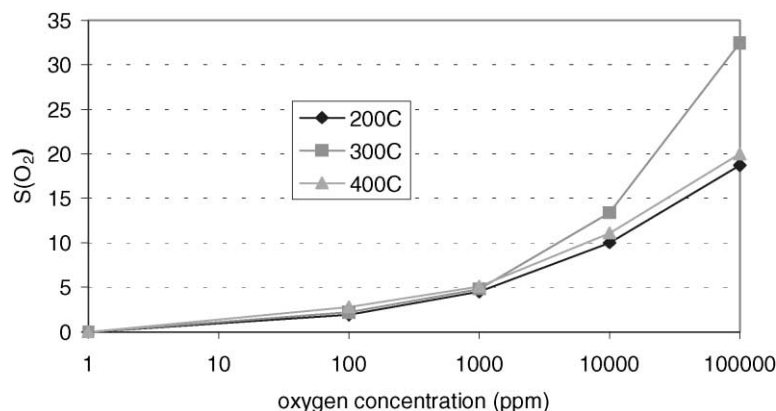


Fig. 6. Static response of the SnO₂ thin film in the oxygen concentration range of 1 ppm to 10%, operating at 200, 300 and 400°C.

temperature of 400°C. The response and decay times also average between 2 and 3 min. Extremely good stability and repeatability is also a key feature of the sensors dynamic response, consistently returning to baseline after being exposed to a broad oxygen concentration range.

From Fig. 6, the optimal operating temperature is dependent on sensing concentration. For fast response and high sensitivity at low ppm oxygen concentration, an operating temperature of 400°C is optimal. However, for higher ppm oxygen concentrations, 300°C sensor operating temperature is best, as can be seen from the static response diagram.

4. Conclusion

Nanocrystalline SnO₂ thin sensing films were successfully prepared by mechanochemical processing and spin coating. Micro characterisation clearly illustrated the uniform nanocrystalline morphology of the material. The mechanochemically processed powder was characterised by an average particle size of 24 nm, which increased to 34 nm after spin coating and annealing. The electrical response to oxygen verified that SnO₂ obtained by mechan-

ochemical processing could indeed be applied to the field of gas sensing. The stable, repeatable and reproducible electrical response indicates the predicability of these sensors, being highly desirable gas sensing properties. Further work will concentrate on reducing the average particle size and characterising the films with various gas agents.

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Biographies

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Kosmas Galatsis received his degree with honours in Computer Systems Engineering from the Royal Melbourne Institute of Technology University, Australia in 1998. His research efforts focus on MoO₃ based MOS gas sensors, gas analysers, vehicle cabin air quality, and smoke-dust IR back scatter detectors.

Wojtek Wlodarski has worked in the areas of sensor technology and instrumentation for over 30 years. He has published four books and monographs and over 200 papers and holds 26 patents. He is a professor at RMIT University, Melbourne, Australia and heads the Sensor Technology Laboratory located in the School of Electrical and Computer Systems Engineering.