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laboratorio  
Espoo 2003

Report 70

## **THE GAS-SENSING POTENTIAL OF NANOCRYSTALLINE $\text{SnO}_2$ PRODUCED BY DIFFERENT CHEMICAL REACTIONS AND MILLING CONDITIONS**

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ISBN 951-22-6727-6

ISSN 1456-6001

Picaset Oy

Helsinki 2003

Kersen, Ü., **The gas-sensing potential of nanocrystalline SnO<sub>2</sub> produced by different chemical reactions and milling conditions.** Helsinki University of Technology, Laboratory of Electromechanics, Report 70, Espoo 2003, 15 p.

Key words: SnO<sub>2</sub> powder, sensor, mechanochemical processing

## **ABSTRACT**

In this work, the mechanochemical processing of undoped nanocrystalline SnO<sub>2</sub> powders and the subsequent preparation of thick films were studied. SnCl<sub>2</sub> powder was milled with Ca(OH)<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> powder respectively in a ball-mill at room temperature and in an air atmosphere. Heat-treatment of milled mixtures at 400 °C resulted in the formation of a tetragonal phase. The Fourier-transform infrared spectra (FTIR) and X-ray diffraction patterns (XRD) for the different powders are reported. A significant feature is that during milling in the presence of water a high number of OH groups are formed at the surface. After heat-treatment the OH bonds of adjacent SnO<sub>2</sub> grains are probably transformed into Sn-O-Sn bridges. On exposure to H<sub>2</sub>S gas, the SnO<sub>2</sub> film, prepared from anhydrous powder, has higher sensitivity than the SnO<sub>2</sub> film, prepared from hydrated powder. It was found that with appropriate selection of milling conditions and chemical reaction, the obtained powder might be successfully applied to a H<sub>2</sub>S gas sensor.



## INTRODUCTION

For gas sensors, where surface reactions produce the change in electrical conduction, the importance of grain size is significant [1]. The most important type of gas sensors with respect to real application utilizes SnO<sub>2</sub> as the sensor material [2]. Several methods are used to produce this material, involving sol-gel chemistry [3], spray pyrolysis [4], pulsed laser ablation [5], chemical vapour deposition [6] or sputtering [7]. On producing nanopowders with the above methods, it is not possible to ensure separation of the particles during the synthesis, resulting in the formation of highly agglomerated particles. In addition, the powders obtained by these methods often have a high synthesis costs.

Mechanochemical processing (MCP) is an alternative low cost method of manufacturing a wide range of nanopowders in a conventional ball mill. The chemical reactions are activated by the repeated ball-powder collisions, which induce structural changes and repeatedly regenerate the reacting interfaces. Plastic deformation of the powder particles is due to the formation of shear bands caused by high deformation rates experienced during mechanical alloying. On further milling, the shear bands coalesce, and the small-angle boundaries are replaced by high-angle grain boundaries [8].

A wide range of materials has been produced by MCP, but the synthesis of SnO<sub>2</sub> nanoparticles is not frequently encountered in the literature. McCormick and co-workers describe the preparation of SnO<sub>2</sub> thin films and the electrical response of the prepared sensor to O<sub>2</sub> was measured [9]. A second paper about the synthesis of SnO<sub>2</sub> nanoparticles by MCP for gas sensing application is reported, but it was published without testing the response to reducing gases [10].

Most of the reports on MCP that have appeared in the literature concern the use of high-energy mills. In a previous study it has been shown that it may be possible to produce nanopowder using a centrifugal mill of the conventional type instead of high-energy one [11]. A much deeper investigation of the milling phase, however, reveals that it is not possible to guarantee separation of all particles during milling, thus resulting in the formation of moderately agglomerated particles. Significant surface treatments due to the high rotation speed (100-200 rpm) and enhanced ball-to-powder mass ratio (10:1) were introduced during milling.

The previous study shows that the milling process itself contributes to the creation of surface hydroxyl groups, and after the subsequent heat-treatment, even at high temperature, there remains a considerable number of hydroxyls [12]. The distinct correlation between the behaviour of the electrical conductance and the intensity of the infrared surface hydroxyl deformation (Sn-OH) band is reported [13].

Thick or thin SnO<sub>2</sub> films have been often used for the detection of H<sub>2</sub>S gas [14-16]. Mixtures of SnO<sub>2</sub> and Ag powder were evaporated with a molybdenum boat, where the granular films with high Ag incorporation were found to show good sensitivity to 500 ppm of gas in air [14]. No response was found in the gas concentration range 1-50 ppm. The Ag and Cu/SnO<sub>2</sub>-based films were prepared by magnetron sputtering on the silicon substrates [15]. The gas response time was especially long at the operating temperature range 140-250 °C. This time is shortened at the operating temperature of 370 °C with a considerably reduced gas response. The low-pressure evaporation method was adopted for preparing SnO<sub>2</sub> thin films [16]. The sensitivity of evaporated film to 10 ppm of gas was much lower than 100, at the operating temperature of 250 °C, with the gas response time of about 20 min. The disadvantage found in this work is that the gas response is strongly dependent on operating temperature.

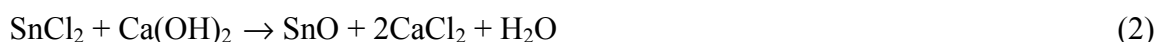
In this paper, the synthesis of SnO<sub>2</sub> nanocrystalline powder for gas sensor applications by different chemical reactions and milling conditions is reported. On exposure to low concentrations of H<sub>2</sub>S gas (20-50 ppm), the SnO<sub>2</sub> film, prepared from anhydrous powder, shows a higher response than the film, prepared from hydrated powder.

## 1 EXPERIMENTAL

Nanosized SnO<sub>2</sub> powder particles were produced by mechanochemical processing, where milling was performed at room temperature in a centrifugal type mill. There were two chemical reactions selected. The first one (Eq. 1) does not produce water. The chemical reaction used is



The starting materials (4.23 g of SnCl<sub>2</sub> and 3.09 g of K<sub>2</sub>CO<sub>3</sub>) were sealed in a non-metal vial in air and milled to produce 3 g of SnO<sub>2</sub>. Milling was performed using steel balls with a diameter of 12.7 mm. A ball-to-powder mass ratio of 10:1 was used. The milled composition was heat-treated subsequently at 400 °C for 1 h to complete the oxidation reaction. For the first milling condition examined, the milling time was kept as three hours, the relationship of ball-to-powder mass was equal to 10:1 and the rotation speed as maintained at 125 rpm. KCl is also added to the system as a starting material in order to obtain the minimum particle size. The second reaction (Eq. 2) produces water



The starting materials (2.33 g of SnCl<sub>2</sub>, 0.91 g of Ca(OH)<sub>2</sub> and 15.45 g of CaCl<sub>2</sub>) were sealed in a non-metal vial in an air and milled to produce 5 g of SnO. Removal of the KCl and CaCl<sub>2</sub> by-products was carried out by water, pure ethanol or ammonia 0.1 M solution.

A Philips PW 1710 X-ray powder diffractometer with a Cu-K<sub>α</sub> radiation (λ=1.54056 Å) was used to follow the crystallisation of the powder. The FTIR spectra are recorded by a Bio-Rad FTS 6000 spectrometer with photo-acoustic output in the range 4000-400 cm<sup>-1</sup>. The mean particle size distribution was measured using a Galai CIS-100 particle analyzer.

Thick film gas sensors were prepared by hand coating of a paste, the SnO<sub>2</sub> powder mixed with a λ-terpineol-based solvent, over the 0.2 mm gap of Au sensing electrodes on the Al<sub>2</sub>O<sub>3</sub> substrate. Subsequently the samples were sintered at 700 °C for 1 h in air. Pt wires were attached on the pads of the heater and sensing electrodes by using an Au-paste with followed by heat-treatment. The gas response test was carried out with a PC-controlled measuring system. Sensors to be tested were placed in a measuring chamber of about 0.5 l in volume. Thick-film sensor were exposed to varying test gas concentrations of H<sub>2</sub>S (20-50 ppm), using a gas flow controller unit with an air flow rate of 0.5 l min<sup>-1</sup>.

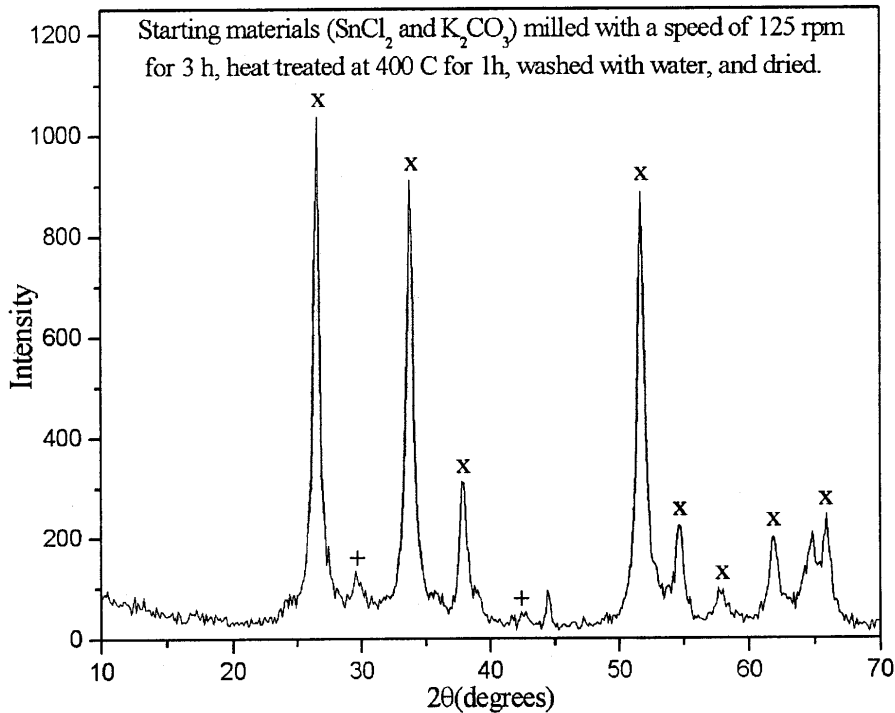
## 2 RESULTS AND DISCUSSION

### 2.1 X-ray Diffraction

Reaction (1) does not produce water and it produces an anhydrous powder. An XRD pattern of the as-milled composition (milling time: 3 h) did not reveal diffraction peaks, indicating the formation of an amorphous structure during processing. The mixture, obtained from milling, was subsequently heat-treated at 300 °C or 400 °C for 1 h, resulting in the exothermic reaction:



An XRD pattern of the final powder (heat-treated at 400 °C, washed by water, and dried) is presented in Fig. 1. The three main peaks are located at 26.6, 33.9, and 51.8 ( $2\theta^\circ$ ) degrees respectively. The tetragonal phase is clearly dominant with the orthorhombic phase, giving rise to one peak at 29.6 degrees and a very weak second one at 42.2 degrees.



**Fig. 1.** X-ray diffraction pattern of the synthesized  $\text{SnO}_2$  powder with a typical distribution of tetragonal (x) and orthorhombic (+) phases.

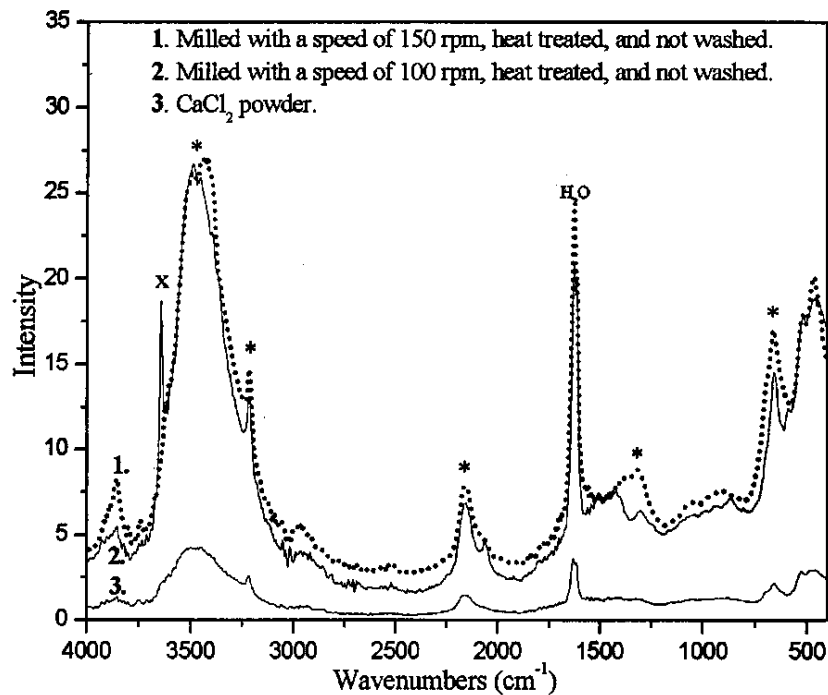
These weak reflections were completely absent after heat treatment at only 300 °C. It may be concluded that the crystallization had occurred at temperature of 400 °C. The crystallite size,  $D$ , was calculated according to the Scherrer equation,

$$L(2\theta) = K\alpha / (D\cos\theta) \quad (4)$$

where  $L(2\theta)$  is the width at half-maximum intensity (in radians) and  $\theta$  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  $K = 0.9$ ),  $\alpha$  is the wavelength of the X-ray source (in the case of Cu radiation  $\alpha = 1.54059 \text{ \AA}$ ) and  $D$  the crystallite size [17]. Crystallite sizes of the final powders (after washing and drying) and estimated by Eq. 4, were of 12.2 and 11.0 nm (washing of the powder respectively with water and ethanol).

## 2. 2 Fourier-transform infrared spectroscopy

The fine  $\text{SnO}_2$  powder was produced by two different chemical reactions, initiated by ball milling. It should be noted that water vapour in the milling vessel or produced by the chemical reaction during milling, have a considerable influence on the milling mechanism. If ball milling produces water (Eq. 2), a large number of OH groups are formed at the surface, contributing considerably to the reactivity of the surface. In Fig. 2 there the infrared spectra of hydrous powders (curves 1 and 2), produced by the second reaction (Eq. 2) are shown. Different milling conditions were chosen for these two powders.

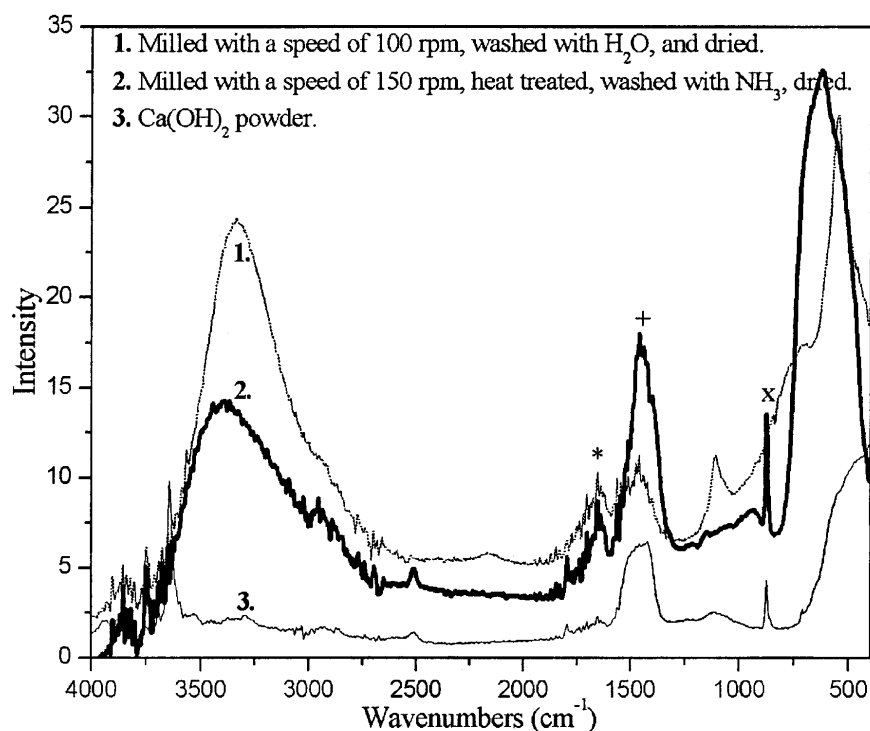


**Fig. 2.** FTIR spectra of hydrous powders milled for 4 h with moderate speed and heat-treated at  $400 \text{ }^\circ\text{C}$  for 1 h. The bands (\*) observed at 653, 1310, 2153, 3217 and  $3500 \text{ cm}^{-1}$  are assigned to  $\text{CaCl}_2$  and band (x) to  $\text{Ca}(\text{OH})_2$ .

Water is responsible for a large component of hydroxyl stretching mode, in the range  $3700\text{-}2000 \text{ cm}^{-1}$ , with a maximum at about  $3500 \text{ cm}^{-1}$ . The molecular water deformation mode is located at about  $1640 \text{ cm}^{-1}$ . Due to the  $\text{CaCl}_2$  added to the starting materials there is an excess of this salt in the system. An interesting effect is that longer milling (5 h) causes the molecular water at the surface to increase. It is most likely that during milling repeated ball-powder collisions have not

reached all the reacting interfaces of particles. The reason may be that the rotation speed of 100 rpm was too low or milling time too short to consume all starting materials loaded into the vial.

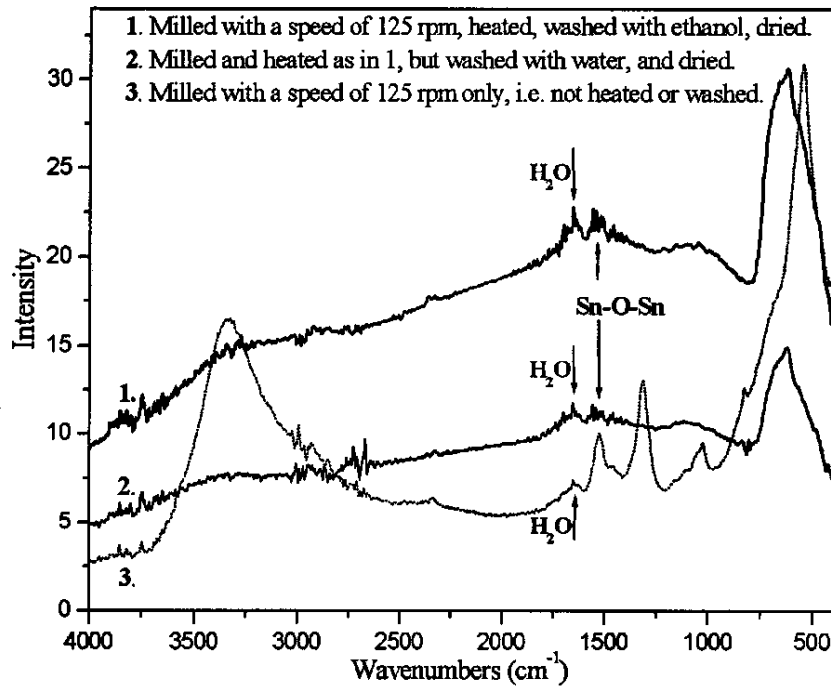
It is known that the dehydration from the  $\text{SnO}_2$  particles occurs via condensation of surface hydroxyl groups on the [100] and [101] planes. Hydroxyl group condensation on these planes will lead to the formation to surface Sn-O-Sn bridges [18]. Fig. 3 shows clearly the formation of the stretching mode of the mentioned bridges at about  $1450\text{ cm}^{-1}$ , where curve 1 represents only the milling phase, followed by washing and drying at  $100\text{ }^\circ\text{C}$  for 5 h.



**Fig. 3.** FTIR spectra of hydrous powders milled with moderate speed, heat-treated and washed with water or ammonium solution. The bands marked as (\*), (+) and (x) are assigned to surface molecular water, Sn-O-Sn bridges and  $\text{Ca}(\text{OH})_2$  respectively.

A weak Sn-O-Sn bond is observed at  $1450\text{ cm}^{-1}$ . The powder milled for 5 h and washed with ammonia 0.1 M solution (curve 2) shows the enhanced intensity of stretching mode at  $1450\text{ cm}^{-1}$ . It seems that in the system has retained some of unreacted  $\text{Ca}(\text{OH})_2$ , indicated by the band at  $875\text{ cm}^{-1}$ . Fig. 3 shows that the location of bands assigned to hydroxyl stretching modes for different powders and washing solutions used, are all in the range  $1425\text{-}1475\text{ cm}^{-1}$ .

Thus, it is reasonable to conclude that the Ca-OH bonds formed during milling, remain there at the surface and that after heat-treatment the two Ca-OH bonds of adjacent grains are transformed to surface Sn-O-Sn stretching mode of a surface-bridging oxide at  $1450\text{ cm}^{-1}$ . It is clear that these surface Sn-O-Sn bonds are not involved in gas adsorption. The induced chemical reaction (Eq. 1), does not produce water, and the IR spectrum of the only milled composition, without the heat-treatment at  $400\text{ }^\circ\text{C}$ , is shown by curve 3 in Fig. 4. There is a large hydroxyl envelope ranging from  $3700\text{ cm}^{-1}$  to  $2500\text{ cm}^{-1}$  with a maximum at about  $3330\text{ cm}^{-1}$ . Bands observed in the range  $1020\text{-}1540\text{ cm}^{-1}$  are assigned to hydroxyl deformation modes.



**Fig. 4.** FTIR spectra of anhydrous powders milled with moderate speed, heat-treated and washed. The term “ $\text{H}_2\text{O}$ ” in figure means the “molecular water”.

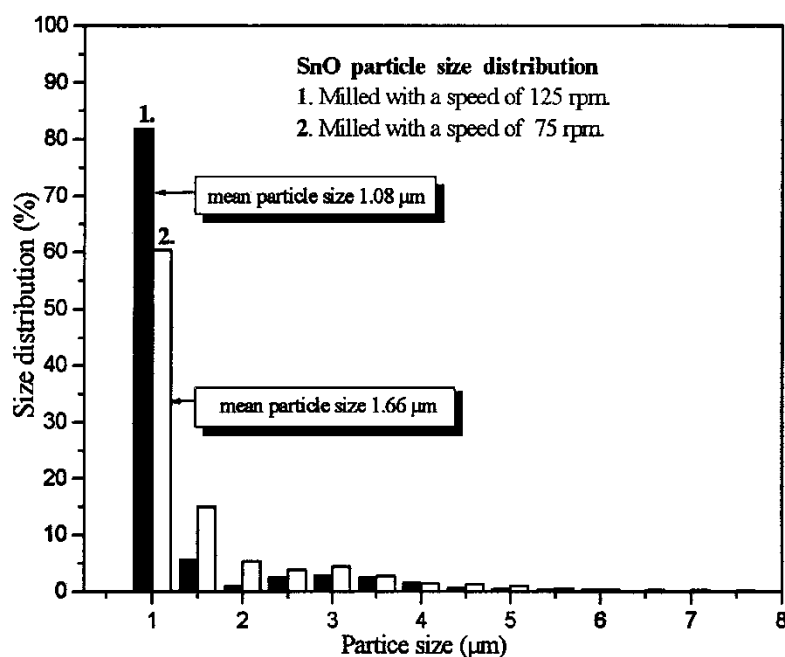
The molecular water deformation mode at  $1640\text{ cm}^{-1}$  is reduced considerably in intensity, showing that initially, during milling, molecular water is not produced on the surface. Since washing of the KCl by-product with ethanol is time-consuming, there is always a probability that some salt will remain at the surface. This means that the surface hydroxyl groups, bound initially to K atoms during milling, are probably transformed into K-O-K bonds during heat-treatment.

The resulting band located at about  $1550\text{ cm}^{-1}$  is assigned to the stretching mode of a surface-bridging oxide. It can be concluded that final  $\text{SnO}_2$  powders (heat-treated and washed), obtained initially by the chemical reaction (Eq. 1), are characterized as the hydroxyl-free particles (curves 1 and 2).

### 2. 3 Nanoparticle size distribution

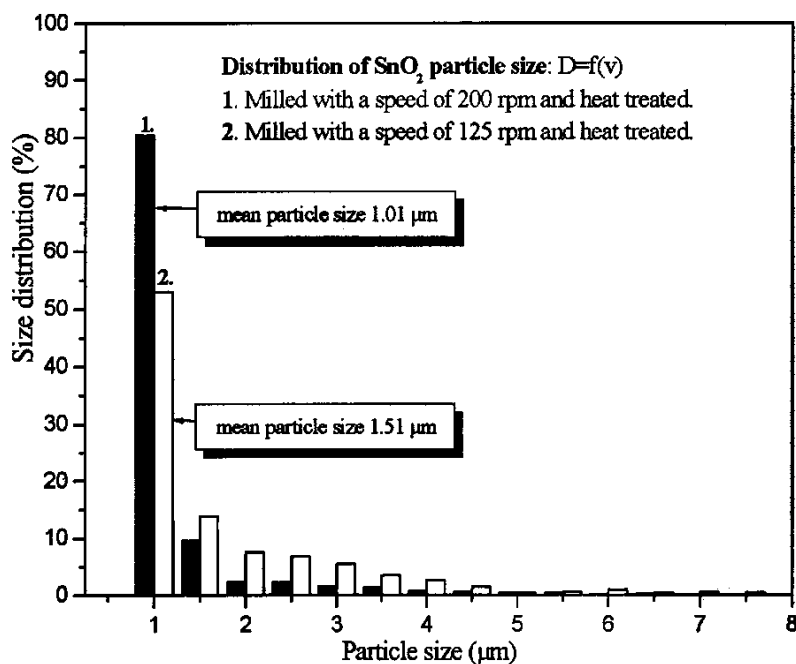
It must be explained that by using mechanochemical processing it is not possible to produce absolutely separated particles; they are always slightly agglomerated.

The formation of  $\text{SnO}_2$  nanoparticles has been investigated in detail, in order to determine, when an agglomeration of the particles takes place. An important feature of MCP is the narrow particle size distribution (Fig. 5 and 6). The particles of only milled powders in the salt matrix were washed with water, dried at  $100^\circ\text{C}$ , and the mean particle size was measured.



**Fig. 5.** Nanoparticle size histogram for only milled (with different speeds) compositions.

Fig. 5 confirms that initially during milling, moderately large particles: the size is about 1.0  $\mu\text{m}$ , are formed, using a rotation speed of 125 rpm. Using higher rotation speeds causes the decrease in the particle size. When milling of the starting materials was performed with a rotation speed of 200 rpm, it resulted in the formation of  $\text{SnO}_2$  particles, much less than 1.0  $\mu\text{m}$  as shown in Fig. 6. When the powder was heat-treated at a temperature of 700  $^\circ\text{C}$ , the particle size increased to 1.9  $\mu\text{m}$ .



**Fig. 6.** Nanoparticle size histogram for the resultant powders. The compositions were milled at different speeds, heat-treated at 400  $^\circ\text{C}$ , and washed with water.

An attempt was made to determine the thickness of the salt layer, surrounding the particles during milling. The full size of milled aggregates was measured to be 2.0  $\mu\text{m}$ . After washing with ethanol, the size reduced to 1.3  $\mu\text{m}$ . Thus the mean thickness of salt, surrounding the  $\text{SnO}_2$  particles, is about 0.7  $\mu\text{m}$ .

## 2. 4 Response to $\text{H}_2\text{S}$ gas

Water released during milling greatly influences the properties of powder and prepared gas sensor. It is of interest therefore, to prepare and test undoped  $\text{SnO}_2$  thick film sensors from both the hydrous and anhydrous powders. It is known that the conduction of  $\text{SnO}_2$  in air, at the temperature range 150-400  $^\circ\text{C}$ , is influenced by the chemisorption of oxygen and water vapor [19]. The region corresponds also to the various temperatures quoted for loss of OH groups from the surface [20]. The sites left by hydroxyls are immediately reoccupied by adsorbed oxygen, increasing the surface coverage of charged oxygen species, resulting in the decrease of electrical conductance. This is of great importance, considering further the gas sensing mechanism at the surface of grains. There are different oxygen species, which may cover the surface:  $\text{O}_2^-$ ,  $\text{O}^-$ , and  $\text{O}^{2-}$ . A relatively low population of single charged oxygen species is reported at temperatures below 280  $^\circ\text{C}$ , compared with the relatively high abundance of  $\text{O}^{2-}$  species [21].

The first interpretation of the chemical sensing mechanism considers the negatively charged surface oxygen ions, which react with the gas. The increase of the conductivity in the presence of  $\text{H}_2\text{S}$  may be explained by the reaction below,



According to this reaction, the interaction of  $\text{H}_2\text{S}$  with previously adsorbed  $\text{O}^{2-}$  ions results in the injection of electrons into the depletion layer of  $\text{SnO}_2$  grains.

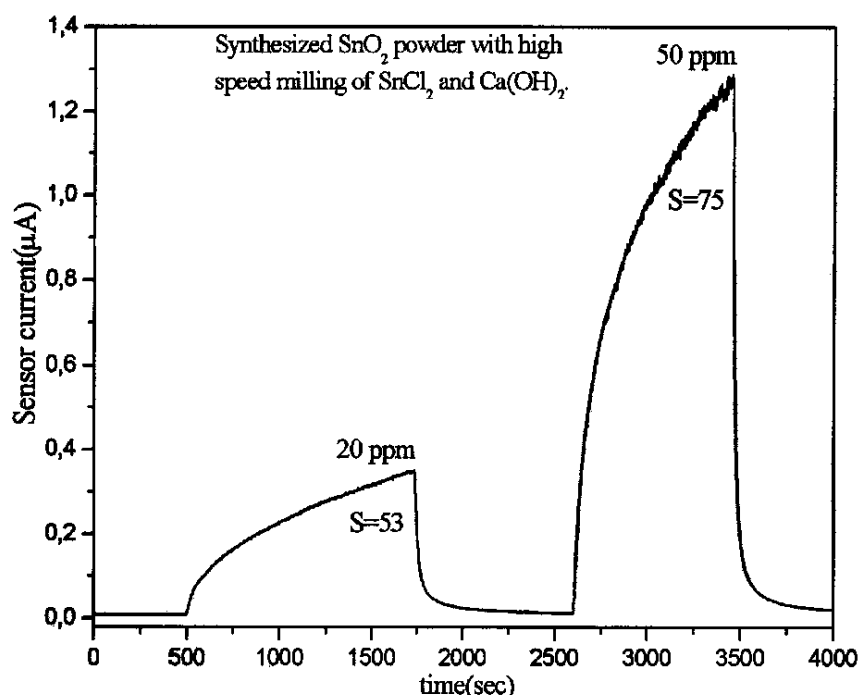
The second interpretation of the chemical sensing mechanism considers the surface chemisorbed oxygen ions and hydroxyl groups formed on the surface in the temperature range 100-500  $^\circ\text{C}$ . Even at the high temperature of 400  $^\circ\text{C}$ , the thermogravimetric study shows that a significant surface hydroxyl concentration remains, whereas the IR study showed almost all lost at this temperature [22].

Response to gas is defined as

$$S = (\text{I}_{\text{gas}} - \text{I}_{\text{air}}) / \text{I}_{\text{air}} \quad (6)$$

where  $\text{I}_{\text{air}}$  is the sensor current in clean air and  $\text{I}_{\text{gas}}$  is the current in the test gas.

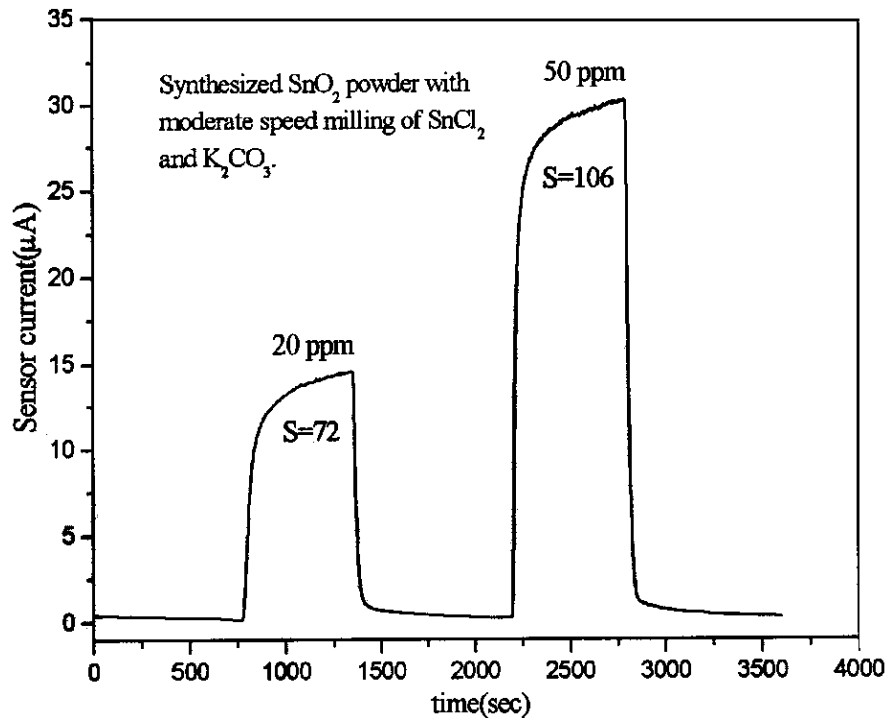
The  $\text{H}_2\text{S}$  gas response of the  $\text{SnO}_2$  thick film, prepared from the hydrous powder, is shown in Fig. 7. The obtained  $\text{SnO}_2$  particles exhibit a large number of surface hydroxyls.



**Fig. 7.** Dynamic response of a SnO<sub>2</sub> thick film sintered at 700 °C in air for 1 h to increasing H<sub>2</sub>S concentrations in air. An airflow rate is maintained at 0.5 l min<sup>-1</sup>.

Several authors have suggested that besides the gas reaction with the surface chemisorbed oxygen species, some reaction can occur due to the oxidation of the gas by means of the oxygen atoms, available in the hydroxyl group. Given this, it should be possible to produce a good gas response for this SnO<sub>2</sub> thick film prepared from hydrous powder.

The H<sub>2</sub>S gas response of the SnO<sub>2</sub> thick film, prepared from the anhydrous powder, is shown in Fig. 8. The chemical sensing mechanism of this SnO<sub>2</sub> thick film, prepared from anhydrous powder, should be described by the first interpretation, given before. The SnO<sub>2</sub> thick film response to the gas should be lower than that in previous case, when the thick film was prepared from the hydrous powder.



**Fig. 8.** Dynamic response of a SnO<sub>2</sub> thick film sintered at 700 °C in air for 1 h to increasing H<sub>2</sub>S concentrations in air. An airflow rate is maintained at 0.5 l min<sup>-1</sup>.

In fact, however, the dynamic responses obtained from the SnO<sub>2</sub> thick films presented in Fig. 7 and 8, showed the opposite effect. At a sufficiently high temperature the surface may be practically free of molecular water, but at the same time it may be partly covered by OH groups [23]. Therefore, the lower gas response, as observed in Fig. 7 compared to that presented in Fig. 8, could be explained by the fact that a certain number of the hydroxyls are entering the oxygen vacancies, which may prevent the oxygen atoms from reaching the surface. Secondly, Ca-OH bonds formed initially during milling of the powder, will be later transformed to surface Sn-O-Sn bridges. This means that probably many Sn atoms occupied by these bonds can not contribute the gas sensing mechanism.

It is clear that the high response to H<sub>2</sub>S gas of the SnO<sub>2</sub> film, prepared from anhydrous powder, is attributed to the operation of the first type of chemical sensing mechanism. The negatively charged surface oxygen ions react with the gas and release the electrons to the conduction band, and OH groups do not contribute the gas sensing mechanism at all.

### 3 CONCLUSIONS

In this work the effect of different milling conditions and the use of different chemical reactions on fine SnO<sub>2</sub> powder quality were investigated in detail. Ball milling of predetermined amounts of starting materials in a centrifugal action resulted in the formation of the desired mass of SnO. After heat-treatment and removal of the salt, slightly agglomerated SnO<sub>2</sub> particles were produced.

The main results obtained are the following: 1) The milling process itself initially results in the formation of moderately large, slightly agglomerated SnO particles (around 1 μm) covered with a

thick layer of the salt ( $\text{CaCl}_2$  or  $\text{KCl}$ ) (around  $0.7 \mu\text{m}$ ). 2) Synthesized powders have a very narrow particle size distribution. 3) If water is produced by the reaction, this changes considerably the surface reactivity. 4) The  $\text{SnO}_2$  thick film prepared from anhydrous powder has much higher response to  $\text{H}_2\text{S}$  gas than that prepared from the hydrous powder.

## ACKNOWLEDGEMENTS

The author is thankful to Dr. Peter Gardner, UMIST, United Kingdom, for his help on reading the manuscript.

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