



The Reactive Surface Sites and the H₂S Sensing Potential for the SnO₂ Produced by a Mechanochemical Milling

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SnCl₂ powder was milled with Ca(OH)₂ and K₂CO₃ powder respectively in a ball mill at room temperature and in an air atmosphere. Pure SnO₂ was obtained by removal of the CaCl₂ or KCl by-product by washing the powder. An initial composition of SnCl₂, K₂CO₃, and Cr(NO₃)₃·9H₂O was milled to produce the doped SnO₂ phase with Cr on the surface. Heat-treatment results in the formation of a tetragonal phase. The infrared spectra for the different powders and from thick films of these materials are reported. An important finding is that during milling in the presence of water, OH groups are formed at the surface in great numbers. After heat-treatment at 400°C or higher, the OH bonds of adjacent grains are probably transformed into Sn-O-Sn bridges. Washing the material with pure ethanol, instead of water, can result in the reduction of intensity for the band at 1450 cm⁻¹ due to the presence of the bridge bonding Sn-O-Sn. On exposure to H₂S and CO gas, the SnO₂ film prepared from anhydrous powder, has higher sensitivity than the SnO₂ film, prepared from hydrated powder. It is shown that the SnO₂ produced by mechanochemical synthesis can be successfully applied to a H₂S gas sensor.

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The current methods of fabrication of semiconductor SnO₂ gas sensors requires the use of nanocrystalline powder with grain size of less than 20 nm. After synthesis the powder is mixed with organic solvent to form a paste. Nanosized SnO₂ powders for gas sensing applications have been produced by several methods, including sol-gel processing, spray pyrolysis, pulsed laser ablation, chemical vapor deposition, and sputtering. Often nanocrystalline structures obtained by these methods have a high state of agglomeration. Mechanochemical processing (MCP) is an alternative method for the production of nanosized powders, where separated nanoparticles can be formed.¹ This method is not time consuming and is of low cost.

Only one previous paper has been published on the uses of SnO₂ thin films prepared by mechanochemical processing as a gas sensor.² Separated tin dioxide nanoparticles, averaging 24 nm, were produced, and examined by X-ray photoelectron spectroscopy (XPS), but in this work, the surface was not characterized by infrared spectroscopy.

In this paper, the synthesis of SnO₂ nanoparticles by MCP is reported. It is found that the details of powder synthesis and processing have a large influence on the final electrical properties of the gas-sensitive layer. Since the surface reactions important to the gas sensing mechanism are complex, involving the transfer of electronic charges, it is important to analyze the reactive surface sites.

Fourier transform infrared (FTIR) spectrometry is a reliable tool for the determination of existing surface species; however, large differences in sensor fabrication lead to very different surfaces, making it difficult to compare results obtained by different authors. The FTIR spectra of SnO₂ powders calcined at 250°C (for use in improved sol-gel fabricated thick film gas sensors) shows bands at 1632 cm⁻¹ indicating the presence of adsorbed water and also hydroxyl absorption bands in the range 2000-3600 cm⁻¹. The water content and associated lattice distortions largely disappear after heat-treatment above 450°C as indicated by the disappearance of the associated absorption bands.³ Another synthesis method based on the microwave treatment of a solution of tin chloride produces powder precursors in a few minutes. In the infrared spectrum at 450°C there are again clear absorption bands from molecular water and hydroxyl groups associated with lattice distortions and defects.⁴ SnO₂ thin films may also be prepared by using a chloride-based

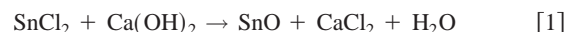
inorganic sol-gel route, where tetrachloride is used as a tin precursor. Heating at 350°C causes complete decomposition of organic compounds, and FTIR shows a broad band in the range 3750-2500 cm⁻¹ due to different O-H stretching modes of alcohol. Molecular water and Sn-OH groups are not present, only the band of SnO₂ vibrations at about 600 cm⁻¹ and that of a lattice mode at about 690 cm⁻¹ is observed.⁵ The measured FTIR spectra in the range 4000-800 cm⁻¹ revealed different bands, assigned to the unsymmetrical hydroxyl stretching, water deformation, and surface hydroxyl stretching modes.^{2,4}

The repeated ball-powder collisions during milling induce structural changes and continually regenerate the reacting interfaces, allowing chemical reactions to occur.⁶ Extensive surface treatment by use of high rotation speeds (100-200 rpm) and enhanced ball-to-powder mass ratio (10:1) during milling give rise to quite different surfaces, which may lead to differences in surface charge and hence intergranular barrier heights. The presence of free water causes a considerable change in the reactivity of the surface. Thus, mechanochemically synthesized SnO₂ surfaces may have considerably different chemical compositions and reactivities than those prepared by other methods.²⁻⁴ It was found in the present work that with appropriate selection of milling conditions and chemical reaction, it is possible to reduce the intensity of the antisymmetric Sn-O-Sn modes of surface-bridging oxide at 1450 cm⁻¹. Hydroxyls attached to Sn atoms are highly electron accepting, causing the resulting complex to be strongly dipolar.⁷ Thus, the consumption of surface OH groups by reacting with gas could lead to an increase in the conductance.

The aim of this work is to present more information about the surface composition and reactivity of SnO₂ powder used in the preparation of a gas sensors. Neither the study of the surface reactivity of mechanochemically synthesized particles, nor the influence of the surface reactivity to the gas-sensing response, have been reported before.

Experimental

Nanosized SnO₂ powder particles were produced by mechanochemical synthesis, where a milling process of duration 4 h was performed at room temperature in a centrifugal type mill. Two chemical reactions were used. The first one is

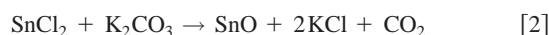


It is important to notice that this reaction produces water. The starting materials (2.33 g of SnCl₂, 0.91 g of Ca(OH)₂, and 15.45 g of

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CaCl₂) were sealed in a nonmetal vial in an air atmosphere and milled to produce 5g of SnO. Milling was performed using steel balls with a diam of 12.7 mm. The ball-to-powder mass ratio of 10:1 was used with a rotation speed of 75 rpm (low speed), 125 rpm (moderate speed), and 200 rpm (high speed). The milled powder was subsequently heat-treated at 400°C for 1 h in air atmosphere to complete the SnO₂ formation. Removal of the CaCl₂ by-product was carried out both, with distilled water and pure ethanol.

The second reaction used is



This reaction does not produce water. The starting materials (4.23 g of SnCl₂ and 3.09 g of K₂CO₃) were sealed in a nonmetal vial in an air atmosphere and milled to produce 3 g of SnO. The ball-to-powder mass ratio of 22:1 was used with a rotation speed of 125 rpm. The milled powder was washed by distilled water.

The starting materials (2.33 g of SnCl₂, 0.91 g of Ca(OH)₂, 0.098 g of Cr(NO₃)₃·9H₂O and 15.45 g of CaCl₂) were sealed and milled to produce the doped SnO phase with Cr distributed on the surface. The ball-to-powder mass ratio of 10:1 was used with a rotation speed of 125 rpm. The milled powder was washed by deionized water. After washing all powders were dried at 65°C for 8 h.

A Philips PW 1830 X-ray powder diffractometer with Cu K α radiation was used to follow the crystallization of the powder as a function of heat-treatment temperature. The crystallite size, *D*, is calculated according to the Scherrer equation

$$L(2\theta) = K\alpha / (D \cos \theta) \quad [3]$$

where *L*(2 θ) is the width at half-maximum intensity (in radians), θ is the Bragg angle of the (110) plane in the diffraction pattern of the peak, *K* is a constant depending on the line shape profile (currently *K* = 1), α is the wavelength of the X-ray source (in the case of Cu radiation α = 1.54059 Å), and *D* is the crystallite size.⁸ The specific surface area and porosity of the synthesized powders are measured with a Coulter Omnisorp 100 CX, using a N₂ gas adsorption method at 77 K. The FTIR spectra were taken with a Bio-Rad FTS 6000 spectrometer with photoacoustic output in the range 4000-400 cm⁻¹. All powders synthesized by MCP were washed both in water and in ethanol, dried, additionally heat-treated at 750°C for 1 h, and cooled down to room temperature before making of the FTIR measurements.

Thick-film gas sensors were prepared by conventional hand coating of a paste, the SnO₂ powder mixed with an α -terpineol-based solvent, over the 0.2 mm gap of Au sensing electrodes on a 7 × 8 mm Al₂O₃ substrate. Subsequently these substrates were sintered at 700°C for 1 h in air. Pt wires were attached to the pads of the heater and sensing electrodes by using an Au paste and heat-treatment. The H₂S and CO gas response tests were carried out with a PC-controlled measuring system. Sensors to be tested were placed in a measuring chamber of about 0.51 in volume. Optimum detection temperatures were determined and thick-film sensors maintained at this fixed temperature were exposed to varying test gas concentrations of H₂S (3 ppm and 10 ppm) and CO (50 ppm and 100 ppm), using a gas flow controller unit with an air flow rate of 0.51 min⁻¹. Sensitivity, *S*, to gas is defined

$$S = [R(\text{air}) - R(\text{g})/R(\text{air})] \quad 100\% \quad [4]$$

where *R*(air) is the sensor resistance in clean air and *R*(g) is the resistance in the test gas.

Results and Discussion

The mixture, produced after 4 h ballmilling with a rotation speed of 125 rpm, was heat treated at 400°C for 1 h, resulting in the exothermic reaction

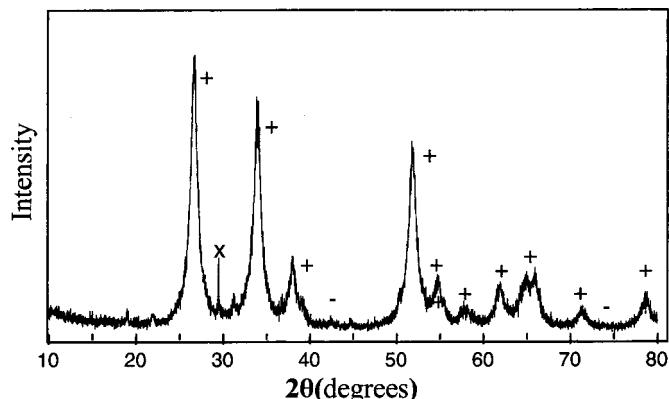


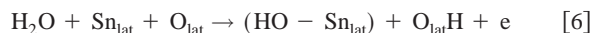
Figure 1. X-ray diffraction pattern of the milled (for 4 h), heat treated (at 400°C for 1 h), and washed powder with a typical distribution of (+) tetragonal and (-) orthorhombic SnO₂ phases. The sharp peak (x) at 29.4 (2 θ°) indicates residual CaCl₂.

An X-ray diffraction (XRD) pattern of the synthesized powder, after removal of the CaCl₂ mass and drying, is presented in Fig. 1. The tetragonal phase is clearly dominant with the orthorhombic phase, giving the rise to only two very weak peaks. It may be concluded that the crystallization has succeeded at this low temperature of 400°C. The main three peaks are located at 26.6, 33.9, and 51.8 (2 θ°) degrees, respectively, and show a high degree of crystallinity. The sharp peak (*) at 29.4 (2 θ°) indicates residual CaCl₂.

X-ray analysis is important for the confirmation of the microstructure of the synthesized powder obtained after washing and removal of all CaCl₂. The SnO₂ crystallite sizes determined using Scherrer's equation were in the range 10-25 nm dependent on the different milling conditions. The sample of powder for Brunauer, Emmett, Teller analysis was milled for 5 h at a speed of 125 rpm. The total pore volume comprised 0.25 mL/g with a measured specific surface area of 79 m²/g.

It should be noted that water vapor present inside the milling vessel or produced by the chemical reaction accompanying milling, has a considerable influence on the milling mechanism. The current work shows that molecular water and hydroxyls are remained on the surface at much higher temperature than 500°C. The hydroxyl groups appear as a result of the acid-base reaction with the OH⁻ sharing its electronic pair with the Lewis acid (Sn) leaving weakly bonded protons. The correlation between the behavior of the conductance and the intensity of the surface hydroxyl deformation band (Sn-OH) in the infrared spectrum shows that the decrease in conductivity in the temperature range 150-450°C is due to loss of hydroxyl groups from the oxide surface.⁹

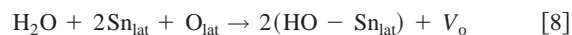
Two types of mechanism, proposed by Heiland and Kohl,¹⁰ to explain the increase in surface conductivity in the presence of water vapor can also result in the formation of two types of OH groups during MCP, one including lattice oxygen O_{lat} the other bound to lattice tin Sn_{lat}



Dissociation of water in the gas phase results in the reaction



The second mechanism is related to the reaction between the proton and the lattice oxygen with subsequent binding of the resulting OH group to the Sn_{lat} atom



The oxygen vacancy created produces electrons in the conduction band. The OH group bound to Sn_{lat} has been detected spectroscopi-

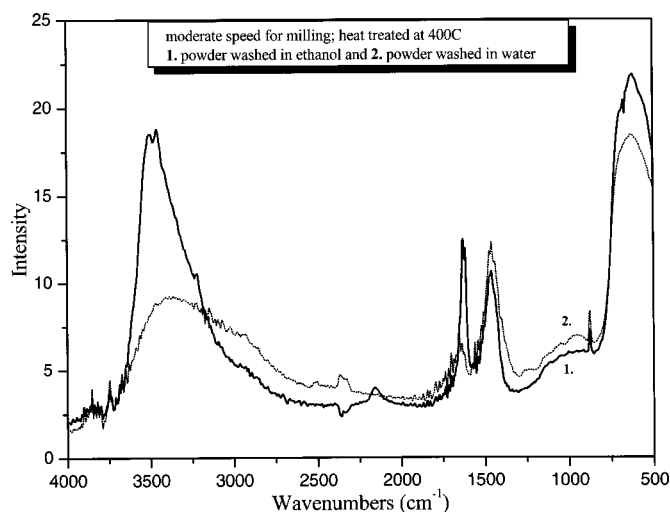


Figure 2. FTIR spectra of SnO₂ powder milled with moderate speed. Curve 1 shows results for a powder heat-treated at 400°C and washed in pure ethanol, and curve 2 the results for a powder washed in distilled water.

cally. Probably during milling the reaction shown by Eq. 8 is initiated and a certain number of OH groups are bound to Sn_{lat}. The reaction shown by Eq. 6 may be partially started by milling, but it is of evident that reaction requires some activation of the composition by heat-treatment at 400°C.

The FTIR difference spectrum of powder, synthesized at moderate speed, using the reaction shown by Eq. 1 is illustrated in Fig. 2. A broad absorption band in the range 3750-2500 cm⁻¹ is due to the asymmetric hydroxyl stretching mode and the band between 820 and 1300 cm⁻¹ is assigned to the hydroxyl deformation mode. The molecular water deformation mode is located at 1640 cm⁻¹. The band at 1450 cm⁻¹ is most probably an overtone of the asymmetric Sn-O-Sn stretching mode of a surface-bridging oxide formed by condensation of adjacent surface hydroxyl groups. The SnO₂ vibrations are observed at 625 cm⁻¹ and lattice modes of SnO₂ appear at 690 cm⁻¹. Washing of the heat-treated powders with pure ethanol leads to lower band intensities compared to washing with water. Of especial importance is the intensity of the band at 1450 cm⁻¹. It has been concluded by Morimoto that dehydration of the surface of SnO₂ occurs principally via condensation of adjacent surface hydroxyl groups on the (100) plane with secondary condensation on the (101) plane.¹¹ Hydroxyl group condensation on these two planes will lead to the formation of surface Sn-O-Sn bridges. It was concluded in previous work that a possible factor, affecting the sensitivity to H₂S gas, is the formation of strong Sn-O-Sn stretching mode deformation and its influence on the H₂S adsorption.¹² It was suggested that strong oxygen bonds, formed during the dehydration, remain on the surface and thus reduce the number of active sites for gas adsorption. At high speed milling (200 rpm) there is no essential difference between OH band intensities, whether the composition was washed by water or ethanol, as shown in Fig. 3. The differences can be found in the intensity of the band at 1450 cm⁻¹. (The sharp peak at 890 cm⁻¹ can be attributed to a surface hydroxyl deformation band.)

The FTIR spectra of powders synthesized with different milling conditions and chemical reactions are presented in Fig. 4. The powder produced by the chemical reaction (Eq. 2) and milled with moderate speed (curve 1) is characterized by the lowest intensities of adsorption bands. The curve 2 is the infrared spectrum of SnO₂ powder with Cr₂O₃ distributed on the surface, where the band at 1450 cm⁻¹ is increased in intensity. Curves 3 and 4 show the FTIR spectra of two undoped SnO₂ thick film sensors, sintered at 700 and 600°C, respectively.

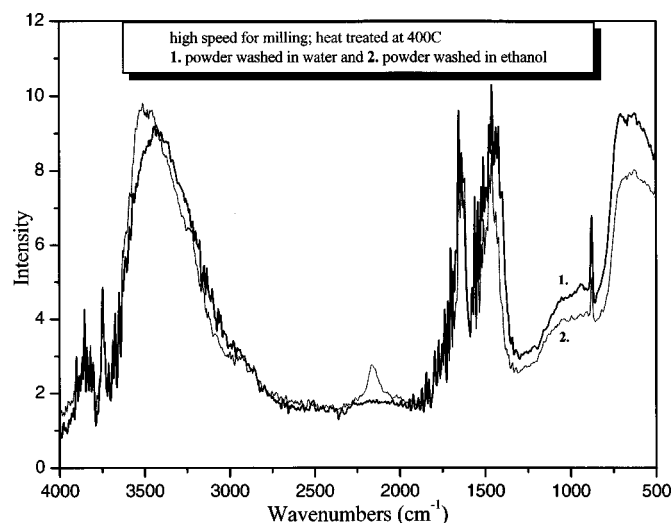


Figure 3. FTIR spectra of SnO₂ powder milled with high speed. For curve 1 the powder was heat-treated at 400°C and washed in distilled water, while for curve 2 the powder was washed in pure ethanol.

Both adsorption of water and hydroxylation are unfavourable at high temperatures. It is possible that at a sufficiently high temperature, the surface may be free from molecular water, but may be partially covered by OH groups. In Fig. 5 there are spectra for five different powders obtained by mechanochemical synthesis and heat-treated at 750°C for 1 h. It can be noticed that the intensities of all the adsorption bands are reduced to some extent after high temperature heat-treatment compared to those in Fig. 4. The powders washed with water and milled with speeds of 75-125 rpm have the highest intensities for the asymmetric Sn-O-Sn stretching and hydroxyl deformation modes in Fig. 5. Treatment of the milled composition with ethanol causes the band at 1450 cm⁻¹ to decrease (curves 3, 4). The milled composition produced by the reaction given by (Eq. 2) contains no water, and therefore the deformation bands are of lowest intensity (curve 5), resulting only from the adsorption of water from the gas phase during the milling.

The response and recovery times of sensors made from the powders depend on the operating temperature, both being slow at low

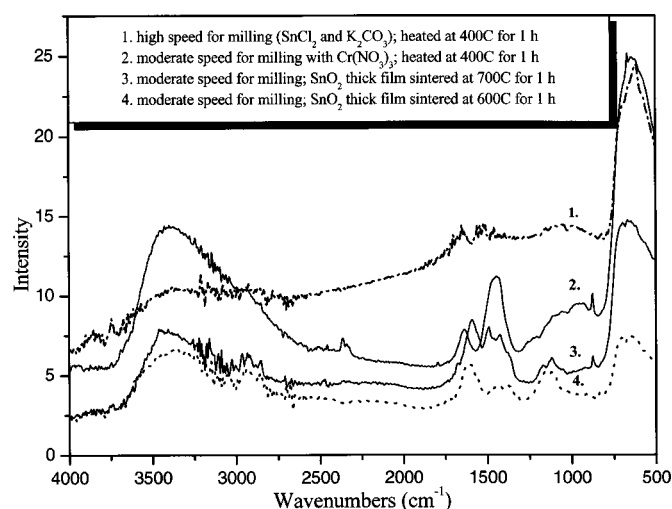


Figure 4. FTIR spectra of SnO₂ powder milled with high speed. Curve 1 shows the spectrum of the anhydrous powder and curve 2 that of the hydrous powder. Curves 3 and 4 show the spectra of the SnO₂ thick films prepared from these powders.

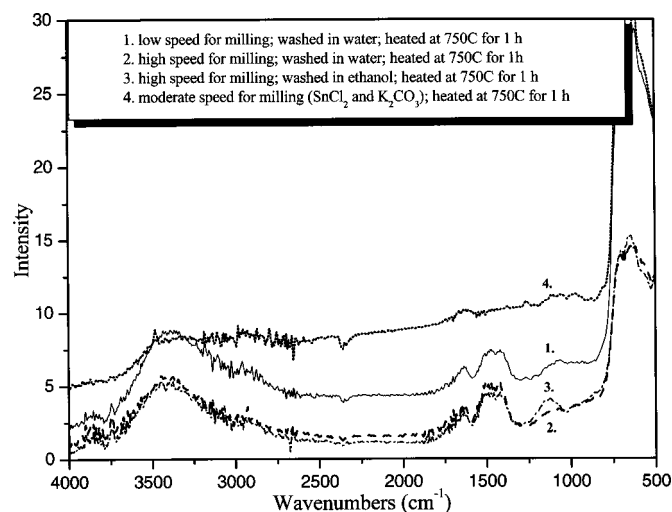


Figure 5. FTIR spectra of SnO₂ powders milled with different speeds and heat-treated at 750°C.

temperatures, and fast at higher temperature. An operating temperature of about 225-250°C was found to give the maximum sensitivity to H₂S gas. The increase of the conductivity in the presence of H₂S may be explained by the reaction between H₂S and oxygen ions on the surface of SnO₂



According to this reaction, the interaction of H₂S with previously adsorbed O²⁻ ions on the surface, is resulting in injection of electrons into the depletion layer of SnO₂ grains.¹³ This reaction reduces the band bending of the intergranular depletion layer and leads to an enhanced conduction of the sensor. Figure 6 shows the gas response to 3 and 10 ppm of H₂S gas. The powder for the sensor was milled at high speed and washed with water. Since the thick film, as prepared, has a low porosity, the reaction in the bulk takes a considerable time. Removal of the salt matrix with ethanol increases, to some extent, the sensitivity to the gas, as shown by curve a in Fig. 7. Comparison with Fig. 6 shows that gas is adsorbed much more quickly. Similar response times, of the order 20-40 min, for H₂S at

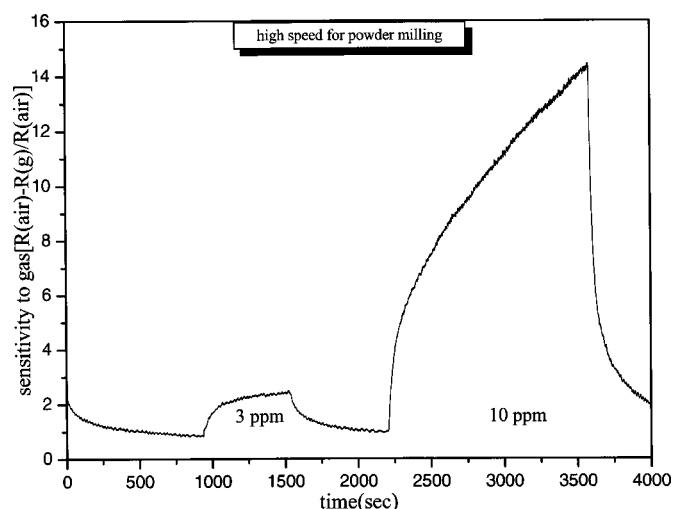


Figure 6. Dynamic response of an SnO₂ thick film to 3 and 10 ppm of H₂S in air. The powder was milled with high speed, heat-treated, and washed in distilled water.

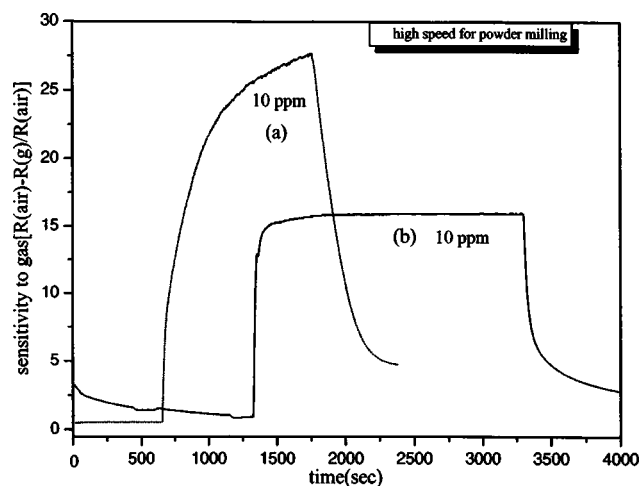
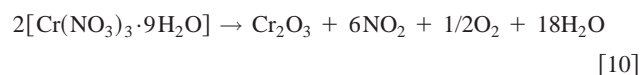


Figure 7. Response of an SnO₂ thick films to 10 ppm of H₂S in air. The powder was (curve 1) milled with high speed, heat-treated and washed in pure ethanol, or (curve 2) milled with moderate speed and washed in pure ethanol.

operating temperatures of 200-250°C have been observed previously.^{14,15} The response time depends considerably on the sensor operating temperature. At a higher temperature of 300°C the sensor current in air is below 2 mA, which corresponds to a sensor resistance of 2.5 kΩ. The current increases to 20 mA in gas (curve b in Fig. 7), and there is a faster gas response of the surface, but the sensitivity to H₂S is decreased to 12.

An attempt was made to Cr dope the SnO₂ particles by ballmilling using chromium nitrate nonhydrate Cr(NO₃)₃·9H₂O. The decomposition of the main starting materials during milling could be followed according to the Eq. 1. By heat-treatment at 400°C, chromium nitrate particles decompose and Sn and Cr ions change their oxidation states as below



Coordination bonds between Cr³⁺ ion and water in the starting material will be transformed into Cr-O-Cr bonds upon heating to

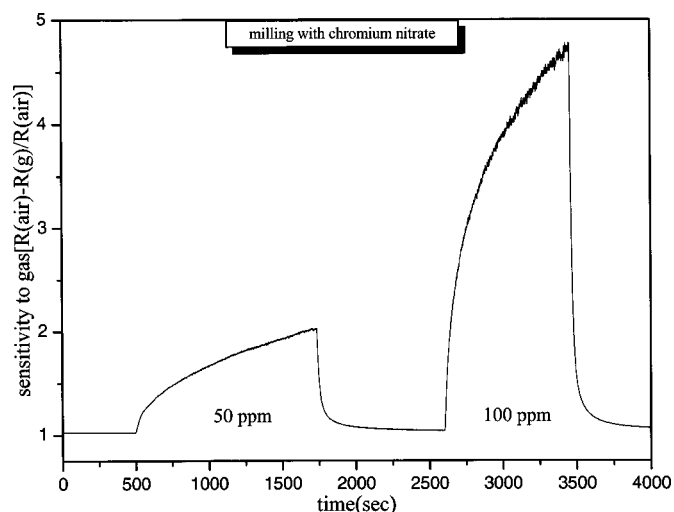


Figure 8. Dynamic response of a Cr doped SnO₂ thick film to 50 and 100 ppm of H₂S in air. The powder used in the preparation was milled with high speed, heat-treated and washed in distilled water.

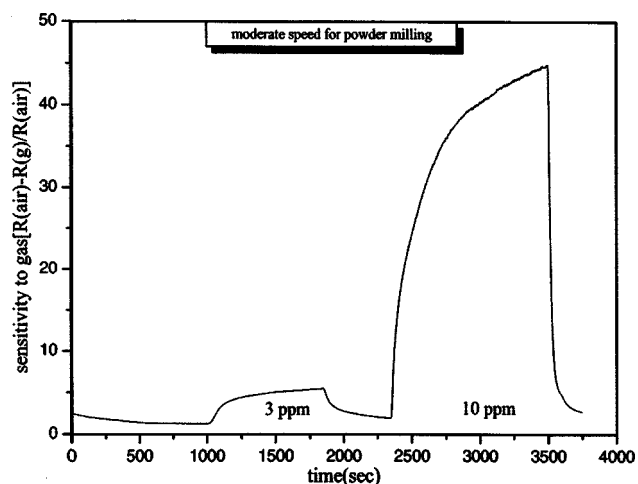
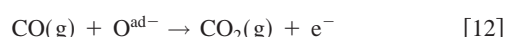
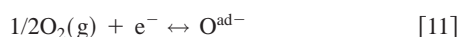


Figure 9. Dynamic response of an SnO₂ thick film prepared from anhydrous powder to 3 and 10 ppm of H₂S in air.

400°C. The occupation of Cr⁶⁺ ion sites by H₂O or OH groups may be one explanation for the reduced sensitivity of this Cr doped SnO₂ thick film as presented in Fig. 8. It is noticeable that there is a considerably higher intensity for Sn-O-Sn stretching mode of surface bridging oxide for this sample (curve 2 in Fig. 4).

The main sensing mechanism may be explained by the reaction between H₂S and oxygen ions adsorbed on the surface of SnO₂. It can be seen in Fig. 9 that enhanced gas sensitivity ($S = 44$) was achieved upon exposure to 10 ppm of H₂S.

A comparison of the sensitivity to H₂S and CO gas for the different types of SnO₂ sensors has been performed in order to get confirmation of the proposed sensing mechanism. The two chemical reactions that underly the chemical sensing mechanism are



where O^{ad-} is the negatively charged surface oxygen that can react with the CO to produce electrons to the conduction band. The response of the SnO₂ thick film, where the powder for the preparation was obtained with high speed milling and washed with water after

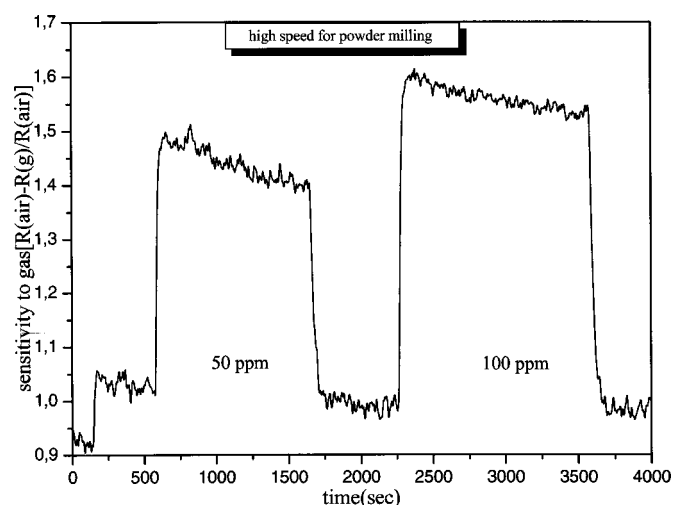


Figure 10. Response of an SnO₂ thick film to 50 and 100 ppm of CO in air. The powder used in the preparation was milled with high speed, heat-treated, and washed in distilled water.

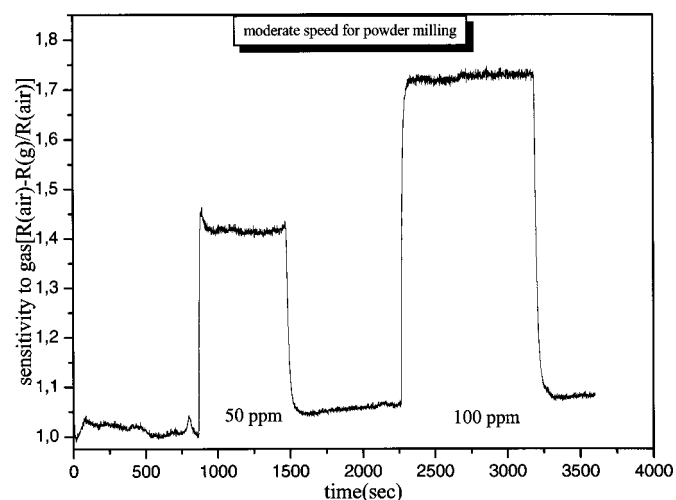


Figure 11. Response of an SnO₂ thick film prepared from anhydrous powder to 50 and 100 ppm of CO in air.

heat-treatment, is shown in Fig. 10. Due to the very small concentrations of CO (50 and 100 ppm), the responses are not high. When the powder was obtained using milling at moderate speed with the chemical reaction given by Eq. 2, the resulting thick film has a more distinct response, shown in Fig. 11, as well as a higher response to CO in comparison to Fig. 10. A possible explanation for this could be that powders manufactured with high and very high milling speeds have greater surface charge due to a large number of surface OH groups. During heat-treatment, however, most of OH groups are transformed into Sn-O-Sn bonds, which are not involved in gas adsorption.

Conclusions

Mechanochemical processing of known stoichiometric amounts of SnCl₂ with Ca(OH)₂ or with K₂CO₃ in a centrifugal action resulted in the formation of the desired mass of SnO. Use of the former reactant results in the production of water, while use of the latter does not. The infrared spectra of the powders produced support the evidence that two mechanisms proposed by Heiland and Kohl to describe the increase of sensor conductance by exposure to water vapor, can be applied to explain the formation of surface hydroxyl groups during the milling. The FTIR spectra of the powders and of the SnO₂ thick film sensors fabricated from them are influenced to a large degree by the energy input in the milling and the type of chemical reaction to be used during of milling. Using K₂CO₃ reactant, the chemical reaction initiated by ball milling does not produce water, therefore the FTIR spectrum of the synthesized powder has no surface hydroxyl deformations, only a small amount of molecular water shown by the band at 1640 cm⁻¹. For this case most of adsorbed oxygen ions are distributed near the Sn ions on the surface of SnO₂ grains. The interpretation of gas sensing mechanism is that H₂S or CO gas reacts with these oxygen ions, releasing electrons into the conduction band, with simultaneous decrease in surface charge and an increase in conductance.

The response of SnO₂ thick film sensors to H₂S gas may be improved by (i) selection of the proper chemical reaction that does not produce water during mechanochemical synthesis; (ii) producing powder grains smaller than 10 nm and (iii) the using FTIR spectroscopy to control the conditions of manufacture of the SnO₂ surface.

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References

1. T. Tsuzuki and P. G. McCormick, *Physica B*, **239**, 378 (1997).
2. L. M. Cukrov, P. G. McCormick, K. Galatsis, and W. Wlodarski, *Sens. Actuators B*, **77**, 491 (2001).
3. A. Dieguez, A. Romano-Rodriguez, J. R. Morante, J. Kappler, N. Barsan, and W. Göpel, *Sens. Actuators B*, **60**, 125 (1999).
4. A. Cirera, A. Vila, A. Dieguez, A. Cabot, A. Cornet, and J. R. Morante, *Sens. Actuators B*, **64**, 65 (2000).
5. P. Siciliano, *Sens. Actuators B*, **70**, 153 (2000).
6. P. G. McCormick and F. H. Froes, *JOM*, **50**, 61 (1998).
7. K. D. Schierbaum, U. Weimar, and W. Göpel, *Sens. Actuators B*, **3**, 205 (1991).
8. B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd ed., p. 102, Addison-Wesley Publishing, Reading, MA, (1978).
9. P. G. Harrison and M. J. Willett, *J. Chem. Soc., Faraday Trans. 1*, **85**, 1928 (1989).
10. G. Heiland and D. Kohl, in *Chemical Sensor Technology*, Vol. 1, T. Seiyama, Editor, p. 15, Elsevier, Amsterdam (1988).
11. K. Morishige, S. Kittaka, and T. Morimoto, *Bull. Chem. Soc. Jpn.*, **53**, 2128 (1980).
12. U. Kersen, *Mater. Sci. Forum*, **386-388**, 637 (2002).
13. J. N. Zemel, *Thin Solid Films*, **163**, 189 (1988).
14. M. Rumyantseva, M. Labeau, G. Delabouglise, L. Ryabova, I. Kutsenok, and A. Gaskov, *J. Mater. Chem.*, **7**, 1785 (1997).
15. L. Jianping, W. Yue, G. Xiaoguang, M. Qing, W. Li, and H. Jinghong, *Sens. Actuators B*, **65**, 111 (2000).